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**The removal of arsenic during drinking
water treatment by sorption
and coagulation processes**

**Uklanjanje arsena u tretmanu
vode za piće primenom sorpcionih
i koagulacionih procesa**

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List of abbreviations used in this dissertation

AA	Activated alumina
AC	Activated carbon
ANOVA	Analysis of variance
BAT	Best available technology
BET	Brunauer–Emmett–Teller
DMA	Dimethylarsonic acid
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDS	Electron dispersive spectroscopy
EPA	United States Environmental Protection Agency
FA	Fulvic acid
GFH	Granulated ferric hydroxide
HA	Humic acid
HPLC	High performance liquid chromatography
IARC	International Agency for Research on Cancer
iAs ^{III}	Inorganic As(III)
iAs ^V	Inorganic As(V)
IBS	Iron based sorbents
ICP-MS	Inductively-coupled plasma mass spectrometry
IEC	Ion exchange chromatography
IOCS	Iron oxide coated sand
MAC	Maximum allowable concentration
MMA	Monomethylarsonic acid
NOM	Natural organic matter
PACl	Polyaluminium chloride
RO	Reverse osmosis
RSM	Response surface methodology
SEM	Scanning electron microscopy
SMIOCS	Sulphate modified iron oxide coated sand
SPE	Solid phase extraction
TMA _o	Trimethylarsinic oxide
WHO	World Health Organisation
ZVI	Zero valent iron

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1 Introduction

One of the most wide-spread problems with current drinking water resources globally is the natural presence of arsenic in groundwaters. Throughout South-East Europe, groundwaters are commonly used as sources for drinking water. The chemical quality of these groundwaters varies greatly, with many different constituents, including not just common minerals (sodium, calcium, magnesium, potassium, chloride, bicarbonate, and sulphate), but also arsenic, boron, iron, manganese, phosphates, silicates and natural organic matter (NOM). Within the Pannonian Basin, the groundwaters are naturally contaminated with particularly high concentrations of arsenic, which poses a severe challenge for public water utilities. Arsenic is a highly abundant element which forms a variety of inorganic and organic compounds, most of which are toxic, and many of which are human carcinogens.

The extremely negative impact of chronic arsenic exposure on human health led the World Health Organisation (WHO) to recommend a maximum allowable concentration (MAC) of 10 $\mu\text{g As/l}$ for drinking water (WHO, 2011). This MAC was adopted into EU law with the implementation of the Drinking Water Directive (Council of the European Union, 1998) and into Serbian law with the introduction of the Regulation on the hygienic quality of drinking water (Official Gazette RS 42/98 and 44/99, 1998). Some countries in Europe are already pushing for even stricter limits in the future. Meanwhile, in parts of Vojvodina, the groundwaters can contain as much as 250 $\mu\text{g As/l}$, and concentrations greater than 10 $\mu\text{g As/l}$ are the norm: it is estimated that almost 1 million people in Vojvodina are currently supplied with drinking water which contains arsenic concentrations which exceed 10 $\mu\text{g/l}$ (Agbaba et al., 2015a). Given the negative health effects of chronic arsenic exposure, there is thus not just a legal, but also a social imperative to reduce the As concentrations to acceptable legally defined levels.

The process of removing As from water is made more complicated by the other water constituents present, which may either indirectly reduce effectiveness of removal mechanisms, or compete directly for adsorption sites. NOM is particularly significant here, as it is known to play a key role in the mobility of As from the mineral layers surrounding aquifers into the water phase. Thus, in groundwaters with high As concentrations, there are often correspondingly high NOM concentrations. Although NOM in drinking water is not directly threatening to human health, it can create several problems: it can act as a substrate in distribution networks, promoting the growth of biofilms which may house pathogenic organisms, and it can also act as a precursor material in the creation of disinfection by-products (DBP). To secure the microbiological and chemical quality of drinking water all the way to the tap, it is therefore necessary to also remove NOM during the treatment process. Depending upon the technologies applied, this may necessitate NOM removal prior to As removal, in cases where NOM significantly interferes with the efficacy of the

As removal process, or an increase in the capacity of the same treatment process capable of removing both, for example in the case of ferric chloride coagulation.

In this context, there is a critical need for research relating to new drinking water treatment technologies, capable of sustainably treating a wide variety of source waters, and providing chemically and microbiologically safe drinking water.

This dissertation, whilst focusing on investigating effective, affordable and sustainable arsenic removal technologies, therefore aims to achieve the following goals:

1. To investigate the interactions between arsenic and natural organic matter, two of the most significant contaminants commonly found in drinking water sources.
2. To develop and investigate the capabilities of new adsorbents based on iron oxides for the removal of arsenic from drinking water, and investigate how certain competitive ions affect their behaviour.
3. To investigate the removal of arsenic by a variety of coagulation and combined oxidation/coagulation processes, in order to identify and optimise the most critical process parameters.
4. To utilise Design of Experiments and Response Surface Methodology (RSM) to develop mathematical models describing the interactions between arsenic and natural organic matter during the process of iron chloride coagulation, to facilitate the optimisation of coagulation processes for waters with different amounts of these contaminants.

These investigations will contribute a better understanding of how As and NOM interact, not just in raw source waters, but also during the treatment process, knowledge which will be extremely significant for efforts to improve the quality of local drinking water supplies via the development, implementation and optimisation of innovative and sustainable drinking water treatment technologies.

2 Arsenic in drinking water: a global problem

The sustainable provision of safe drinking water is one of the most important challenges facing society today. This challenge is only going to become more difficult to solve in the future, as the global population continues to grow, and climate change and pollution affect the availability and distribution of suitable fresh water resources. In Europe alone, the population is expected to increase from more than 508 million in 2015 to 523 million by 2050 (Eurostat, 2013). This increase in demand for potable water means that as well as utilizing existing water resources more rationally, new resources must also be explored and exploited.

Furthermore, even as many countries already struggle to comply with their own existing drinking water quality regulations, more information becomes available about the negative health effects which result from the consumption of water contaminated with a wide variety of natural and artificial compounds, such that drinking water quality standards trend towards becoming even more stringent in the future. In this context, there is a critical need for research relating to new drinking water treatment technologies, capable of sustainably treating a wide variety of source waters, and providing chemically and microbiologically safe drinking water.

One of the most wide-spread problems with current drinking water resources is the natural presence of arsenic in groundwaters. Globally, the WHO estimates that approximately 130 million people are supplied with drinking water which contains more than 50 µg As/l, which was the previous recommended maximum allowable concentration (MAC) for arsenic, prior to 1993 (WHO, 2001). Arsenic, the group 15 metalloid, is the 20th most abundant element on earth, the 34th most abundant element in the human body (Freitas, 1999), and is found in a variety of oxidation states in nature, with 0, +3 and +5 being by far the most common. As explained below, many of its compounds are extremely toxic, so that in most countries, the current WHO recommended limit for drinking water of 10 µg As/l has been adopted into law as the MAC (WHO, 2011). This includes the EU (Council of the European Union, 1998) and the Republic of Serbia (Official Gazette RS 42/98 and 44/99, 1998). Furthermore, the possibility of lowering the MAC for As even further, to as low as 1 µg As/l, has recently been discussed by water professionals in some EU member countries (Halem et al., 2009). It is therefore necessary to remove arsenic from drinking water in many countries, as the concentrations in groundwaters used as drinking water sources can exceed the MAC by several orders of magnitude.

Some examples of typical arsenic concentrations reported in groundwaters globally are given in table 1, along with estimates of the populations adversely affected where possible. The countries with the largest adversely effected problems are Bangladesh and India, but as can be seen from the table, arsenic contamination is extremely widespread.

Table 1. Typical arsenic concentrations in groundwaters around the globe.**Tabela 1.** Uobičajene koncentracije arsena u podzemnim vodama u svetu.

Country	Reported As concentrations (µg/l)	Estimated pop. effected (millions)	Reference
Argentina	10–5300	2	Smedley et al., 2005; McClintock et al., 2012
Bangladesh	> 1000	35	Meng et al., 2002; Yunus et al., 2011
Chile	470–700	1.5	Alem et al., 2009
China	1–2400	5.6	Kong et al., 2013; Wu et al., 2011
India	50–3600	40	Roy et al., 2014
Hungary	1–174	0.6	Rowland et al., 2011
Pakistan	10–200	20	Baig et al., 2009
Serbia	1–270	1	Tubić et al., 2010; Papić et al., 2012
Taiwan	170–800	unknown	Smith et al., 1992
USA	> 50	2.5	Focazio et al., 1999

The natural contamination of local groundwaters by arsenic is one of the most pressing health issues facing Serbia, with almost 1 million people in Vojvodina still being supplied with drinking water which contains more than 10 µg/l As (Agbaba et al., 2015a).

2.1 Arsenic in the environment

In addition to the arsenic stored in minerals in the Earth's crust, and the arsenic dissolved in the adjacent aquifers, arsenic is also found in the atmosphere, due to wind erosion processes, volcanic emissions, and volatilization due to biological processes (Lièvrement et al., 2009). Arsenic is therefore very widespread throughout the environment, which is reflected in the fact that it may be found in plants in concentrations up to 5 µg/g dry plant matter, depending on the plant uptake and soil arsenic concentrations. Wherever arsenic is present in water, it can also enter the food chain, with rice and sea food being particularly relevant sources of arsenic exposure in many parts of the world (Oberoi et al., 2014).

Anthropogenic sources of arsenic in the environment include pesticides and herbicides, leaching from chemical wastes from the paper industry, mine tailings and the combustion of fossil fuels (Jain and Ali, 2000; Chakravarty et al., 2002).

2.1.1 Origins of arsenic in groundwater

Ultimately, the sources of arsenic which cause problems for drinking water resources are geological. Arsenic is present in more than 245 different types of mineral (Sharma and Sohn, 2009), with typical crustal concentrations ranging from 0.5–2.5 mg/kg. The most common arsenic bearing minerals include arsenopyrite (FeAsS), orpiment (As₂S₃) and

realgar ($\alpha\text{-As}_4\text{S}_4$), with arsenic being found occasionally in elemental form, but more often as sulphides and oxides, either as arsenate or arsenite (Jain and Ali, 2000; Lièvremon et al., 2009).

Arsenic concentrations in the sediments of groundwater aquifers are typically higher than the crustal average, and vary widely depending upon the nature and location of the aquifer. Typical arsenic concentrations in aquifer sediments range from 5–10 mg/kg (Smedley et al., 2005). Under the correct geochemical and hydrogeological conditions, the arsenic stored in the aquifer sediments can be released into the aquifer water. Favourable conditions for the contamination of aquifer water by arsenic are found in relatively "young" sediments, with strongly reducing or oxidising high pH conditions, either allowing arsenic to desorb from metal oxides, or the complete dissolution of those metal oxides. In this context, "young" implies aquifers found in deposits no later than the Late Quaternary, formed around 0.5 to 2.6 million years ago.

The aquifers in Vojvodina which are contaminated with arsenic are those formed in the sediments of what was once the Pannonian sea. The Pannonian Sea existed during the Miocene and Pliocene epochs, extending into what is now Northern Serbia, Hungary, Romania and Croatia. The sediments of the Pannonian Basin are heterogeneous, thick and complex, with the average thickness of the Neogene and Quaternary sediments in the basin being 2 – 3 km. Three categories of aquifer have been identified within the Pannonian Basin sediments (Rowland et al., 2011).

1. aquifers with strong geothermal and saline influences with low levels of As (mean average 33.1 $\mu\text{g/l}$, range <0.5 to 240 $\mu\text{g/l}$),
2. dug wells with very low As (mean average 1 $\mu\text{g/l}$, range <0.5 to 2.1 $\mu\text{g/l}$).
3. general groundwaters (mean average 123 $\mu\text{g/l}$, range 23.4 to 208 $\mu\text{g/l}$) in contrast to group 2 (mean average 11.5 $\mu\text{g/L}$, range <0.5 to 58.0 $\mu\text{g/l}$),

2.1.2 Natural arsenic species and their toxicity

In the various laws and regulations which govern the concentrations of arsenic in drinking water (Council of the European Union, 1998; Official Gazette RS 42/98 and 44/99, 1998; WHO, 2011), maximum allowable arsenic concentrations are always expressed in terms of total arsenic. However, arsenic is in fact present in nature in numerous different species, all of which have different chemical properties and toxicities. Speciation analysis allows the different types of arsenic in a water sample to be quantified, but is very complicated, time consuming and expensive, hence the use of total arsenic in the global regulative.

The toxicity of arsenic in humans can be expressed in a variety of ways, with chronic exposure being linked to increased likelihoods of cardiovascular disease, respiratory illness, skin lesions, and cancers of the skin, liver, kidney, lung and bladder (McClintock et al., 2012). The inorganic arsenic species are generally more toxic than the organic ones, with the toxicity of the compounds of arsenic decreasing in the series arsine > inorganic As

(III)> organic As (III)> As inorganic (V)> organic As (V)> arsonium compounds and elemental arsenic (Thirunavukkarasu et al., 2001).

For acute exposure, the oral LD₅₀ for inorganic arsenic ranges from 11–293 mg As/kg in a variety of laboratory mammals, and the ingestion of 70–80 mg arsenic trioxide, which is believed to be more toxic than arsenic pentoxide, has been reported to be fatal for humans (Sharma and Sohn, 2009). Note that trivalent and pentavalent inorganic forms of arsenic are often given the nomenclature *iAs*^{III} and *iAs*^V in the literature.

Table 2 provides some basic information about some of the most commonly occurring arsenic compounds (Yu et al., 2003). In order to illustrate their relative toxicities, where found in the literature, the table includes reported lethal doses (LD₅₀) for each compound.

Table 2. Structures, *pK_a* values and toxicities of the most common arsenic compounds.

Tabela 2. Strukture, *pK_a* vrednosti i toksičnost najzastupljenijih jedinjenja arsena.

Name	Strucutre	<i>pK_a</i>	LD ₅₀ for human cells (μM)
Arsenous acid (As(III))	H ₃ AsO ₃	9.2	5.49
Arsenic acid (As(V))	H ₃ AsO ₄	2.3, 6.8, 11.6	571
Monomethylarsonic acid (MMA ^V)			
Monomethylarsenous acid (MMA ^{III})	HAsCH ₄ O ₃	3.6, 8.2	
Dimethylarsinic acid (DMA ^{III})			2.16
Dimethylarsenous acid (DMA ^V)	HAs(CH ₄) ₂ O	6.2	843
Trimethylarsinic oxide (TMAO)	(CH ₃) ₃ AsO	4	
Tetramethylarsonium ion			
Arsenobetaine	AsC ₅ H ₁₁ O ₂	2.18	
Arsenocholine bromide	AsC ₅ H ₁₄ OBr	N.A.	

Other arsenic compounds which can be found in nature include dimethylarsinoylribosides and other arsenosugars (Sharma and Sohn, 2009).

The methylated forms MMA^V and MMA^{III} are the metabolites of their inorganic analogues. For a long time, the fact that humans and other animals metabolise inorganic arsenic to the methylated forms was considered evidence for the fact that MMA and DMA are less toxic than the inorganic forms (Sharma and Sohn, 2009). However, more recent research suggests that MMA^{III} and DMA^{III} is in fact toxic than *iAs*^{III} due to its genotoxicity (Mass et al., 2001). The greater toxicity of DMA^{III} is reflected by its LD₅₀ in human cells, which is the lowest of all the arsenic species (see table 2) investigated. The larger organic compounds such as arsenobetaine and arsenocholine are considered to be virtually nontoxic.

Arsenic in food, especially fish and shellfish, is mainly in the form of the less toxic organic compounds, although about 25% of the arsenic in food is present in inorganic form (IPCS,

2001). However, the greatest exposure to arsenic is still via drinking water, where arsenic is mainly present in inorganic forms. Drinking water supplies in which the concentration of arsenic is higher than 10 µg/l are the dominant sources of exposure for humans (IPCS, 2001).

Arsenic toxicity is expressed when the metalloid binds to sulfhydryl functional groups of proteins (enzymes), causing them to coagulate, inhibiting the production of ATP, and therefore inhibiting metabolism, particularly respiration. Arsenic inhibits more than 200 enzymes and influences multisystem health effects by interfering with enzyme functions and the regulation of transcription (Lage et al., 2006). Due to its chemical similarity to phosphorus, the high toxicity of arsenic is attributed to the fact that it can be exchanged for phosphorus in the body, interfering with a large number of chemical reactions (Wolfe-Simon et al., 2009). Replacement of phosphate ions in DNA molecules could explain the mutagenic, teratogenic and carcinogenic effects of arsenic. Intracellular reduction of As(V) to As(III) can also lead to the formation of free radicals responsible for chromosome damage (Lièvreumont et al., 2009).

Acute toxicity is related to the chemical form and oxidation state of arsenic. In adult humans, the lethal dose of arsenic is estimated at 1–3 mg As/kg (De Zuane, 1996). The characteristics of acute toxicity include gastrointestinal symptoms (loss of appetite, vomiting), disorders of the nervous system and cardiovascular system (spasms of the heart muscle), and death (Smith et al., 2000; Abernathy, 2001).

Different organ systems within the human body suffer different changes due to chronic exposure to inorganic arsenic. One common symptom of chronic toxicity in humans originating from oral exposure to arsenic are skin lesions, characterized by hyperpigmentation and hyperkeratosis. Black foot disease is a vascular disease which causes gangrene of the lower extremities and is also detected in people with chronic exposure to arsenic in drinking water (Sharma and Sohn, 2009). Long-term consumption of drinking water with high concentrations of arsenic can lead to the development of arsenicosis. Arsenicosis is the common name for disease symptoms due to chronic arsenic exposure (Das et al.; Halem et al., 2009) and may develop after years of exposure to arsenic (Petruševski et al., 2008).

Arsenic can damage internal organs without visible external symptoms, which makes it difficult to diagnose arsenic poisoning. However, increased concentrations of arsenic in the hair, nails, urine and blood may be indicators of exposure to arsenic before the onset of visible external symptoms (Rasmussen and Andersen, 2002).

Regardless of the different approaches and methodologies used, there is broad acceptance of the fact that consuming water with a high arsenic content can lead to the development of malignant diseases. Increased risk was observed in the case of consuming drinking water containing more than 50 µg/l of arsenic (WHO, 2011). However, there is still debate about the risk of cancer posed by exposure to low to moderate concentrations of arsenic in drinking water (Smith et al., 1992; Celik et al., 2008)

Evidence of a link between an increased risk of cancer and exposure to arsenic compounds led the International Agency for Research on Cancer (IARC) to classify inorganic arsenic compounds as carcinogenic (Group 1) to the population, while pentavalent inorganic arsenic and organic arsenic, as well as their compounds, are classified as toxic substances (IARC, 2004).

Most countries in the world, including members of the European Union, USA, Japan and Serbia, have adapted the 10 µg/l limit recommended by the WHO (USEPA, 2001). Several countries (e.g. Bangladesh, Bolivia, China, Egypt, India, Indonesia, Sri Lanka, have kept the older 50 µg/l standard, mostly due to difficulties in satisfying the stricter 10 µg/l standard. Currently, the strictest standard for the MAC of arsenic in drinking water is 7 µg/l in Australia (O'Brien et al., 2003; Petrusevski et al., 2007)), although as mentioned above, discussions in some EU member states such as the Netherlands have already begun on lowering their MAC to less than 1 µg/l (Halem et al., 2009).

2.2 Arsenic mobility in the environment

In groundwater, arsenic is usually present in inorganic form as As(III) or As(V), which as explained above, differ significantly in terms of toxicity. The ratio of arsenite and arsenate in groundwater can vary considerably, and depends on the presence of redox active substances (especially organic carbon), the activities of microorganisms and oxygen uptake from the atmosphere. As(III) is usually dominant in very anoxic aquifers where the reduction of Fe(III) and sulphate can occur (Sasaki et al., 2009).

The concentration of arsenic in groundwater depends upon the concentration of arsenic in the aquifer minerals and the conditions in the aquifer (pH, redox potential, ionic strength, presence of other ions, natural organic matter content), which dictate which physical processes such as adsorption and desorption occur at the boundary between the solid and liquid phases in the aquifer (Bundschuh, 2012). Arsenic present in aquifers is in a dynamic equilibrium between these two phases, either dissolved in the aquifer water or adsorbed onto the minerals. Iron oxide is one of the most dominant minerals responsible for arsenic sorption. The sediment arsenic is linked to the oxy(hydroxides) of iron, and also aluminum, and thus these control the the amount of arsenic in groundwater.

The pH is one of the most critical parameters dictating the degree to which arsenic is sorbed onto iron oxides, and the behaviour of arsenic in water in general. Figure 1 shows how the disassociation of arsenite and arsenate changes depending upon the pH.

The local groundwaters tend to be neutral or slightly alkaline. This results in a very significant difference between arsenite and arsenate, as inside the pH range of the groundwaters, the great majority of arsenite present is neutral (H_3AsO_3 form), whereas the vast majority of arsenate present is in its doubly negatively charged (HAsO_4^{2-} form). This makes arsenate considerably more likely to interact with positively charged ions.

As explained below in section 2.5.6, the isoelectric point of most iron hydroxides is such that between pH 5–7, the surface of iron hydroxides is positively charged. This means electrostatic interactions may occur between the iron hydroxide and arsenate in the water, increasing the likelihood that arsenate will remain sorbed on the aquifer minerals rather than being dissolved in the water. Other significant minerals in the sorption and desorption behaviour of arsenic include aluminium oxides and hydroxides, calcium carbonate and clays like kaolinite and montmorillonite.

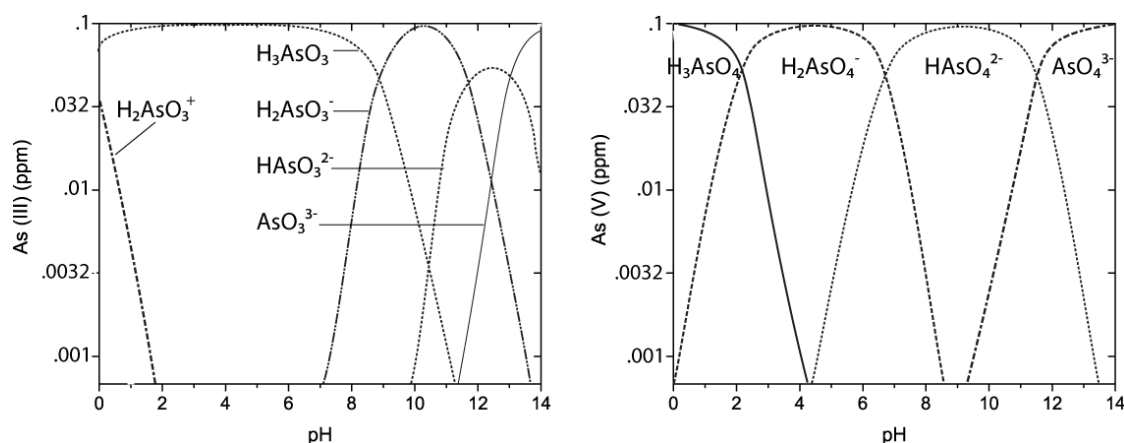


Figure 1. Speciation of As(III) and As(V) compounds at different pH.

Slika 1. Specijacija jedinjenja As(III) i As(V) na različitim pH vrednostima.

(Sharma and Sohn, 2009)

Natural organic matter likely plays a role in releasing arsenic from minerals (Halim et al., 2009). Arsenic adsorbed onto the surface of iron oxyhydroxides (FeOOH) can be reduced due to the microbial oxidation of the organic matter, resulting in desorption from the surface of arsenic oxide and its release into the groundwater (Venkataraman, 2010). Whether arsenic will ultimately enter into groundwaters depends up on many factors (Halim et al., 2009): the age of the aquifer (mobilization of arsenic is less likely in younger sediments); the water velocity in the aquifer; water pH (at pH < 8.5, arsenic is desorbed from minerals); and the redox potential of the system (under anoxic conditions, and at pH ~7, (oxy)hydroxides of iron can be reduced, leading to coprecipitation of arsenic, increasing its mobility).

The role of redox potential (E_h) and pH in defining which species of arsenic are present in the environment is summarized in figure 2.

Under oxidizing conditions (high E_h values), inorganic arsenic occurs primarily as H_3AsO_4 at pH < 2, and both $H_2AsO_4^-$ and $HAsO_4^{2-}$ species exist in the pH range from 2–11. At low E_h values, H_3AsO_3 is the predominant inorganic arsenic species under reducing conditions. At E_h values below -250 mV, in the presence of sulphur or hydrogen sulphide compounds, As_2S_3 can be formed but these conditions are not environmentally relevant, whilst conditions which are sufficiently reducing to form arsine and elemental arsenic are also very rare in the environment (Wang and Mulligan, 2006; Sharma and Sohn, 2009).

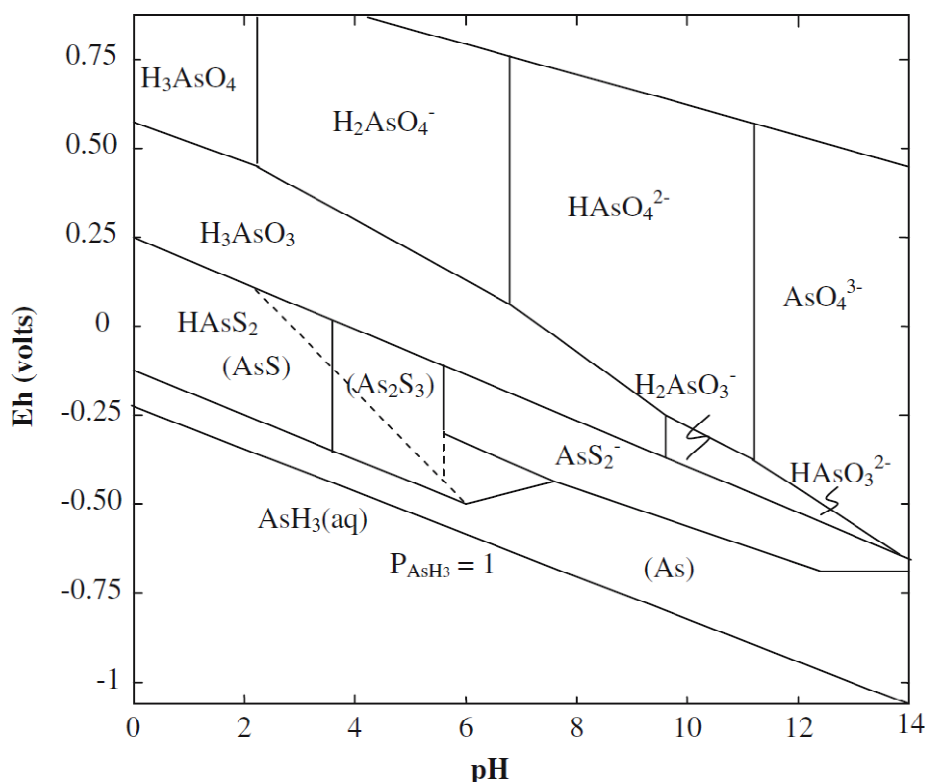


Figure 2. Eh-pH diagram for inorganic arsenic in the environment.

Slika 2. Eh-pH dijagram za neorganski arsen u životnoj sredini.

In reducing conditions, in the absence of oxygen and nitrate, trivalent arsenic dominates. In waters which contain oxygen and nitrate, pentavalent arsenic dominates. This is extremely important during the preparation of drinking water, as As (III) and As (V) behave differently during water treatment and express different toxicities in humans, with As(III) being more mobile and more toxic than As(V) (Guan et al., 2009).

2.3 The role of natural organic matter in arsenic mobility

Some form of natural organic matter (NOM) is present in all natural waters. NOM originates mainly from the chemical and microbial decomposition of land and aquatic animals and plants (Wang and Mulligan, 2006). When present in the aquatic environment, dissolved organic matter (DOM) is a complex mixture of heterogeneous macromolecular substances, the nature and structure of which, as well as the amount present, varies widely from water to water. NOM may be classified as belonging to either hydrophobic (such as humic acids and fulvic acids, see figure 3) or hydrophilic (further characterised as acidic or non-acidic) NOM fractions (Sharp et al., 2006).

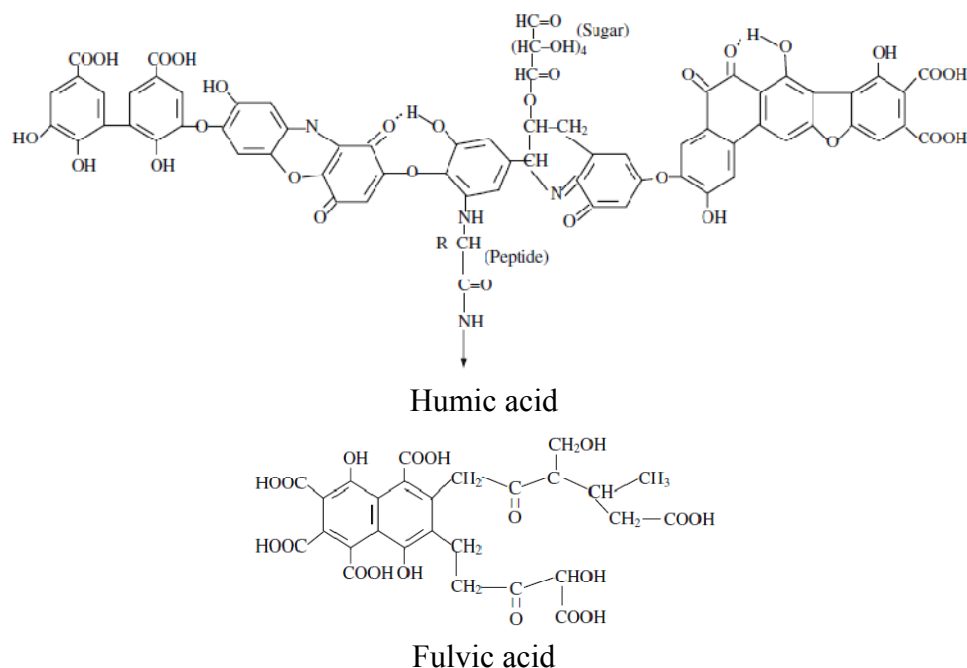


Figure 3. Generalised structures of the hydrophobic NOM fractions.

Slika 3. Opšte strukturne formule hidrofobnih frakcija POM (Wang and Mulligan, 2006).

The chemical structures of these fractions are very complex, with multiple aromatic rings and a wide variety of functional groups (Ghabbour, 2001; Matilainen et al., 2011). It is these functional groups which allow NOM to participate in redox reactions with arsenic and other water constituents.

In general, the deeper the aquifer, the more anoxic the conditions. Deep wells are therefore more likely to contain As(III) than As(V) (Kim et al., 2002). However, the NOM present in all aquifers is theoretically able to both oxidise and reduce arsenic in groundwater, acting as either an electron acceptor or an electron donor, depending upon the functional group involved in the reaction, and the surrounding conditions in the aquifer.

2.3.1 Effects of NOM on drinking water quality

The influence of NOM on the quality of drinking water is multifaceted (Ghabbour, 2001). NOM affects the organoleptic properties of water, giving it a specific colour (brown-yellow) and an unpleasant odour and taste. More significantly, NOM drinking water can act as a source of precursor material for a broad spectrum of disinfection by-products, many of which, such as the trihalomethanes and other organochlorine compounds, are human carcinogens (Molnar et al., 2013; Tubić et al., 2013). Furthermore, NOM can act as a substrate promoting the growth of microorganisms, potentially leading to microbiological contamination of water in distribution systems.

NOM can also interfere with water treatment processes designed to remove other water constituents, such as coagulation or adsorption technologies for the removal of arsenic. As explained in more detail in sections 2.5 and 2.6, NOM can either consume process

chemicals or adsorption sites intended for arsenic, or its multiple reactive functional groups, such as phenolic and carboxylic acids, can directly interact with the arsenic in solution, changing its behaviour in physical-chemical processes (Redman et al., 2002; Buschmann et al., 2006; Liu et al., 2008).

2.3.2 Interactions between arsenic and natural organic matter

The influence of NOM on the behaviour of arsenic has been investigated by many authors, who have focused on its effect of arsenic adsorption, speciation and mobility (Ko et al. 2004; Bauer and Blodau, 2006; Ruiping et al., 2009; Pallier et al., 2010), but little is known about the interaction of natural organic matter and arsenic in the water, despite those interactions playing a key role in deciding whether or not a certain drinking water treatment technology will be effective (Wang and Mulligan, 2006).

The effect of the presence of NOM on the adsorption of arsenic onto goethite and hematite were examined by Weng et al. (2009) and Redman et al. (2002) respectively. Weng et al. (2009) concluded that the interactions between fulvic acid and arsenate were stronger than the interactions between humic acid and arsenate, due mainly to differences in the particle size of fulvic (FA) and humic acids (HA). FA particles are smaller than HA particles, and when present on the goethite surface, contributed to stronger repulsive electrostatic interactions between the adsorbed FA and arsenate. Redman et al. investigated six different types of NOM and found that four formed complexes in water with both arsenate and arsenite. The degree of complexation depended on the origin of the NOM. Redman et al. (2002) concluded that the presence of NOM promotes the mobility of arsenic, in particular As(III), such that in aquifers located in arsenic-bearing iron minerals, NOM may lead to elevated concentrations of dissolved arsenic in the water.

Both FA and HA can theoretically act as electron acceptors or donors in the redox reactions of arsenic. In general, oxidation of As(III) to As(V) is more common, but the opposite reduction reaction has also been observed (Redman et al., 2002; Ko et al., 2005; Bauer and Blodau, 2006).

Fulvic and humic acids form stable complexes with mineral surfaces, effectively blocking the adsorption of arsenic on iron oxides, aluminum, quartz and kaolinite. They can therefore increase the desorption of arsenic from the soil material with which arsenic is usually associated, namely the metal oxide fractions. Bauer and Blodau (2006) reported a small but significant increase in the mobility of arsenic, concluding that pore waters rich in NOM could release 3 times more arsenic from soils than in waters poor in dissolved organic matter (DOM).

In addition to the competitive effects of adsorption, NOM may affect the distribution of arsenic through some other mechanisms. In many situations, the degradation and oxidation of NOM can be associated with a reduction of arsenate to arsenite. Some authors believe that arsenic can also form complexes with NOM via a bridging metal ion. For example, iron oxides and hydroxides are considered major adsorbents for As(V) in many sandy

aquifers (Smedley and Kinniburgh, 2002). The formation of complexes between NOM and arsenic on the surface of minerals can reduce or increase the solubility of arsenic in groundwater (Weng et al., 2009).

Ko et al. (2005) identified humic acid in particular as playing a strong role in the speciation, i.e. the oxidation state of arsenic, thus affecting its future fate and transport. They reported that twice as much As(III) complexed with HA as As(V), under the same experimental conditions, and that HA also acted as an electron acceptor in the oxidation of As(III). Wang and Mulligan (2006) proposed a possible structure for As:NOM complexes, given in figure 4.

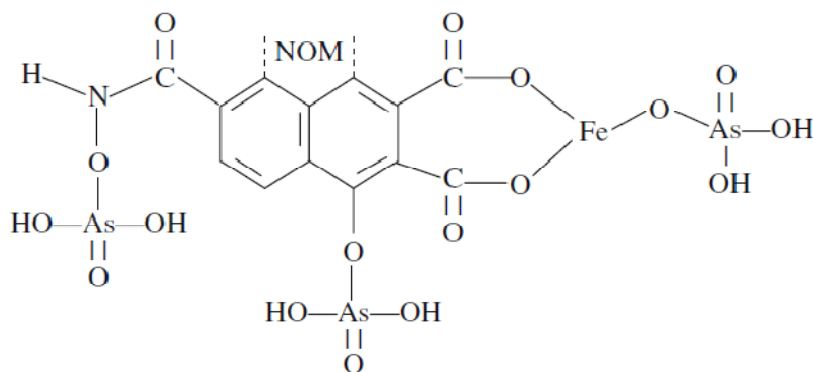


Figure 4. Hypothetical structure for As:NOM complexes.

Slika 4. Predložene strukture As:POM kompleksa. (Wang and Mulligan, 2006)

Water pH plays an important role in reactions between NOM and arsenic because it controls the charge of the reactive functional groups. The effect of organic matter on the adsorption and mobility of arsenic depends in part on the solubility under certain environmental conditions (e.g. pH and ionic strength) (Ko et al., 2004). For example, Liu et al. (2008) demonstrated that the presence of 8 mg C/l NOM in simulated raw water significantly reduces the adsorption of arsenic on TiO₂. Without NOM, arsenic adsorption increased with increasing solution pH in the range from pH 4.0 to 9.4, whereas in contrast, in the presence of NOM they found arsenic adsorption was greatest at pH 7.4, and fell at higher pH values (Liu et al., 2008)

In addition to the pH, the mass ratio of NOM also plays an important role in the mobilization of arsenic. In investigations using humic acid (HA) as a model NOM substance, Wang and Mulligan (2009) concluded that at concentrations less than 2 mg As/g HA, arsenic mobilization was inhibited in acidic environments, and that arsenic mobilization increased with increasing NOM/As ratio. At neutral pH, HA increased arsenic significantly. The effects of NOM on adsorption of arsenic speciation and mobility are now therefore subjects of great interest to the scientific community, and an understanding of the interactions between NOM and arsenic is seen as a key factor for the selection of technologies for drinking water treatment (Mulligan and Wang, 2006).

2.4 Technologies for the removal of arsenic from drinking water

Given the ubiquitous nature of the problems with arsenic contamination throughout the world, a large number of treatment technologies have been developed for the removal of arsenic from drinking water. In 2005, the US Environmental Protection Agency (USEPA) updated their list of Best Available Technologies (BATs) for arsenic removal, which include the following technologies (USEPA, 2005): ion exchange resins, activated alumina, reverse osmosis, enhanced lime softening, enhanced coagulation/filtration, iron removal by oxidation and filtration, and several alternative adsorption media still under development. As explained below, USEPA also names pre-oxidation and pH adjustment as BATs for arsenic removal, due to the fact their application is frequently necessary to improve the efficacy of the other BATs. The combination of enhanced coagulation and micro-filtration (MF) is not named as a BAT due to lack of pilot data. However, EPA have acknowledge that this technology meets the other criteria for BAT classification (Wickramasinghe et al., 2014).

Preoxidation is necessary in many cases, to facilitate the removal of inorganic As(III) via conversion to As(V). This step is often necessary to achieve optimal performance of unit processes. Chlorine, permanganate, ozone, and manganese dioxide media are all effective oxidizing agents for this process (Bissen and Frimmel, 2003; Sancha, 2006; Cui et al., 2015).

pH Adjustment: removal performance for many arsenic removal technologies is pH dependent. Therefore, pH adjustment may be necessary to optimize arsenic removal, especially where the groundwaters are naturally basic (Baskan and Pala, 2009; Pallier et al., 2010).

Ion Exchange is a physical-chemical process in which ions are exchanged between a solution phase and solid resin phase. Ionisable groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e. selectivity) for the resin. This technology is not effective for As(III) removal, and therefore requires a preoxidation step (Möller and Sylvester, 2008)

Activated Alumina (AA). Activated alumina is a sorption process which uses porous, granular material with ion exchange properties. In drinking water treatment, packed-bed AA adsorption is commonly used for removal of natural organic matter and fluoride. The removal of both As(V) and As(III) by adsorption may be accomplished by continuously passing water under pressure through one or more beds (Singh and Pant, 2006).

Reverse Osmosis (RO). RO is a pressure-driven membrane separation process capable of removing arsenic from water by means of particle size, dielectric characteristics, and hydrophilicity/hydrophobicity (George et al., 2006). RO also effectively removes other constituents from water, including organic carbon, salts, dissolved minerals, and colour.

Enhanced Lime Softening. Lime softening is a precipitative process commonly used to remove calcium and magnesium cations from solution. To remove arsenic, lime is added to

increase the pH above 10.5 to form magnesium hydroxide. In this pH range, magnesium hydroxide and As(V) are removed by co-precipitation (McNeill and Edwards, 1997).

Enhanced Coagulation/Filtration. Coagulation/filtration is a precipitative process which can be optimized to remove dissolved inorganic As from water. The mechanism involves adsorption and co-precipitation of As(V) to an aluminum or ferric hydroxide precipitate. Preoxidation may be required to effectively remove As(III) because of its overall neutral charge under natural pH. Optimized coagulation-filtration systems are capable of achieving over 90% removal of As(V) (see section 2.6 below).

Oxidation/Filtration (Iron Removal). A precipitative processes designed to remove naturally occurring iron and manganese from water. The process involves the oxidation of the soluble forms of iron and manganese to their insoluble forms that are then removed by filtration. Arsenic is removed via adsorption and coprecipitation. First, soluble iron and As(III) are oxidized. The As(V) then adsorbs onto the iron hydroxide precipitates that are ultimately filtered out of solution. In general, the Fe:As mass ratio should be at least 20:1, which assumes 1 mg/Fe removes 50 µg/As (USEPA, 2005).

Alternative Adsorption Media. Several adsorption media have been accepted for investigation as BATs: titanium based media, zirconium based media, and iron based media. Adsorption on Iron Based Sorbents (IBS) is an emerging treatment for arsenic (see chapter 2.5.3 below). IBS can very effectively treat waters without the need for pH adjustment, unless the pH is >8.

The experimental phase of this work will focus on investigating the application of adsorption technologies and enhanced coagulation for the removal of arsenic and NOM from groundwater. These two technologies are therefore discussed in more detail below.

2.5 Application of adsorption processes for arsenic removal

Adsorption is the process of applying a solid phase for the removal of substances from gaseous or liquid states, whereby the substances in one phase may be separated, and undergo accumulation or concentration on the surface of the second stage (Choong et al., 2007).

One of the key advantages of adsorption processes is their simplicity of implementation. Straightforward process control, scalability, ease of operation, potential for sorbent regeneration, minimum sludge production and ease of sludge handling all combine to make adsorption processes highly efficient methods for removing arsenic from aqueous solutions (Maji et al, 2012).

However, although adsorption technology is considered extremely promising in the treatment of drinking water, the expense of commercially available sorbents, and the expense of the regeneration processes required, has limited its widespread implementation to date, especially in developing countries (Ruiping et al., 2009). In recent years, many

researchers have therefore attempted to identify and use locally available materials to develop inexpensive methods for arsenic removal (Vu et al., 2003; Kumar et al., 2008).

Adsorption using low-cost adsorbents is thus considered to be much cheaper to implement in comparison with membrane separation or ion exchange technologies (Chen et al., 1999). One particularly promising strategy for the development of low-cost adsorbents is the coating of inexpensive and available materials with iron compounds, which have high affinities for arsenic. As discussed below, quartz sand is an example of a cheap material which can be readily coated with iron oxide. This so called iron oxide coated sand (IOCS) shows good promise for the cheap and effective removal of As both (V) and As (III) and may be a suitable alternative to more expensive commercial adsorbents (Feenstra et al., 2007, Vaisha and Grupta, 2003; Benjamin et al, 1996).

2.5.1 Adsorption mechanisms

All water purification technologies have their advantages and drawbacks, and adsorption processes are no exception. Advantages include high removal efficiencies for pollutants, especially organic pollutants; the ability to regenerate the adsorbents; simple installation and maintenance; potential for complete automation; and the availability of a large number of adsorbents. Disadvantages include adsorbents losing their adsorption capacity over time; the resulting requirement for expensive regeneration processes, and the need to dispose of the solid and liquid wastes generated (Yadanaparathi et al., 2009; Inglezakis, 2006).

Adsorption is based on the nature of the interactions between adsorbent and adsorbate particles. Depending on the type of interaction, adsorption may be physical adsorption (physisorption) or chemical (chemisorption). Physisorption is based on van der Waals forces, whereas chemisorption involves electron clouds interactions, charge redistribution and the establishment of chemical bonds. For any specific combination of adsorbent and adsorbate, whether physisorption or chemisorption prevails depends on the nature of the adsorbate and adsorbent and the temperature of the system. In many cases, adsorption mechanisms are mixed, partly physisorption and partly chemisorption (Roy et al., 2014).

Desorption occurs in parallel with the process of adsorption, whereby the primary adsorbed particles return into the liquid phase. The degree of desorption increases as the surface of the adsorbent is covered with the adsorbate. At a certain point, a dynamic balance between adsorption and desorption is reached, the adsorption equilibrium. The rate at which equilibrium is reached depends on a number of factors such as temperature, pH, the type and concentration of the adsorbate and the quality of the adsorbent surface.

Many mathematical models are used to describe the dependence of the quantity of adsorbate bonded per unit mass of adsorbent, known as the load q (usually expressed in mg/kg) and the equilibrium concentration c_e of the adsorbate (mg/l). These models are called adsorption isotherms, to indicate that the dependency expressed applies only at a constant temperature (Dada et al., 2012).

Experimentally, the adsorbate load at equilibrium for a particular mass of adsorbent is calculated using equation 1:

$$q = \frac{(c_0 - c_e) \cdot V}{m}, \quad \text{Eq. 1}$$

whereby c_0 is the initial concentration of adsorbate, V is the volume of adsorbate, and m the mass of adsorbent.

For the purposes of assessing adsorption capacities of sorbents for particular sorbates, the load q is most commonly modelled with the Langmuir and Freundlich isotherms (Dada et al., 2012). The Brunauer–Emmett–Teller (BET) isotherm is also commonly used, during surface area analyses (Rouquerol et al., 1999).

2.5.1.1 Freundlich isotherm

The Freundlich isotherm is described by the following exponential equation:

$$q_e = K_F \cdot c_e^{\frac{1}{n}} \quad \text{Eq. 2}$$

where the load q is usually expressed in mg/kg), K_F is the Freundlich isotherm constant, and n the Freundlich exponent, also known as the adsorption intensity (Dada et al., 2012). K_F and n are specific empirical constants that depend on the nature of the adsorbent and adsorbate and upon the temperature. K_F approximately indicates adsorption capacity, whereas n is a function of the strength of adsorption. When n is 1, the isotherm is linear and the free energy of adsorption is the same for all concentrations, such that adsorption is independent of concentration. When $n < 1$, the isotherm is concave, and the free energy of adsorption decreases with increasing adsorbate concentration. When $n > 1$, the isotherm is convex, increasing concentration increases the free energy of adsorption, and cooperative adsorption is indicated.

The linear form of equation 2 allows experimental data to be fit to the Freundlich isotherm by linear regression, and the coefficients calculated:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad \text{Eq. 3}$$

The Freundlich isotherm assumes multi-layer adsorption on the surface of the adsorbent is possible.

2.5.1.2 Langmuir isotherm

Depending upon the system being investigated, the Langmuir isotherm may be more appropriate (Langmuir, 1918). The Langmuir equation is expressed as

$$q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \quad \text{Eq. 4}$$

whereby K_L is the Langmuir constant, and q_{max} is the maximum adsorption capacity of the adsorbent at equilibrium in mg adsorbate/g adsorbent). The Langmuir equation is linearised as follows:

This allows q_{max} and K_L to be calculated from the slope and intercept of a plot of $1/q_e$ versus $1/c_e$. In order to facilitate interpretation of the parameters obtained by fitting the Langmuir isotherm, the separation factor R_L may also be calculated:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq. 5}$$

The separation factor is effectively defined by the shape of the isotherm, and yields information about the nature of the adsorption process. For $R_L > 1$ adsorption is unfavourable; for $0 < R_L < 1$ adsorption is favourable; for $R_L = 1$ adsorption is linear; and for $R_L = 0$, adsorption is irreversible.

The Langmuir isotherm assumes that only mono-layer coverage of a homogenous surface is possible, and that there are no interactions between adsorbate molecules on adjacent surface sites. It also assumes that the change in free energy, enthalpy and entropy due to adsorption is constant for all concentrations of the solid phase, although this condition is often not met, whereby the adsorption enthalpy changes with increasing concentration of the solid phase.

2.5.1.3 Brunauer–Emmett–Teller (BET) isotherm

The Brunauer–Emmett–Teller (BET) isotherm is an extension of the Langmuir isotherm which allows for multilayer adsorption. It is widely used in surface area analysis, in which the amount of a noble gas adsorbed onto the surface being analysed, is related to the surface area of the sorbent investigated (Rouquerol et al., 1999). BET theory assumes that the gas molecules can physically adsorb onto a solid in layers indefinitely, that no interaction exists between layers, and that each layer obeys the Langmuir isotherm. The BET equation is expressed as:

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c} \quad \text{Eq. 6}$$

where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v the adsorbed gas quantity, v_m the monolayer adsorbed gas quantity and c_B the BET constant calculated as:

$$c_B = \exp\left(\frac{E_1 - E_L}{RT}\right) \quad \text{Eq. 7}$$

where E_1 and E_2 are the heat of adsorption for the first layer and subsequent layers respectively. Plotting $1/v[(p_0/p) - 1]$ against p/p_0 allows the BET isotherm coefficients v_m and c_B to be calculated, from which the specific BET surface area S_{BET} may be obtained from the total surface area S_{total} :

$$S_{total} = \frac{(v_m N_s)}{V} \quad \text{Eq. 8}$$

$$S_{BET} = \frac{S_{total}}{a} \quad \text{Eq. 9}$$

N is Avogadro's number, s the adsorption cross section, V the molar volume of the adsorbate gas, and a the mass of adsorbent.

BET specific surface area determinations are commonly carried out using nitrogen physisorption at low temperatures (77 K). Vacuum dried samples are brought into contact with the gas at different pressures, and the relative pressures measured to determine the volume of gas adsorbed.

2.5.2 Adsorption processes for arsenic removal

In a review of recent literature by Yadanaparathi et al. (2009), which covered the removal of cadmium, arsenic and lead, papers relating to more than 30 different adsorbents for the removal of arsenic were identified. These included different activated and other carbons, activated alumina, bauxite, iron minerals, iron oxides, iron–manganese binary oxides, and many others. The wide variety of adsorbents highlights the importance of the search for cost-effective arsenic removal solutions, whereby inexpensive, easily and locally available adsorbents have been prioritised for investigation.

Activated carbon (AC) is one of the most widely investigated adsorbents for arsenic removal (Mohan et al, 2007; Wennrich and Weiss, 2004; Huang and Fu, 1984; Gimbel and Hobby, 2000). Lorenzen et al., (1995) examined the influence of pH, activated carbon type and various pretreatments on the mechanisms of arsenic adsorption onto activated carbon. They found that As(V) removals were significantly better with ACs with high ash contents, and that pretreatment of AC by Cu(II) increased adsorption capacity. They found an optimum pH value for arsenic adsorption onto Cu(II) enriched AC to be around pH 6, at which pH, in addition to being adsorbed onto the AC, the arsenic could also form an insoluble complex with the Cu(II) (Lorenzen et al., 1995 Mohan, et al., 2007).

ACs impregnated with Fe(II) and Fe(III) have also been investigated, and shown to have higher adsorption capacities for As(III) and As(V) in comparison to non-impregnated carbons (Muniz et al., 2009).

Certain natural **zeolite minerals**, such as clinoptilolite and cabazite, have also been shown to exhibit a strong affinity for arsenite and arsenate. Zeolites are crystalline hydrated aluminosilicate minerals, some of which occur in sufficient quantities and purities to warrant their application in water purification (Kesraoui-Oukiet al., 1994, Mohan et al., 2007). Zeolites have also been successfully modified with organic compounds to improve As adsorption (Misalides et al., 1998).

As explained above, **aluminum oxide (Al_2O_3)** was classified as a BAT for arsenic removal. For effective arsenic removal, preoxidation of As(III) to As(V) and pH adjustment to < 6.5 is required. Above this pH, the presence of competing ions interferes more significantly with the arsenic adsorption process.

The application of **iron based sorbents** for arsenic removal has also been extensively studied, due to their high affinity for As(III) and As(V) (Driehaus et al., 1998; Guo et al,

2005 ; Guan et al., 2008). Iron oxides, oxyhydroxides and hydroxides (collectively, iron oxides), contain Fe, O and/or OH. There are many different types, which differ in their crystal structures, composition, and Fe valence state. Some examples of iron based sorbents are given below.

Ferrihydrite has been extensively studied for the removal of arsenic. It is composed of very small crystals, with a crystal structure of $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ (Michel et al., 2007). Its small particles (around 5 nm) are responsible for its very high specific surface area (200–500 m^2/g), making it ideal for adsorption of many anions and cations from aqueous solutions (Yavuz et al., 2006; Pinney et al., 2009; Gilbert et al., 2009).

Granulated ferric hydroxide (GFH) is a commercially available porous Fe-based adsorbent made up of iron hydroxide and admixtures of crystalline goethite. It is very porous adsorbent (micropore volume $\sim 0.0394 \pm 0.0056 \text{ cm}^3/\text{g}$, mesopore volume $\sim 0.0995 \pm 0.0096 \text{ cm}^3/\text{g}$), with a BET surface area of $235 \pm 8 \text{ m}^2/\text{g}$ (Giles et al., 2011). GFH has a high adsorption capacity, and may be applied in simple fixed bed reactors, like aluminum oxide or activated carbon. A key benefit of GFH is that pH correction or chemical pretreatment is not required (Naidu and Bhattacharya, 2006). Arsenic adsorption by GFH is a proven method that provides high operational reliability with minimal demand for process monitoring (Jekel and Seith, 2000).

SORB 33 is another commercially available iron oxy hydroxide adsorbent, specifically designed to remove arsenic from water (Dennis and Simms, 2004). At high pH, high concentrations of vanadium, phosphate and silicate may compete with arsenic for adsorption sites, reduce process efficacy (Selvin et al., 2002).

Iron minerals such as hematite (Fe_2O_3) (Redman et al., 2002), goethite ($\alpha\text{-FeOOH}$), magnetite (Fe_3O_4) and amorphous iron oxide (Dixit and Hering, 2003) have been studied. Commercially available goethite and hematite have been shown to remove over 80% of arsenic (Mamindy-Pajany et al., 2009), with impregnation of the goethite surface with Cu(II), Ni(II) and Co(II) ions increasing the As(V) removal capacity (Mohapatra et al., 2006)

Zero valent iron (ZVI) is an adsorbent which can also act as a reducing agent, make it suitable for the removal of organic and inorganic arsenic (Kiem et al., 2003, Tyrovola et al., 2007). Lackovic et al. (2000) demonstrated that ZVI can simultaneously remove As(III) and As(V), with removal capacities of 298 mg/g ZVI or 669mg/g ZVI respectively, without the need for additional As(III) oxidation (Sun et al., 2006). The removal mechanism for As(III) and As(V) includes the formation of Fe(II) and Fe(III) corrosion products on the surface of ZVI. These corrosion products are amorphous mixtures of Fe(III)oxides/hydroxides, magnetite and/or maghemite (g-FeOOH) (Farrell et al, 2001; Kane et al., 2005; Manning et al., 2002; Melitas et al, 2002). Other studies suggest that precipitation processes are the dominant mechanism for arsenic removal by ZVI (Lackovic et al, 2000; Nikolaidis et al., 2003). ZVI is often applied in water treatment in the form of iron filings.

Iron oxide based sorbents developed by coating/impregnating a variety of materials with iron oxide are a final subset of the iron based sorbents, and are described in the next section.

2.5.3 Arsenic removal by iron oxide based sorbents

Iron oxide has great affinity for As(III) and As (V). However, it is generally in the form of a very fine powder, making its separation from solution after the adsorption treatment difficult, limiting its use in continuous column operations (Maiti et al., 2012). Head loss during passage through the column and the difficulties with regeneration are additional disadvantages which limit the application of iron oxide (Kundu and Gupta, 2006).

In order to overcome these problems, recent work has focused on coating different materials with Fe(III) oxides/oxyhydroxides, including sand (Hsu et al., 2008a), coal (Chen et al., 2007, Gu et al., 2005; Fierro et al., 2009), cellulose (Guo and Chen, 2005), chitosan (Gupta et al., 2009), cement (Kundu and Gupta, 2007) active aluminum (Kuriakose, 2004) and others.

One benefit of iron oxide coated sand (IOCS) is its particle size makes it suitable for packing in columns, and applicable as a permeable reactive barrier (Higgins and Olson, 2009). Fixed bed IOCS reactors have been proposed by the EPA (USEPA, 2000; Thirunavukkarasu et al., 2003; Mohan et al., 2007). Filtration using coated sand provides several advantages, including high sorption capacity, and high porosity media with a minimal risk of clogging and easy regeneration (Ko et al., 2007). IOCS filters have been successfully applied in rural areas of developing countries (Petruševski et al., 2002).

Note that by itself, quartz sand is relatively ineffective at removing arsenic due to its very low isoelectric point (pH 2) meaning its surface is generally negatively charged (Scholl et al., 1990). In contrast, IOCS have higher isoelectric points, and also very large surface areas due to their amorphous structure (Hsu et al., 2008a, Korshin et al., 1997, Lo et al., 1997). Gupta et al. (2005) compared the removal of As(III) by IOCS and raw quartz sand, and found IOCS to have an adsorption capacity of 0.029 mg/g, five times greater than the uncoated sand.

IOCS has been made in the laboratory by two main methods, one using iron chloride (IOCS1, Joshi and Chaudhuri, 1996), and the other using iron nitrate and higher temperatures during the coating process (IOCS2) (Thirunavukkarasu et al., 2002; Thirunavukkarasu et al., 2003). These IOCS have subsequently been investigated and found to be effective for the removal of arsenic and other heavy metals by a number of authors (Bailey et al. 1992; Benjamin et al. 1996; Lai and Chen, 2001; Ko et al., 2002; Vaishya and Gupta 2003a ; Vaishya and Gupta 2004). Hsu et al. (2008a) have shown that the use of IOCS can achieve high removal efficiency of both As(V) (99.5%) and As(III) (79%) at pH 5, from an initial arsenic concentration of 300 µg/l.

In addition to inorganic arsenic, Thirunavukkarasu et al. (2002) demonstrated that IOCS2, and to a lesser extent IOCS1, is also effective at removing organic arsenic (DMA), concluding that the improved performance of IOCS2 is due to the higher temperatures applied during the coating process.

Sulphate modified iron oxide coated sand (SMIOCS) was investigated by Vaishya and Gupta (2003c, 2004). Prepared by coating silica sand with BaSO₄ and Fe, maximum removals of As(III) were achieved in the pH range 7–9, whereas maximum removals of As(V) were achieved at acidic pH values.

2.5.4 Arsenic adsorption mechanisms by iron oxide-based adsorbents

The mechanism of arsenic removal by natural iron oxide minerals (magnetite, hematite, goethite and laterite) was investigated by Aredes et al. (2012). They measured the surface charge of the adsorbents to explain the electrostatic interactions between iron oxides and arsenic. The surface charge of iron oxides depends on the protonation and deprotonation of the surface hydroxyl groups (Schwertmann and Cornell, 2003):



The equilibrium of these reactions depends on the pH value. Acidic pH values shift the H⁺ balance to the left, such that positive and neutral groups prevail, making the surface of the oxide positively charged. Reduction in the number of protons, under basic conditions, shifts the equilibrium of the reaction to the right, and the surface becomes negatively charged. However, depending upon the isoelectric point of the surface, positive, negative and neutral functional groups can coexist on the surface of the iron oxide at any pH value. The isoelectric point of most iron oxides is in the range pH 6–10 (Cornell and Schwertmann, 1996). At pH values lower than the isoelectric point, Fe(OH)₂⁺ is the predominant form, and the adsorbent surface is positively charged, increasing the affinity of the surface for arsenate oxyanions.

The adsorption of arsenate anions (H₂AsO₄⁻, HAsO₄²⁻) on the surface of the iron oxide can occur via three mechanisms: the creation of inner sphere complexes (specific adsorption), outer sphere complexes (non-specific adsorption) and ion–diffusion adsorption (Stumm, 1992).

Evidence for specific adsorption is found when arsenate adsorption on the surface of iron oxide causes a displacement of the isoelectric point. This movement of the isoelectric point is a good indication of the high sorption affinity of the iron oxide surface for arsenic and the formation of inner sphere complexes between the arsenate and the surface. The reduction in the surface charge in the presence of arsenic reveals the adsorption of negative arsenate ions on the surface of the adsorbent (Schwertmann and Cornell, 2003).

Non-specific adsorption of anions (outer sphere complexes) occurs only between oppositely charged species, and is insignificant above the isoelectric point, when the surface of iron oxide is negatively charged.

Grössl et al. (1999) investigated the kinetics of adsorption/desorption of arsenate on goethite, and proposed a two-stage arsenate adsorption mechanism leading to the formation of inner sphere bidentate surface complexes (figure 5). In the first step, rapid ligand exchange occurs between the H_2AsO_4^- oxyanion and the OH groups on the goethite surface, forming the inner spherical monodentate complex. The second step involves a slow ligand exchange which forms the inner sphere surface bidentate complexes.

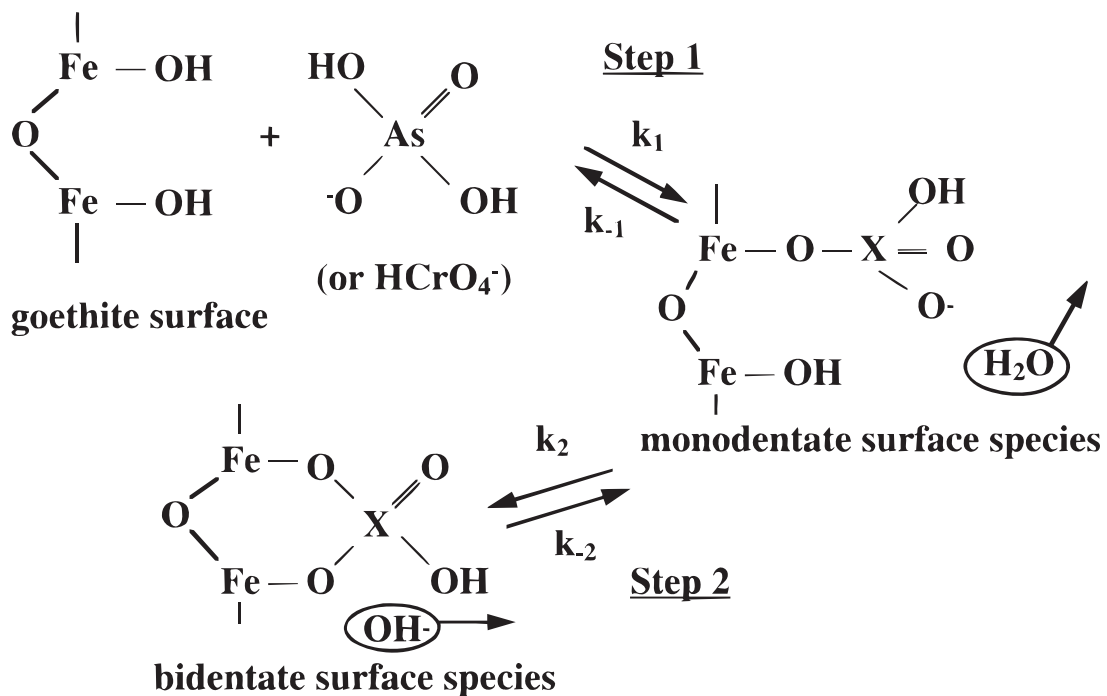


Figure 5. Proposed mechanism for adsorption of oxyanions on goethite; X = As(V).

Slika 5. Predloženi mehanizam adsorpcije oksijaniona na geotitu; X = As(V).

(Gross et al. 1997)

Jain et al. (1999) also found evidence for the formation of bidentate complexes, this time on the surface of ferrihydrite. Bidentate complexes were favoured between pH 4.6–8, whereas above pH 8, monodentate complexes between ferrihydrite and arsenate were more dominant.

According to Thirunavukkarasu et al. (2003), the iron oxide on the surface of IOCS is a combination of goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). These iron oxides are stable compared to other iron oxides, and are usually the end products of the transformation (dehydration and dehydroxylation) of many other iron oxides (Schwertmann and Cornell, 1996). Oxyanions such as arsenite and arsenate are adsorbed onto the surface by specific adsorption, forming inner spherical oxyhydroxide complexes. Adsorption therefore involves substitution of ligands to the outside of the hydroxyl groups on the surface of the adsorbent.

2.5.5 Competition from silicates, phosphates and other ions

As shown above, under optimum conditions, careful adsorbent selection may remove metals from solution to very low levels over a wide pH range. However, the applicability of the adsorption process depends largely on the chemical characteristics of the groundwater, which may contain a wide variety of different chemical constituents. Phosphates, bicarbonates, sulphates, chlorides, silicates, calcium and humic acid are among the major ions usually present in groundwaters (Katsoyiannis and Zouboulis 2002). One of the most significant disadvantages of adsorption processes is that some of those other water constituents can interfere with the removal of the target compound. Many authors have reported that the presence of competing anions and cations can negatively influence arsenic adsorption. In the case of arsenic, high levels of natural organic matter (NOM), orthophosphates, and silicates have been shown to weaken arsenic removal efficiency by competing for sorption sites on iron hydroxide precipitates and/or by changing the electrostatic charge on the surface of the adsorbent. (Katsoyiannis and Zouboulis, 2002; Zhang et al., 2003; Vaishya and Gupta, 2003a, 2003b, 2004; Radu et al., 2005).

The adsorption of arsenic is thus a complex function of not just the concentration of arsenic, the water pH and the species of arsenic, but also of the presence of competing ions. Most research related to competitive adsorption is carried out in single component systems. However, arsenic contamination occurs in waters with a number of ions that may affect its efficient removal by adsorbents (Mohan et al, 2007).

Adsorption in multi-component systems is complicated by ion-ion competition and the interaction of ions with a specific surface area. Multi-component interactions occurring at specific adsorption sites, where they establish a solid–liquid equilibrium depending on the different adsorption capacities of the adsorbent for the individual ions. The interpretation of multi-component systems is complex, as they are effected by many parameters, such as ionic radius, electronegativity, pH and the availability of active sites on the adsorbent (Chiban et al., 2012).

Chiban et al (2011) quantified the effect of ionic interactions on adsorption by determining the maximum adsorption capacities for arsenic in mixtures with other ions (q_{mix}) and calculating ratios of q_{mix} with the adsorption capacity for arsenic in the absence of competitive ions (q_0). Where $q_{mix}/q_0 > 1$, adsorption is improved by the presence of other ions, when $q_{mix} = q_0$, there are no mutual interactions, and when $q_{mix}/q_0 < 1$, arsenic adsorption is suppressed by other ions.

Hsu et al. (2008) investigated the adsorption of arsenic on IOCS in the presence of phosphate, and found that 1 mg/l phosphates was sufficient to inhibit arsenic adsorption. Greater phosphate concentrations lead to more pronounced inhibitory effects. Phosphorus and arsenic are in the same group of the periodic system and the molecular structure of phosphorous ions, which are tetrahedral anions, is very similar to the structure of arsenate ions (Yiran et al., 2010). Phosphates therefore directly compete with arsenic for adsorption

sites, reacting with the functional (hydroxy) groups to form spherical complexes with iron oxide surfaces (Mamindy-Pajany et al., 2011). The degree of complex formation between Fe(III) and phosphates is a function of the pH, such that increasing the pH favours the formation of Fe-HPO_4^{2-} complexes on the surface of the adsorbent, resulting in reduced arsenic removals (Katsoyiannis and Zouboulis, 2002).

Zhong et al. (2007) attributed the adsorption of phosphate ions onto goethite as a ligand exchange reaction on the surface of the adsorbent, in which the phosphate ion replaces surface hydroxyl groups. Phosphate adsorption onto goethite formed inner sphere bidentate complexes ($(\text{FeO})_2\text{PO}_2(\text{H})$) over a range of pH values (pH 3.5–8), whereas higher pH values lead to the prevalence of monodentate complexes ($\text{FeOPO}_3(\text{H})$). Similarly, the adsorption of phosphate onto hematite takes place by the formation of monodentate complexes (Elzinga and Sparks, 2007).

Silicate species are another common oxyanion present in natural waters in concentrations of 0.45–14 mg/l (Meng et al., 2000). Like arsenic, orthosilicates (H_4SiO_4 and H_3SiO_4^-) have a high affinity towards the surface of the iron (hydr)oxides and also form inner sphere complexes via ligand exchange (Doelsch et al., 2001, 2003; Hansen et al., 1994b; Vempati et al., 1990).

Jeong et al. (2007) and Meng et al. (2002) both investigated arsenic adsorption in the presence of silicates, and found that at silicate concentrations above 1.4 mg/l, adsorption of silicates on the surface of iron oxide reduced the number of sites available for arsenate and also increased the electrostatic repulsion between arsenate ions and the surface. Lower silicate concentrations did not interfere with arsenic adsorption, as silicate has a much smaller binding constant than arsenate (Meng et al., 2002). Singh et al. (2005) also reported complexation between Fe(III), Si(IV) and As(V) and competition between As(V) and Si(IV) for sorption onto ferrihydrite.

According to Davis et al. (2002), at $\text{pH} > 8.5$, about 50% of soluble silicate is polymerised, of which about 99% is in dimeric form ($\text{Si}_2\text{O}_2(\text{OH})_5^-$). Polymerisation increases the effect of ligand competition (Doelsch et al., 2001, 2003; Hansen et al., 1994b). Gebreyowhannes (2009) also reported that silicate polymerisation inhibited arsenic removal by IOCS, and noted that at lower pH values where the majority of silicate is not polymerised, the adsorption of As(V) in the presence of silicate is more efficient, as the affinity of $\text{Si}(\text{OH})_4$ for the positively charged IOCS surface is much weaker.

Finally, from pH 6 to 8, humic acids (a fraction of NOM, see section 2.3) are present in the anionic form (Bob and Walker, 2001). Humic acids have a strong tendency to adsorb onto the surface of iron oxide via ligand exchange between the NOM carboxyl/hydroxyl groups and the functional groups of iron oxide (Saito et al., 2004; Vermeer et al., 1998).

Mak et al. (2011) investigated the removal of arsenic by a combination of IOCS and ZVI in the presence of humic acids. They observed the adsorption of humic acid onto the adsorbents, blocking As(V) adsorption sites, preventing its removal.

2.5.6 Characterisation of adsorbents

In order to understand the adsorption mechanisms involved, the physical-chemical characterisation of adsorbents is required. The isoelectric point and BET specific surface area have already been mentioned several times in the text above, and the use of scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) are also significant.

Isoelectric point

The adsorption of ions onto solid phases depends on the charge of the solid phase. In general, metal oxides and oxyhydroxides have variable surface charges at different pH values. The isoelectric point (pH_{pzc}) or point of zero charge of a solid is the pH at which the solid is neutral in an aqueous solution. When solution pH is less than the pH_{pzc} , the surface of the solid surface is positively charged, increasing its affinity for arsenic oxyanions due to electrostatic interactions. Metal oxides and oxyhydroxides with high As(V) adsorption capacities tend to have pH_{pzc} in the range pH 7–9 (Dzombak and Morel, 1990; Sigg and Stumm, 1981; Davies and Kent, 1990; Fuller et al., 1993). The amorphous iron oxyhydroxide has the highest adsorption capacity for the largest area. However, size is not the only criterion for the high capacity of removing metal ions because other mechanisms (precipitation, ion exchange) have an important role (Mohan et al., 2007).

BET specific surface area

As explained in the section on isotherms above (section 2.5.1.3), the BET isotherm is regularly used to determine the specific surface area of a sorbent. In general, the larger the specific surface area of a sorbent, the greater the number of adsorption sites available, so that sorbents with large specific surface areas are more effective. During the determination of BET surface areas, additional data analysis via the application of Barrett-Joyner-Halenda (BJH) theory can also yield information about the micro and mesopore volumes (Lu et al., 2012).

Scanning electron microscopy and energy dispersion spectroscopy

A scanning electron microscope (SEM) produces images of a sample by scanning it with a very focused beam of electrons. The electrons interact with the atoms in the sample, producing signals which can yield information about the topography and composition of the surface of the sample. Images with resolutions < 1 nm may be scanned, and the large depth of field is responsible for the 3D appearance of the images (Goldstein, 2003).

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique which is related to SEM, and which is used for elemental analysis of a sample. It uses the focused electron beam of a SEM to excite the atoms on the surface of the sample. When the beam of electrons excites an electron in an inner shell it creates an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, releasing energy in the form of an X-ray. The exact energy of the X-ray emitted is characteristic of the difference in energy between the two electron shells and the atomic structure of the

emitting element, allowing a detector to determine the elemental composition of sample (Goldstein, 2003).

2.6 Coagulation processes for arsenic removal

Coagulation and flocculation are among the most frequently applied methods for removing arsenic during the preparation of drinking water. One particular advantage they have over adsorption is they also effectively remove NOM, which is often present together with arsenic, and which itself requires removal in order to provide safe, hygienic tap water. Coagulation is the destabilization of colloids by neutralizing the forces that hold them together, with cationic coagulants providing a positive charge to reduce the negative charge (zeta potential) of colloids. As a result of this process, colloidal particles are grouped in the form of large mass particles. Fast mixing is required to spread the coagulant throughout the volume of liquid. In contrast to coagulation, flocculation does not involve charge neutralization, but instead uses polymers to aid the formation of bridges between the large mass particles, giving rise to larger agglomerates (Choong et al., 2007).

Coagulation and flocculation is one of the most common techniques for removing arsenic from water because of its high efficiency and low cost, leading to the USEPA naming it a BAT for arsenic removal (Song et al., 2006; Baskan and Pala, 2009).

There are three mechanisms by which the removal of arsenic is carried out during the coagulation process:

- a) precipitation: the formation of insoluble compounds $\text{Al}(\text{AsO}_4)$ or $\text{Fe}(\text{AsO}_4)$,
- b) co-precipitation: the incorporation of dissolved arsenic in the precipitate,
- c) adsorption: the formation of a complex between dissolved arsenic and the surface of insoluble metal hydroxide.

The main mechanisms for the removal of arsenic are co-precipitation and adsorption, while precipitation is less significant (Pallier et al., 2010).

The arsenic removal mechanism involves adsorption of As(V) onto the aluminum or iron hydroxide flocs. As(III) is not be effectively removed by this method as it is present in neutral forms at drinking water pH (Pallier et al., 2010). The efficiency and cost-effectiveness of coagulation for arsenic removal depends on many factors, including the type and dose of coagulant applied, the water pH and the presence of other water constituents.

According to Han et al. (2003), optimized systems for coagulation and filtration can achieve better than 90% As(V) removals with just 20 mg FeCl_3/l , in water containing 68 $\mu\text{g}/\text{l}$ As. Although arsenic can also be removed by aluminum-based coagulants, iron-based coagulants (iron chloride or iron sulphate) have generally given better results (Feroze, 2001).

Water pH has a large effect on the arsenic removal mechanism, as does the presence of other anions such as phosphates and silicates, bicarbonates, and the presence of NOM. The optimum pH value for the removal of arsenic by aluminum based coagulants is in the range pH 6–7, with removal efficiency falling sharply outside this range. According to Baskan and Pala (2009), coagulation and flocculation with iron salts works best at pH 7.

Where large amounts of As(III) are present, it is necessary to introduce an oxidation pre-treatment to increase the efficiency of coagulation and flocculation (Lee et al., 2003). As(V) is considerably easier to remove by coagulation and flocculation than As (III). Jiang (2001) found that the use of oxidation, coagulation/flocculation and adsorption can be achieve arsenic removals from 500 µg/l to below 10 µg/l. The most effective treatment, wherein 100% arsenic removal was achieved, combined chlorine oxidation, FeCl₃ coagulation, sedimentation, and sand filtration.

Pallier et al. (2010) demonstrated competition for hydroxide adsorption sites between NOM and As during coagulation, whereby the presence of 10 mg C/l DOC doubled the FeCl₃ dose required to reduce arsenic concentrations from 100 µg/l to 10 µg/l.

In order to maximise process efficiency and efficacy for arsenic and NOM removal, the choice of coagulant is very important. Residual iron and aluminium concentrations after treatment must also be taken into account. Letterman and Pero (1990) reported that, residues from coagulation and flocculation in drinking water can cause various diseases in humans, such as Alzheimer's disease (Wade and Cooper, 1995). The residual content of aluminium in drinking water is therefore limited to 0.2 mg/l, while the allowable concentration of iron is 0.3 mg/l (Official Gazette RS 42/98 and 44/99, 1998).

2.6.1 Combining coagulation with preoxidation

In order to improve the removal of arsenic by coagulation or other removal technologies, it is common to apply a preoxidation step to convert As(III) to As(V) (Terracciano et al., 2015). Preoxidation is also used for the removal of other inorganic compounds, colour, taste, odour, turbidity and suspended particles. Preoxidation can also lead to partial degradation of NOM and inactivation of microorganisms, as well as to the improvement of coagulation and flocculation processes.

Preoxidation may be carried out using chlorine, permanganate, hydrogen peroxide, ozone, or manganese dioxide, all of which can be effective oxidizing agents (Bissen and Frimmel, 2003; Sancha, 2006; Cui et al., 2015).

Ozone in particular is very widely applied as a preoxidation step. Originally used within treatment plants for water disinfection, ozone was soon found to achieve many positive effects. Oxidation by ozone affects the organoleptic qualities of water (removing components that give water colour, smell and taste), oxidizes iron, manganese and sulphides, improving their removal and can increase the level of turbidity removal. (Matilainen and Sillanpää. 2010).

However, the application of ozone can have some disadvantages: it can lead to the formation of oxidation by-products (aldehydes, ketones, and in cases where bromide is present, bromate and a number of brominated disinfection byproducts), it is expensive to implement, ozone generation requires high energy and must be generated on-site, and ozone itself is very corrosive and toxic (Treguer et al., 2010).

Preoxidation with ozone has been successful in combination with coagulation and flocculation processes. A number of authors report that ozone affects the behaviour of particles present in the water, changing the distribution of particle sizes (they become larger), forming colloidal particles from previously dissolved organic matter. This improves the removal of TOC and turbidity during the subsequent flotation, sedimentation or filtration whilst decreasing the amount of coagulant necessary to achieve the desired results, increases the rate of settling by formed flocs and extends the operating time of filters as a result of their slower saturation (Singer, 2003; von Gunten 2003). This effect is usually termed microfloculation, and most often occurs at preozonation doses of 0.4–0.8 mg O₃/mg TOC.

However, some authors have shown that preozonation may have negative effects on the process of coagulation. According to Yan et al. (2007), although low ozone doses benefit coagulation, applying high levels of ozone can result in NOM with more lower molecular weight hydrophilic components, which are harder to remove by coagulation. It is therefore necessary to carefully optimize preozonation doses to achieve the more efficient removal of As and NOM.

As an alternative to ozone, preoxidation with hydrogen peroxide has one very major advantage, and that is price. It is however a weaker oxidising agent than ozone, and the arsenic oxidation reaction with hydrogen peroxide therefore proceeds much more slowly than it does with ozonation (Pettine et al., 1999; Sharma and Sohn, 2009). The choice of the most economically feasibly yet technically effective preoxidation treatment for a particular water must therefore be the subject of careful study.

2.7 Arsenic analysis: speciation techniques

The discovery of widespread arsenic poisoning due to arsenic contaminated groundwater in Bangladesh and India galvanised research into the development of analytical techniques to monitor arsenic in its various chemical forms. The different degrees of toxicity and carcinogenicity expressed by the different species of arsenic mean that for adequate risk assessment of the threat posed by arsenic in groundwater, total arsenic concentrations are not sufficient (Akter et al., 2005b). Given the additional fact that the arsenic speciation also affects the physical-chemical properties of arsenic, affecting how it is removed by treatment technologies, and it becomes clear that the arsenic species present in a particular groundwater require separate quantification (Bednar et al., 2004).

Such a speciation method would ideally be capable of being applied for routine analysis, i.e. it should be fast, reliable, inexpensive and easy to use (Hymer and Caruso, 2004).

However, due to the different chemical and physical properties of arsenic compounds, reliable separation of the different types has proven difficult. As a result various separation procedures and detection methods have been developed. Hydride generation of As(III), liquid chromatography, gas chromatography and capillary electrophoresis have all been used to separate particular kinds of arsenic, with ion exchange chromatography (IEC) being most commonly applied (Akter et al., 2005a).

In IEC, the mobile phase is used to transport the sample (and analyte) through a column where the individual compounds enter into competition with oppositely charged ionic functional groups on the stationary phase and the separated analyte ions, replacing them with ions of the mobile phase. IEC separation is often used in combination with inductively-coupled plasma mass spectrometry (ICP-MS) as a detector, thanks to its multi-elemental abilities, low detection limits and wide linear range (Hung et al., 2004; Dressler et al., 1998).

HPLC-ICP-MS using anion exchange columns is perhaps the most versatile method for analysis of organic and inorganic arsenic compounds (Hymer and Caruso, 2004). However, such systems are very expensive to buy and run. A much cheaper alternative to HPLC is to perform the separation of arsenic species by standard solid phase extraction (SPE). SPE methods which apply several different strengths of anion exchange resins in sequence have been recently developed (Yalçın and Le, 1998; Bednar et al., 2004). As well as being much cheaper than HPLC separation, the SPE based separation techniques are also more portable, allowing separation to be carried out in the field, overcoming one of the other difficulties of arsenic speciation analyses, which is the need to preserve the distribution of species in a sample before analysis (Yu et al., 2003).

2.8 Application of Design of Experiments for statistical modelling

To successfully test a hypothesis, and obtain clear, unambiguous and statistically significant results, careful thought must be given to the design of an experiment. During the planning stage of an experiment, the main questions to consider are:

1. What is the hypothesis to be tested?
2. Which responses need to be measured (e.g. reaction yield, percentage contaminant removal, analyte recovery, etc.)
3. Which factors should be held constant during the experiment, and which factors should be variables?
4. What values do the variables need to take to ensure the experiment encompasses the full range of possible conditions?

Once these questions have been answered, a plan of experiments may be drawn up to ensure that enough combinations of factors will be tried to provide sufficient data to draw significant conclusions.

To facilitate this process, Fisher proposed a set of statistical principles called Design of Experiments back in 1935 (Fischer, 1935). His work was developed further by Box and Wilson (1951). Since then, the actual use of Design of Experiments in everyday research has grown steadily in popularity, with the development of statistical software such as Statistica and R playing a major role in increasing its accessibility to scientists outside the field of statistics.

Nowadays, Design of Experiments is most commonly utilised for two closely related problems of experimentation (Kuehl, 2000; Montgomery, 2012):

- to plan the experiment (measurement of relevant process variables)
- statistical (numerical) processing of measurement results in order to obtain a mathematical model.

Experimental design can be defined as a planned approach a scientific problem, in order to determine the causal relationship between the dependent and independent parameters of a process. Its main purpose is to collect the maximum amount of relevant information, with a minimum expenditure of time and extraction equipment and raw materials (Antony, 2010). Experimental design should be as simple and consistent, while fulfilling the requirements set problem (Lazić, 2004).

One area in which Design of Experiments is broadly utilised is in experiments for process optimisation. In such cases, Response Surface Methodology (RSM) is applied as a simple and widely used method for examining the relationship between the independent process parameters and the different characteristics of the resulting product. RSM is an empirical statistical technique that used regression analysis of data obtained in the experiments to solve systems of equations. Each equation represents a response function which is dependent on the variables investigated, and which can be graphed as a response surface (Del Castillo, 2007). Successful use of RSM requires several stages of investigation (Bezerra et al., 2008):

- selection of independent variables which have the greatest impact on response investigated, and definition of the extent of the experimental region or domain,
- choice of experimental design and its implementation in accordance with the selected experiment matrix,
- mathematical and statistical treatment of experimental data to obtain polynomial functions,
- evaluating the appropriateness (fit) of the model,
- verification of whether variable displacement is required in the direction towards the optimum region,
- final optimization of each studied variable.

The benefits of RSM over one-factor-at-a-time experimental design include the ability to identify interactions between the variables studied, a reduction in the number of measurements which need to be performed, a way to quantify systematic error in the procedures applied, and sound statistical treatment to ensure that the results of one's investigation are significant (Bezerra et al., 2008; Baskan and Pala, 2010; Roy et al., 2014).

Figure 6 gives examples of common response surfaces generated during the optimisation of two variables utilising a quadratic response. Figures 5 a) and b) show typical response surface maximums within the experimental domain, whereas in 5 c) the maximum is outside the experimental domain. The response surface in Figure 5 d) has a minimum point, and Figure 5 e) shows critical inflection points.

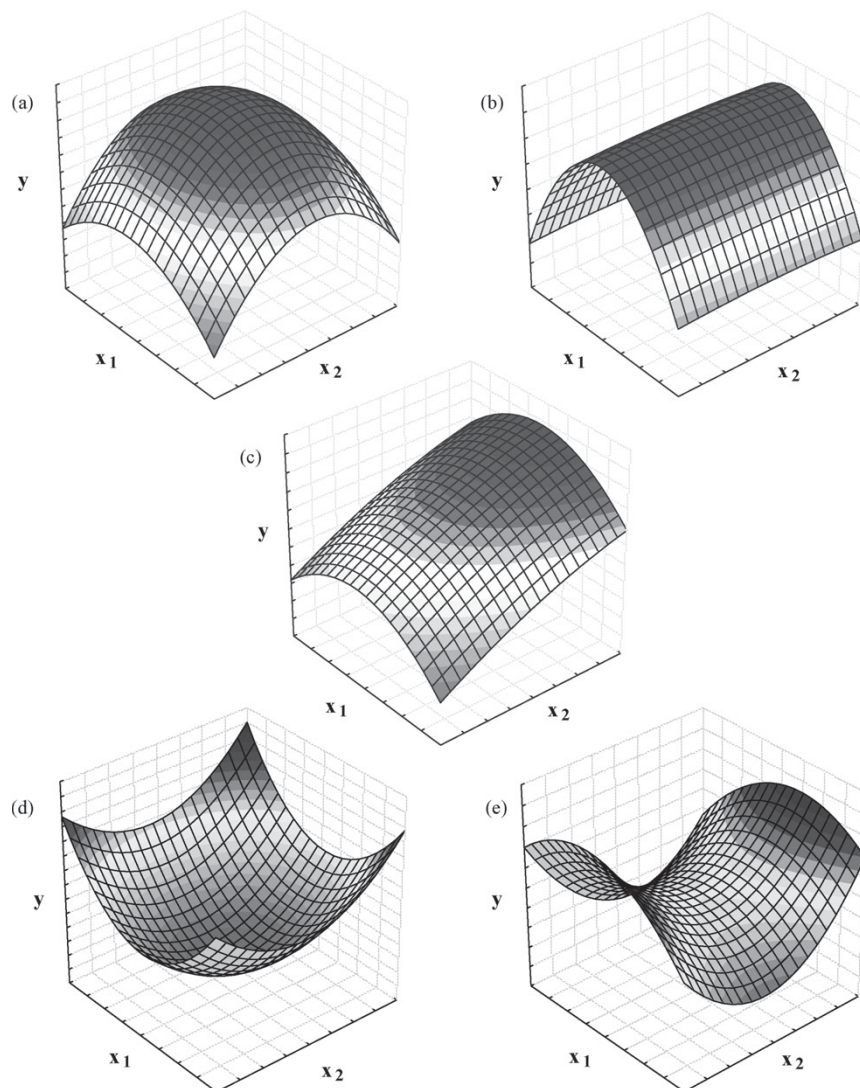


Figure 6. Response surfaces generated by the quadratic model for optimization of two variables: (a) maximum, (b) plateau, (c) maximum outside the experimental region, (d) minimum, and (e) saddle surfaces.

Slika 6. Profili površina dobijenih primenom kvadratnog modela za optimizaciju dve promenljive: (a) maksimum, (b) plato, (c) maksimum izvan eksperimentalnog opsega, (d) minimum, i (e) površina u obliku sedla. (Bezerra et al., 2008)

According to the literature, despite its increasingly widespread use, for example in analytical chemistry for method optimisation, applications of RSM to investigate coagulation in drinking water treatment are still limited. Trinh and Kang (2011) demonstrated that RSM can be applied to minimise the compromises necessary to simultaneously remove turbidity and DOC by coagulation–flocculation. On the other hand, Baskan and Pala (2009, 2010) investigated As removal and indicated how RSM may be applied to optimise the pH and coagulation conditions during the coagulation processes. Papers which utilize RSM to investigate the removal of both As and NOM are still lacking. This is an issue, since they are present together in many water sources around the world (Nordstrom 2002), including the Republic of Serbia, whereby both NOM and As are simultaneously present in groundwaters at levels necessitating their removal. This is the problem which will be examined in the final phase of research in this dissertation (see section 5.5)

3 Research objectives

The focus of this dissertation is on investigating effective, affordable and sustainable technologies for the removal of arsenic from groundwater. However, as explained above, arsenic is generally not the only groundwater contaminant requiring removal during the preparation of drinking water. Furthermore, some of those other contaminants, such as NOM in particular, not only have the potential to interfere with arsenic removal processes, but may also themselves require removal in order to supply chemically and microbiologically safe drinking water.

In order to meet the four goals given in chapter 1, the research carried out was split into 5 experimental phases with the following specific objectives.

Phase 1. Preliminary investigations

Objective 1. Define the range of chemical properties required to make appropriate synthetic water matrices as models for local groundwaters.

Phase 2. Investigating interactions between As and NOM

Objective 2. Test the hypothesis that given sufficient time to react, As and NOM form complexes together under conditions commonly found during the preparation of drinking water from groundwater sources.

Objective 3. Test the hypothesis that NOM is capable of acting as an electron acceptor during the oxidation of As(III) to As(V) under conditions commonly found during the preparation of drinking water from groundwater sources.

Phase 3. Development, characterisation and investigation of iron oxide based adsorbents for arsenic removal

Objective 4. Choose and develop appropriate iron oxide based adsorbents.

Objective 5. Characterise the physical and chemical properties of the adsorbents to be investigated.

Objective 6. Investigate the arsenic removal capacities of the adsorbents, and the effects of the presence of certain competitive ions on the arsenic removals achieved.

Phase 4. Removing arsenic using coagulation and coagulation combined with oxidation

Objective 7. Identify the most appropriate oxidation technology to be combined with coagulation for the removal of As and NOM from groundwater.

Phase 5. RSM investigation into interactions between As and NOM during iron chloride coagulation

Objective 8. Investigate how the interactions between As and NOM impact their combined removal from water by coagulation.

Objective 9. Create and test a model for their combined removal using Design of Experiments and Response Surface Methodology.

4 Materials and Methods

The experimental work carried out for this dissertation was organised into 5 research phases, with a series of preliminary investigations into the quality of the local groundwaters, followed by investigations into the interactions between As and NOM, and the application of adsorption and coagulation technologies for the removal of As. A general overview of the experiments carried out in each phase is given in figure 7.

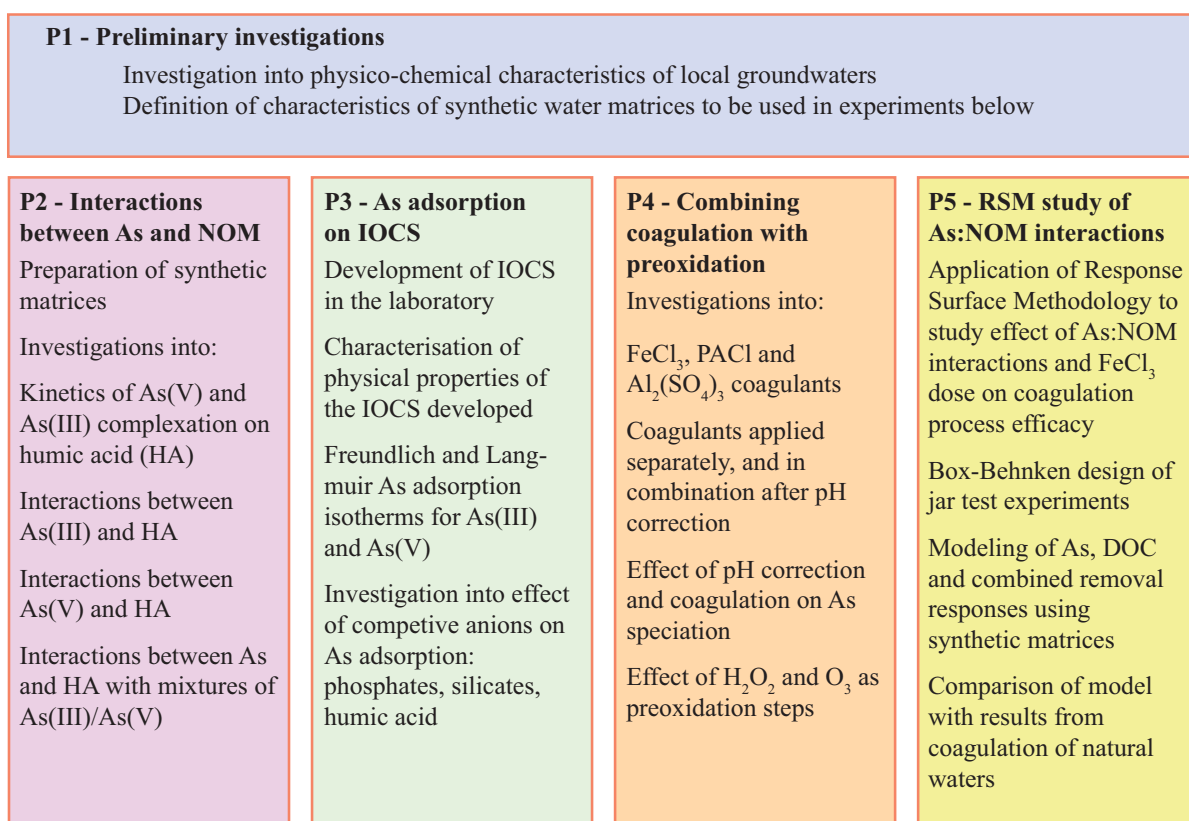


Figure 7. Overall structure of the experimental work carried out.

Slika 7. Šematski prikaz eksperimenta.

The procedures relevant to every phase of this dissertation are given in the first two sections of this chapter, with additional specific methods detailed in the subsequent sections.

4.1 Syntetic water matrices

4.1.1 Humic acid as a model substance for NOM

As explained in section 2.2.1., investigations into the behaviour of NOM are made complicated by its complex and highly variable structure. In order to gain better control over the experimental conditions, it is therefore common practice to use a simpler model

substance. In this case, a commercial humic acid (Fluka, CAS No. 1415-93-6) was used, and prepared according to Mosteo et al. (2009): Before the dissolution of 0.3 g of HA in 250 ml of deionised water, the pH of the deionised water was adjusted to pH 10, allowing for the dissolution of the humic acid in an alkaline environment. After dissolution of the HA, the solution was stirred for 24 hours. The solution was filtered, first through a glass fiber filter ($<1\mu\text{m}$) and then through a membrane filter ($0.45\mu\text{m}$) to obtain a standard HA solution with a specific content of dissolved organic carbon (DOC). The DOC content of this stock solution was determined by diluting a 1 ml aliquot in 25 ml deionised water and analysed as given in section 4.1.2 below.

4.1.2 Arsenic spikes

1 g/l As(V) and As(III) stock solutions were prepared in deionised water from commercial ACS reagent grade arsenic pentoxide (As_2O_5) or arsenic trioxide (As_2O_3) (Sigma–Aldrich). Further dilutions of these stock solutions were prepared in deionised water before spiking into water samples.

4.1.3 Other water constituents

ASTM type I ultrapure deionised water was used for preparation of the stock standards and synthetic matrices, from a LABCONCO treatment system (WaterPro RO/PS Station). Ionic strength in the synthetic matrices was maintained constant via the addition of 10 mmol/l NaNO_3 . pH was adjusted with HCl and NaOH. Where required, alkalinity of the synthetic matrices was adjusted with the addition of 10 mg/l CaCO_3 .

In the adsorption experiments which investigate the effect of competitive anions, humic acid (as above), silicates ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and phosphates (Na_2HPO_4) were added to the synthetic matrices in the following concentrations:

- HA: 2–12 mg C/l,
- SiO_3^{2-} : 4–12 mg/l,
- PO_4^{3-} : 1–9 mg/l.

These silicate and phosphate anion concentrations were taken from literature as representing typical environmentally relevant concentrations (Redman et al., 2002; Hsu et al., 2008; Weng et al., 2009).

All chemicals were reagent grade or better and were purchased from Sigma-Aldrich or J.T.Baker.

4.2 Analytical methods

Arsenic concentrations were determined either by inductively coupled plasma mass spectrometry (ICP/MS; ELAN 5000, PerkinElmer-SCIEX) or graphite furnace atomic adsorption spectroscopy (GFAAS; AAnalyst 700, PerkinElmer), using EPA methods 200.8

and 7010 respectively (USEPA, 1994, 2007). The PQL for both arsenic methods was 0.5 µg As/l.

DOC contents of samples were determined after acidification with cc. HCl to pH 2 followed by sparging under a flow of synthetic air to remove inorganic carbon dioxide. The sparged samples were then analysed by Elementar LiquiTOCII, using a two-stage platinum-catalysed combustion process at 850°C (SRPS ISO, 2007).

pH, conductivity and **turbidity** measurements were carried out using the InoLab pH/ION 735, WTW Cond 3210, and Hanna HI 93703 portable instruments.

Water alkalinity (p- and m-alkalinity) was measured according to Standard Methods (AWWA, 2012).

4.3 Preliminary investigations

Groundwaters were sampled from Zrenjanin, Senta, Temerin, Kikinda, Kulpin, Bački Petrovac, Maglić and Gložan, and analysed for As, NOM (as DOC) and alkalinity.

4.4 Investigating interactions between As and NOM

In order to observe the two different types of arsenic:NOM interaction hypothesised in Objectives 1 and 2 in Chapter 3, the following experiment was devised (shown in figure 8): Synthetic matrices containing different concentrations of NOM were spiked with known concentrations of As(V), As(III) or a combination of both, and shaken on an orbital shaker. 16 ml aliquots of the arsenic-spiked matrices were then taken at regular intervals, and analysed for different arsenic species (method given below): total arsenic (As_{Tot}), organically bound arsenic (As_{Org}), and the inorganic arsenic (As_{In}) species, separated into As(III) and As(V).

The ionic strength of each synthetic matrix was held constant by the addition of sodium nitrate with a final concentration of 10 mM, and the pH was adjusted to pH 7.0 using concentrated HCl and NaOH.

4.4.1 Speciation analysis

The speciation method was developed from methods given in papers by Bednar et al. (2004) and Yu et al. (2003), and was published in Watson et al. (2011). The method utilises two different solid phase extraction (SPE) resins to perform the separation of the different arsenic species: ENVI 18 and LC-SAX (obtained from Supelco). The ENVI 18 resin has a very strong adsorption affinity for organic compounds, and a very low adsorption affinity for inorganic species. Any organically bound arsenic in a sample which is passed through the ENVI 18 resin is therefore retained on the resin, whilst the inorganic arsenic passes through. After acidification to pH 5.6 (so that the As(V) is fully protonated and the As(III) fully deprotonated), the inorganic arsenic sample is passed

through the strong anion exchange LC-SAX resin. The As(V) is retained on the LC-SAX, from which it may be eluted with 1M nitric acid, and the As(III) passes through.

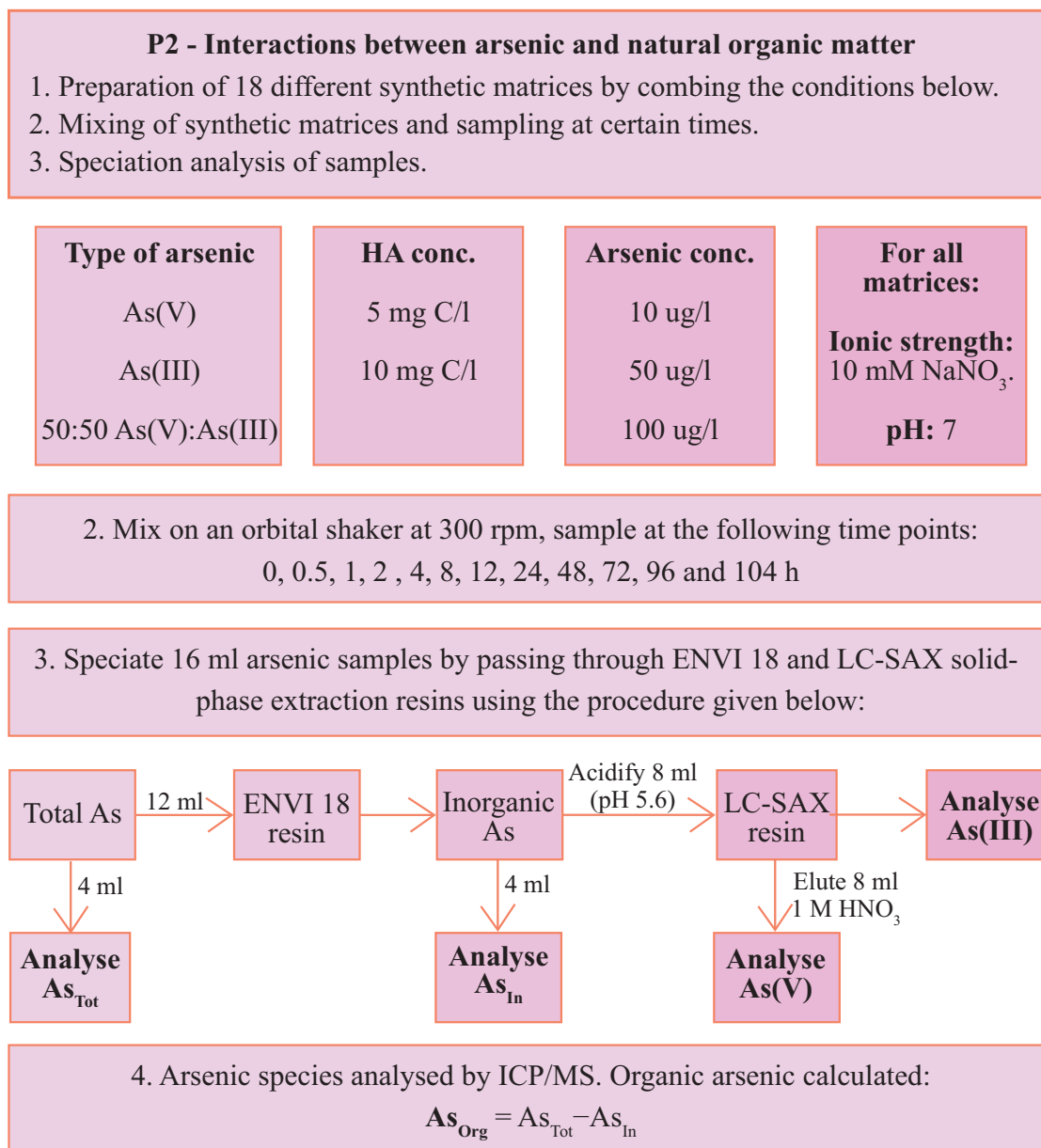


Figure 8: Experimental design of Phase 2: As:NOM interactions.

Slika 8. Dizajn eksperimenta u fazi 2: As:POM interakcije.

The procedure for arsenic speciation is therefore as follows (depicted in figure 8):

- a) 4 ml of sample is set aside for determination of the total arsenic content As_{Tot} .
- b) 12 ml of sample is passed through 0.5 g ENVI 18 resin.
- c) 4 ml of the resulting inorganic arsenic sample is set aside for determination of the total inorganic arsenic As_{In} . As_{Org} is then calculated: $As_{Org} = As_{Tot} - As_{In}$.
- d) The remaining 8 ml is acidified to pH 5.6 and passed through 0.5 g LC-SAX resin. The As(III) sample is collected and analysed.
- e) As(V) is eluted with 8 ml of 1M HNO₃ and analysed.

Due to the synthetic nature of the sample matrices, at the beginning of each experiment it is known that there is no organic arsenic present. Any organic arsenic detected during the speciation analysis may therefore be attributed to the complexation of arsenic with the humic acid used as a model for NOM. Using the speciation method above, it is also possible to observe changes in the distribution between inorganic As(III) and As(V). This speciation method may therefore be used to examine both of the hypotheses given in Objectives 1 and 2 of Chapter 3.

4.5 Development, characterisation and investigation of iron oxide based adsorbents for arsenic removal

Phase 3 of the experiential work, the investigation into the application of iron oxide based adsorbents for arsenic removal, is shown in figure 9.

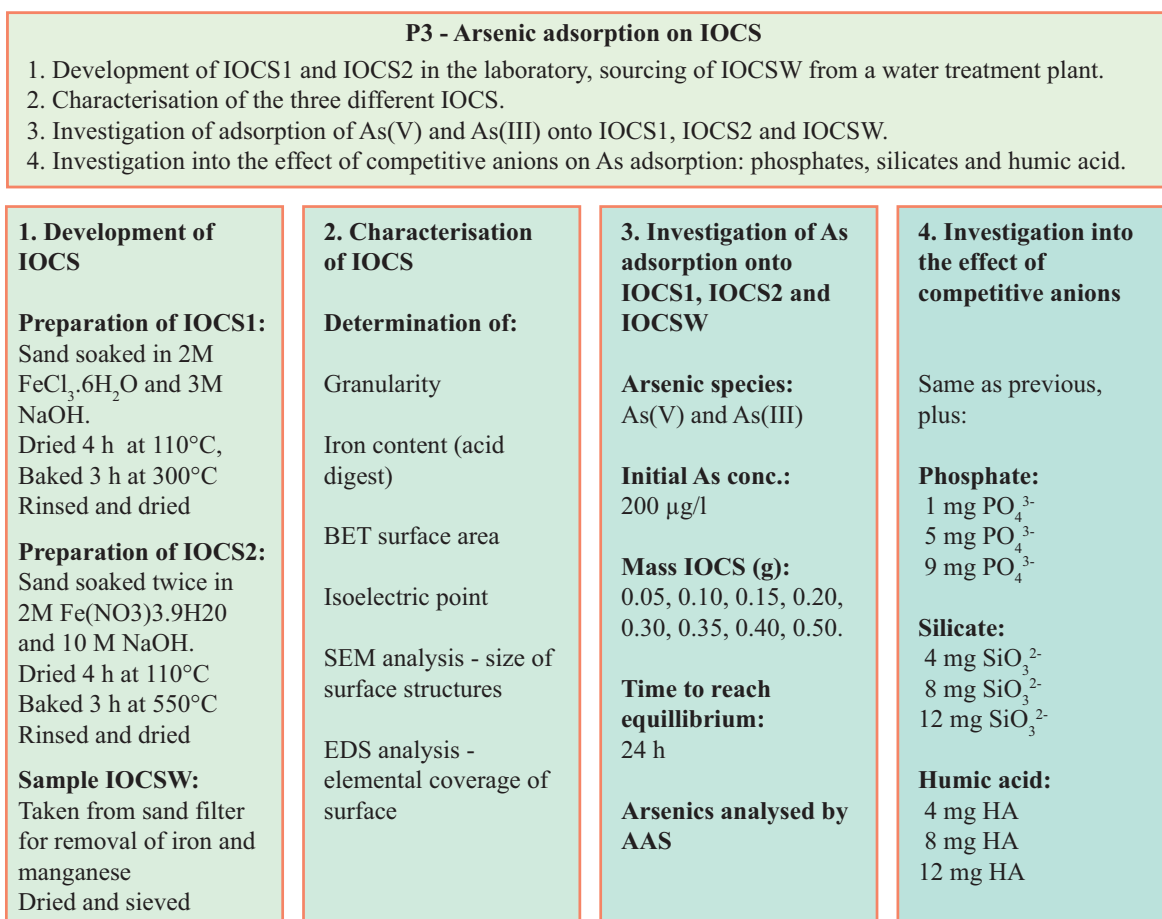


Figure 9. Experimental design of Phase 3: Arsenic adsorption on IOCS.

Slika 9. Dizajn eksperimenta u fazi 3: adsorpcija arsena na IOCS.

4.5.1 Development of the iron oxide coated sands

Thirunavukkarasu et al. (2001) were one of the first groups to investigate in depth the capabilities of iron oxide coated sands (IOCS) for the removal of arsenic. The two laboratory-prepared IOCS investigated in this dissertation are based on their work,

following the modified methods suggested by Dongmei et al. (2011). The origins of the third IOCS investigated are also explained below.

4.5.1.1 Preparation of the acid-washed sand used in the coating process

Dry quartz sand with a particle size of 0.5–0.8 mm was soaked overnight in 0.1 M hydrochloric acid. This acid-washed sand was rinsed with deionised water until the rinsing water reached a neutral pH 7. The sand was then dried overnight at 110°C.

4.5.1.2 Preparation of IOCS1

200 g of dry acid-washed sand was soaked in a solution containing 66 ml 2M FeCl₃·6H₂O and 60 ml 3M NaOH. The FeCl₃·6H₂O used was analytical grade obtained from Poch SA, Poland. After gentle mixing, the mixture was dried at 110°C for 4 hours, and then baked at 300°C for 3 hours. The mixture was then allowed to cool to room temperature, and dried overnight at 110°C. Once the sand is again allowed to cool to room temperature, the IOCS thus prepared was labelled IOCS1 and stored in a closed polyurethane plastic bottle.

4.5.1.3 Preparation of IOCS2

200 g of dry acid-washed sand was soaked in a solution containing 80 ml 2M Fe(NO₃)₃·9H₂O and 1 ml 10M NaOH. The Fe(NO₃)₃·9H₂O used was analytical grade and was obtained from Sigma-Aldrich. After gentle mixing, the mixture was dried at 110°C for 4 hours. After cooling to room temperature, the sand was rinsed with distilled water until clear. The sand was then again soaked in the same volume of the same solution, dried overnight at 110°C, and baked in a furnace at 550°C for 4 hours. After cooling to room temperature, the resulting IOCS was labelled IOCS2 and stored in a closed polyurethane plastic bottle.

4.5.1.4 Preparation of IOCSW

Iron oxide coated sand was obtained from a local waterworks. This sand is a waste material from a common process for the removal of iron and manganese from water. After aeration/oxidation, water is passed through a sand filter, whereby iron and manganese oxides are adsorbed onto the surface of the sand. Eventually (after several years of operation), the surface of the sand is fully saturated with iron and manganese oxide, and the sand is replaced. The resulting iron and manganese oxide coated sand is therefore a waste product of the water treatment process, and requires disposal by the waterworks.

The raw iron and manganese oxide coated sand obtained from the waterworks was damp, and had a wide particle size distribution. The sand was therefore dried overnight at 110°C, and then passed through a series of sieves. The resulting particle size distribution is given in table 3 below.

Table 3. Particle size distribution of IOCSW, the iron and manganese coated sand obtained from the waterworks.

Tabela 3. Distribucija veličine čestica peska dobijenog iz vodovoda, obloženog gvoždem i manganom.

Particle size (mm)	Mass fraction (%)
>2.0	4.66
1.6–2.0	3.89
1.0–1.6	83.3
0.8–1.0	6.86
0.5–0.8	0.55
0.315–0.5	0.08
<0.315	0.66

In order to maximise the efficiency of re-using the IOCS reclaimed from the sand filter, the two greatest mass fractions (0.8–1.0 and 1.0–1.6) were combined, and stored in a polyurethane bottle. This IOCS was labelled IOCSW (to represent its status as a Waste material).

4.5.2 Characterisation of the IOCS investigated

The following methods were used to characterise IOCS1, IOCS2 and IOCSW.

4.5.2.1 Iron content of the coatings

The iron contents of the IOCS were determined by acid digest (AWWARF, 1993) followed by Fe analysis by flame atomic adsorption spectroscopy. 0.5 g of IOCS was heated in 25 ml 10% HNO₃ solution until boiling, and held at boiling temperature in a sand bath for a further 2 h. The resulting solution was diluted in 500 ml deionised water, filtered through a 0.45 µm membrane filter and analysed for total Fe.

Note that the digest method applied is not capable of dissolving quartz, so the results are really the iron contents of the sand coatings.

4.5.2.2 BET specific surface areas

The BET specific surface areas were determined by Quantachrome Autosorb IQ/ASiQWin. 0.5 g IOCS samples were dried under vacuum at 414 K until constant mass. Nitrogen adsorption isotherms were then analysed at 77 K, and a 5–point BET analysis performed.

4.5.2.3 SEM and EDS analysis

SEM and EDS analyses were carried out by JEOL JSM 6460 LV scanning electron microscope. The EDS analyses were carried out at 20 kV, and optimisation was carried out using nickel.

4.5.3 Arsenic adsorption isotherms

The efficacy of the arsenic removal processes by adsorption onto IOCS were determined by adsorption isotherm. An initial kinetics experiment confirmed that 24 hours was more than sufficient to achieve equilibrium in the following system. Different doses of IOCS (0.05, 0.10, 0.15, 0.20, 0.30, 0.35, 0.40 and 0.50 g) were placed into 35 ml dark glass vials. For each series of experiments, 20 ml of solution containing 200 µg/l of either As(V) or As(III) was added to each vial, and the vials placed on an orbital shaker at 160 rpm for 24 h. The samples were then decanted, and analysed for total arsenic concentration.

4.5.4 Effect of competitive anions on the arsenic adsorption

Three different competitive anions were investigated: phosphates, silicates and humic acid. Stock solutions of phosphates and silicates were prepared in deionised water from $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (reagent grade, SigmaAldrich). HA stock solution was prepared as given in section 4.1.1. 18 different synthetic matrices containing 200 µg/l of either As(V) or As(III) were made up containing different concentrations of the competitive anions, as given in table 4. 20 ml aliquots of these solutions were then added to vials containing the same doses of IOCS investigated in 4.3.3 and placed on an orbital shaker at 160 rpm for 24 h. The samples were then decanted, and analysed for total arsenic concentration.

Table 4. Concentrations of competitive anions investigated.

Tabela 4. Koncentracije ispitivanih kompetitivnih jona.

Anion	Concentrations (mg/l)		
PO_4^{3-}	1	5	9
SiO_3^{2-}	4	8	12
HA	4	8	12

4.6 Removing arsenic using coagulation and coagulation combined with oxidation

An overview of the work carried out in the fourth phase of this dissertation, in which different combinations of coagulant, pH adjustment and preoxidation were investigated, is given in figure 10.

For these experiments, groundwater from Zrenjanin was used. In the very last series, waters from Kulpin, Bački Petrovac, Maglič and Gložan were also investigated.

All coagulation experiments were carried out by jar tests performed on a JAR-test FC6S Velp Scientific apparatus. 600 ml samples were placed in 800 ml beakers, and the coagulant and flocculant dosed in suitable aliquots. Coagulation was carried out with rapid stirring at 120 rpm for 2 min, after which flocculation was conducted with slow mixing at 30 rpm for 30 minutes. Magnaflok LT27 flocculant was dosed at 0.2 mg/l. After the

mixing was finished, samples were settled for 60 minutes, after which the supernatant was separated. Water samples were filtered through a 0.45 μm membrane filter and analyzed for total arsenic and DOC concentrations.

P4- Investigation into combining coagulation with preoxidation for arsenic and NOM removal

1. FeCl_3 , PACl and $\text{Al}_2(\text{SO}_4)_3$ coagulants, alone and with pH correction
2. Changes in As speciation after pH correction and coagulation
3. Preoxidation by hydrogen peroxide or ozone prior to coagulation and combinations of coagulants

<p>1. FeCl_3, PACl and $\text{Al}_2(\text{SO}_4)_3$ coagulation</p> <p>Coagulation: 18-300 mg FeCl_3/l 3-50 mg Al/l PACl 3-50 mg Al/l $\text{Al}_2(\text{SO}_4)_3$</p> <p>pH correction + coagulation: pH: 7.8, 7.0, 6.5 FeCl_3 doses: 100, 120, 150, 175, 190, 200 mg FeCl_3/l</p>	<p>2. As speciation analysis (see 4.2.1)</p> <p>pH correction: from 7.8 to 7.0, 6.5</p> <p>Coagulation: PACl doses: 10, 20, 30 mg Al/l FeCl_3 doses: 100, 150, 200 mg FeCl_3/l</p> <p>pH correction + coagulation: pH: 7.8, 7.0, 6.5 FeCl_3 doses: 100, 120, 150, 175, 190, 200 mg FeCl_3/l</p>	<p>3. Preoxidation and coagulation</p> <p>Hydrogen peroxide: 2.4, 5.0, 7.5, 10.0 mg $\text{H}_2\text{O}_2/\text{l}$ or Ozone: 2, 5.0, 7.5, 10.0 mg O_3/l</p> <p>Coagulant doses: 18, 30, 60, 120, 180, 300 mg FeCl_3/l</p> <p>3, 5, 10, 20, 30, 50 mg Al/l PACl or $\text{Al}_2(\text{SO}_4)_3$</p> <p>Combinations: PACl-FeCl_3, and $\text{Al}_2(\text{SO}_4)_3$-$\text{FeCl}_3$</p>
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Figure 10. Overview of experimental work in phase 4 of this dissertation.

Slika 10. Pregled eksperimentalnog rada u fazi 4.

The speciation of the groundwater in Zrenjanin was carried out (see section 4.4.1 for speciation method) at the natural pH of the water (pH 7.8) and at pH 7.0 and 6.5, after pH adjustment by concentrated HCl.

4.6.1 Coagulation by FeCl_3 , PACl and $\text{Al}_2(\text{SO}_4)_3$

The following coagulants were used: a 4% solution of iron (III) chloride (prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in doses of 50–200 mg FeCl_3/l (0.1–2.0 mmol/l); a 1% solution of polyaluminium-chloride (Bopac®; $\text{Al}_n(\text{OH})_m\text{Cl}_{3(n-m)}$; referred to as PACl in the text) in doses from 2.5 to 30 mg Al/l (0.1–2.0 mmol/l); and 1% $\text{Al}_2(\text{SO}_4)_3$ in doses from 2.5 to 30 mg Al/l (0.1–2.0 mmol/l).

For coagulation by FeCl_3 and PACl, the effect of filtration on coagulation efficacy was also investigated, by analysing the settled supernatants before and after membrane filtration through a 0.45 μm filter.

4.6.2 Effect of coagulation on the speciation of arsenic

The arsenic speciation method given in section 4.4.1 was applied to waters coagulated with a range of FeCl₃ or PACl doses: 100, 150 and 200 mg FeCl₃/l and 10, 20 and 30 mg Al/l. The experiments were also carried out for coagulation after pH correction from pH 7.8 to 7.0 and 6.5.

Altogether, arsenic speciation analysis was carried out on the following samples:

- Zrenjanin raw water.
- pH corrected Zrenjanin raw water: pH 7.8, 7.0 and 6.5.
- Zrenjanin raw water coagulated with PACl at 10, 20 and 30 mg Al/ doses.
- Zrenjanin raw water coagulated with FeCl₃ at 100, 150 and 200 mg FeCl₃/l doses.
- pH corrected (pH 7.8, 7.0 and 6.5) coagulated with FeCl₃ at 100, 120, 150, 175 and 200 mg FeCl₃/l doses.

4.6.3 Enhanced coagulation using pH correction

The effect of pH correction on ferric chloride coagulation was investigated, using HCl to adjust the water pH from its natural pH 7.8 down to pH 7.0 and pH 6.5. The investigated coagulant doses were 100, 120, 150, 175, 190 and 200 mg FeCl₃/l.

4.6.4 Enhanced coagulation with preoxidation by hydrogen peroxide or ozone

Finally, possible improvements to the coagulation process using different coagulant and oxidant combinations were investigated. The following doses of hydrogen peroxide or ozone were investigated with the coagulant combinations in table 5 below:

H₂O₂ doses: 2.5, 5.0, 7.5, 10.0 mg H₂O₂/l.

O₃ doses: 2.5, 5.0, 7.5, 10.0 mg O₃/l.

Note that the doses of aluminium-based coagulants and the ferric chloride coagulant are equivalent in terms of the molar concentrations of the units which perform the coagulation: Al or FeCl₃.

Table 5. Applied doses in the combined coagulation/preoxidation experiments.

Tabela 5. Primenjene doze kombinovanih koagulanata u eksperimentima sa preoksidacijom.

	Coagulant	Dose mg FeCl ₃ /l	Dose Al/l	Dosed first
1	FeCl ₃	18, 30, 60, 120, 180, 300	–	–
	PACl	–	3, 5, 10, 20, 30, 50	–
	Al ₂ (SO ₄) ₃	–	3, 5, 10, 20, 30, 50	–
	PACl – FeCl ₃	5, 10, 20, 30, 50	20, 30	PACl
4	Al ₂ (SO ₄) ₃ – FeCl ₃	5, 10, 20, 30, 50	20	Al ₂ (SO ₄) ₃

4.7 RSM investigation into interactions between As and NOM during iron chloride coagulation

In order to investigate the interactions between arsenic and NOM during the ferric chloride coagulation process, whilst optimizing the experimental conditions, response surface methodology was used to design the experiment. A Box-Behnken design was selected, which allows for the efficient estimation of second-order models (Bezerra et al., 2008). In Box-Behnken designs, experimental points are located on a hypersphere equidistant from the central point, as shown in figure 11. All factors are investigated at three equally spaced levels, coded as -1 , 0 , $+1$.

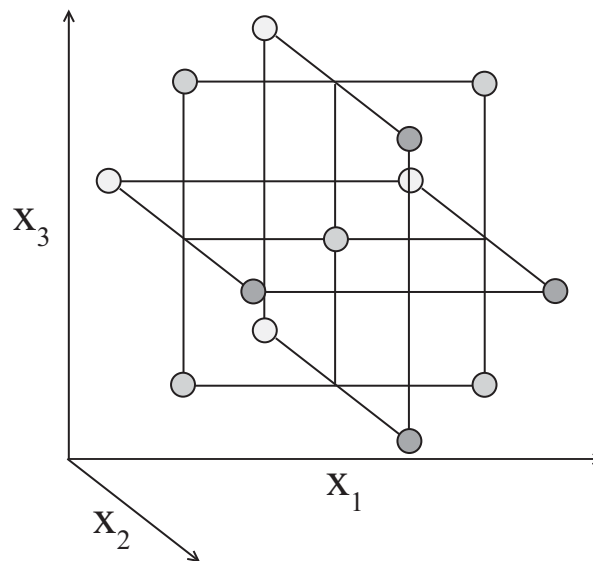


Figure 11. The three-factor Box-Behnken experimental design.

Slika 11. Box-Behnken dizajn eksperimenta sa tri faktora.

The three factors investigated were the initial arsenic concentration (As), the initial humic acid concentration (HA) and the iron chloride dose applied during coagulation (FeCl_3). The actual values of the coded levels of each factor are given in table 6.

The initial arsenate and HA concentrations were chosen to encompass the full ranges found in the groundwaters used for drinking water supply in Vojvodina, and the range of coagulant doses chosen reflects previous coagulation experiments (Molnar et al., 2013; Agbaba et al., 2015b). The Box-Behnken design provided 18 runs with different combinations. Jar tests with the runs were carried out in a randomised order to minimize the effect of uncontrolled variables on the responses, with the central point of the model repeated 6 times in order to quantify the error.

The Jar tests were carried out using a FC6S Velp Scientific apparatus, with 0.4 l samples in 0.8 l beakers at room temperature ($22\text{-}25^\circ\text{C}$). During the experiments, an iron(III)-chloride solution concentration of $72.6 \text{ g FeCl}_3/\text{l}$ was used as coagulant at applied doses of 50, 150 and $250 \text{ mg FeCl}_3/\text{l}$. Magnaflok LT27 flocculant was dosed at 0.2 mg/l . The tests were conducted at an adjusted pH of 7. Coagulation was carried out with rapid stirring at 120

rpm for 2 min, after which flocculation was conducted in slow stirring mode at 30 rpm over the course of 25 minutes. Upon completion of the stirring, samples were settled for 60 minutes, after which the clear supernatant above the sediment was withdrawn from each jar, and analyzed for DOC and As contents, after filtration through a 0.45 μm membrane filter.

Table 6. Relationship of the actual and coded values for each factor.

Tabela 6. Veza između stvarne i kodirane vrednosti za svaki faktor.

Factor	Unit	Symbol used by the model	Coded factor level (x_i)		
			-1	0	+1
Initial As conc.	($\mu\text{g/l}$)	A	20	110	200
Initial HA conc.	(mg/l)	B	2	7	12
FeCl_3 dose	(mg/l)	C	50	150	250

Regression analysis was performed on the data thus obtained, using the Design-Expert software (Version 9, Stat-Ease Inc., Minneapolis, USA). The statistical significance of the models was analyzed by analysis of variance (ANOVA) in Design-Expert, which was also used to depict the 3D response surfaces.

5 Results and discussion

This chapter presents the results of the five phases of experimental work carried out for this dissertation, and discusses their significance.

5.1 Preliminary investigation

This dissertation focuses on the removal of arsenic from groundwaters during the treatment of drinking water. Natural groundwaters are very complex mixtures of constituents, all of which are present together in dynamic equilibrium. To better control experimental conditions and gain clarity on the parameters which are most important to an investigation, it is often therefore necessary to isolate them, using synthetic matrices prepared in the laboratory. In Design of Experiments (see chapter 5.5), the complete range of possible values which different variables can hold is referred to as the design space or experimental domain. To create appropriate synthetic matrices with environmentally relevant concentrations, it is necessary to ensure that the design space of an experiment fully encompasses the range of values possible in the real world. The goal of the preliminary phase of this dissertation was therefore to define the extent of the design space which will be used in the later experiments.

Table 7 illustrates typical average values of arsenic, NOM and alkalinity which can be found in the groundwater wells in cities throughout Vojvodina.

Table 7. *Typical maximum values for As, NOM and alkalinity found in the groundwaters of Vojvodina.*

Tabela 7. *Uobičajene maksimalne vrednosti za arsen, POM i alkalinitet u podzemnoj vodi sa teritorije AP Vojvodine.*

Location	As ($\mu\text{g/l}$)	NOM (mg C/l)	Alkalinity (mg CaCO_3/l)
Zrenjanin	135	9.85	745
Senta	< 10	7.46	631
Temerin	39.2	2.20	451
Kikinda	28.9	5.16	475
Kulpin	8.46	5.28	953
Bački Petrovac	18.0	5.59	1321
Maglić	11.8	6.50	764
Gložan	3.69	3.00	752

From these figures, it is clear that Vojvodina has a severe problem with arsenic and NOM contamination in groundwater. As the most extreme example of arsenic contamination, the water from Zrenjanin was chosen as the main natural water matrix to be used when required, primarily in the investigations into the application of coagulation for the removal

of arsenic. For the synthetic matrices, the results above suggest that arsenic concentrations in the range 10–200 µg/l will be sufficient to adequately represent the majority of local groundwaters.

A previous study of the structure of the NOM in the Zrenjanin groundwater revealed the following fractions: 68% fulvic acid fraction, 14% humic acid fraction, 6% hydrophilic acid fraction and 12% hydrophilic non-acid fraction (Tubić et al., 2013). Of these fractions, humic acid (HA) has the most readily commercially available makes it the most suitable for use as an NOM analogue during the preparation of synthetic matrices. The results presented in table 8 suggest HA concentrations of 2–12 mg C/l will be appropriate for the synthetic matrices.

Depending upon the nature of the investigation, other additional water constituents will be added to the synthetic matrices in the concentrations given in the materials and methods, section 4.1.3.

5.1.1 Groundwater quality in Zrenjanin

A more in depth investigation into the groundwater in Zrenjanin was conducted. The raw water used for drinking water supply is blended from 21 wells, from depths of 40–80 m and 100–150 m. The key water quality parameters for the blended well water are given in Table 8 (Tubić et al., 2011; Watson et al., 2016).

Table 8. *Water quality of blended well water from Zrenjanin.*

Tabela 8. *Kvalitet podzemne vode zbirnog uzorka sa teritorije Zrenjanina.*

Parameter	Unit	Mean value	n
pH	–	7.48±0.10	19
Conductivity	µS/cm	1202±16	19
Turbidity	NTU	0.49±0.02	19
Alkalinity	mg CaCO ₃ /l	745±12	19
As	µg/l	134±4.5	44
DOC	mg C/l	9.85±0.99	8
Br ⁻	µg/l	60±8	5

An analysis of the arsenic concentrations in each well was carried out. The distribution of the total arsenic concentrations in the 21 wells and in the blended water (which was sampled on 44 occasions), are shown in figure 12. The number of measurements of the blend was normalised to the number of wells (21) in order to aid comparison. The arsenic concentrations in the wells range from 4.0 to 344 µg/l, with 86% of the wells bearing water with arsenic concentrations greater than the 10 µg/l MAC (Official Gazette RS 42/98 and 44/99, 1998).

In general, the deeper wells are those which show the greatest natural arsenic contamination. The waterworks controls which wells are exploited in order to minimise the concentration of arsenic whilst ensuring enough water is extracted to satisfy demand. The

total arsenic concentration in the resulting blend of water supplied varied from 82.7–221 $\mu\text{g/l}$ in the 44 samples taken over the course of this phase of investigation. As can be seen from figure 12, despite favouring the least contaminated wells, the median arsenic concentration of the blend is around 125 $\mu\text{g/l}$, which is still an order of magnitude greater than the MAC for arsenic in drinking water (Official Gazette RS 42/98 and 44/99, 1998).

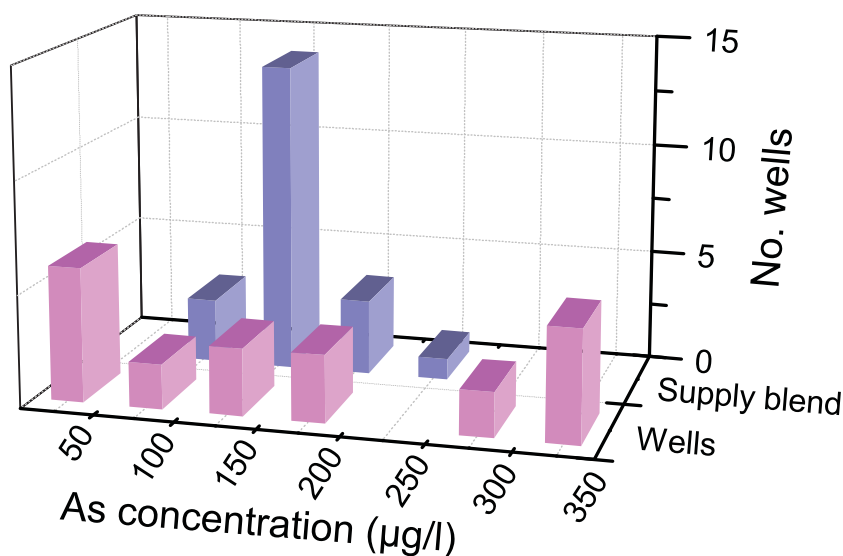


Figure 12. Normalised distributions of arsenic concentrations in the well waters of Zrenjanin and in the blend used for water supply ($n = 21$).

Slika 12. Normalizovana distribucija sadržaja arsena u podzemnoj vodi sa teritorije Zrenjanina i zbirnog uzorka podzemne vode koja se koristi za vodosnabdevanje ($n = 21$).

5.1.2 Arsenic speciation of the Zrenjanin raw water and after adjusting pH

The speciation of the arsenic present in a groundwater can play an important role in its behaviour during treatment processes, due to the different physical and chemical properties of the various arsenic species (see section 2.1.2). Part of the investigations carried out relating to coagulation therefore focused on which arsenic species were present in the water before and after treatment. The speciation of arsenic in the raw water, which was sampled on two separate occasions (Sample 1 and Sample 2), is given in table 9.

These speciation analyses were performed at the natural pH of the water, pH 7.8, on samples which had been passed through a 0.45 μm membrane filter using the method given in section 4.2.1. The dissolved As samples are passed sequentially through two solid phase chromatography columns: the first packed with C18 resin, which separates the organic-bound As, and the second packed with LC-SAX, a strong anion exchange resin, which separates the As(III) from the As(V). The total arsenic concentrations in the two water samples before filtration were 192 and 143 $\mu\text{g/l}$. After filtration, the dissolved arsenic in the samples was measured as 148 and 124 $\mu\text{g/l}$. In both samples, the proportion of arsenic bound to organic matter was roughly the same, around 22%, with the remaining 78% being inorganic. However, the distribution of inorganic species within the two samples was quite

different: in sample 2, the inorganic arsenic is almost entirely As(III), as might be expected from deep wells with anoxic water conditions. On the other hand, sample 1 has a much more even distribution of inorganic species, with 52 µg/l of As(III) and 62 µg/l As(V). We can suppose that the conditions in the different depths of aquifer, for example different NOM concentrations, have a strong influence on the distribution of arsenic species.

Table 9. Arsenic speciation of Zrenjanin groundwater sampled on two separate occasions.

Tabela 9. Specijacija arsena sirove vode sa teritorije Zrenjanina, uzorkovane u dva različita perioda.

As species	Raw water sample 1		Raw water sample 2	
	Conc (µg/l)	Share (%)	Conc (µg/l)	Share (%)
Total As	192		143	
Dissolved As	148	100	124	100
As(III)	52.0	35	96.8	78
As(V)	62.0	42	1.55	1.2
Organically bound As	33.8	23	25.7	21

The effect of changes in the pH on the speciation of arsenic in the Zrenjanin groundwater was also investigated. For this series of experiments, the natural groundwater pH of 7.8 was adjusted to pH 7.0 and pH 6.5. The changes in the distribution of arsenic species in the water samples after pH adjustment samples are shown in figure 13 and table 10.

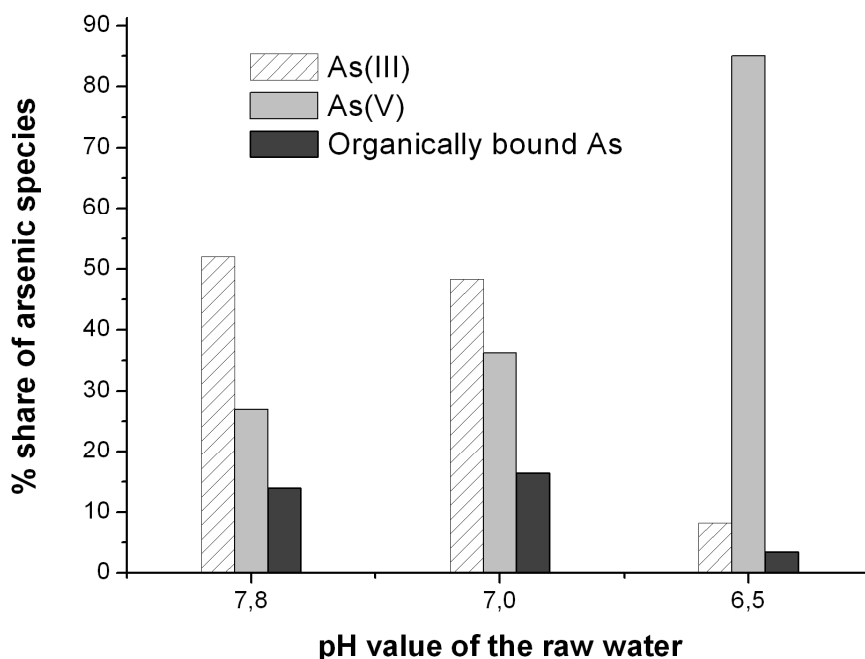


Figure 13. Effect of pH on the distribution of arsenic species in the Zrenjanin groundwater.

Slika 13. Uticaj pH na distribuciju različitih oblika arsena u podzemnoj vodi sa teritorije Zrenjanina.

At pH 7.8, 52% of the dissolved arsenic present was As(III). As the pH is lowered, the percentage of As(III) present is reduced, with corresponding gains in the amounts of As(V) present, such that at pH 6.5, only 11% of the arsenic is As(III), and the share of As(V) has increased to 85%. The increasing share of As(V) at lower pH values is in agreement with the results reported by Katsoyiannis et al. (2007), who report that As(V) has greater stability than As(III) in the pH range investigated.

Table 10. *Effect of pH adjustment on the distribution of arsenic species in the Zrenjanin groundwater*

Tabela 10. *Uticaj korekcije pH na distribuciju različitih oblika arsena u podzemnoj vodi sa teritorije Zrenjanina*

As species	pH 7.8		pH 7.0		pH 6.5	
	[As] (µg/l)	Share (%)	[As] (µg/l)	Share (%)	[As] (µg/l)	Share (%)
Total As	73.4		83.2		91.1	
Diss. As	72.4	100	80.2	100	80.3	100
As(III)	38.0	52	38.8	48	8.58	11
As(V)	19.5	27	29.0	36	67.9	85
Org. As	14.5	20	19.3	24	3.68	4.6

5.1.3 Quality of the other groundwaters investigated

The additional waters investigated during the coagulation experiments in section 5.4 were from Kulpin, Bački Petrovac, Maglić and Gložan. The groundwater from Bački Petrovac is a mixture of waters from five different wells (80.5–400 m deep). The piezometer in Kulpin is located at a depth of 144 m, and intakes water from a depth of 82–94 m. The groundwater from Maglić is from a 110 m deep well, and the well at Gložan has a depth of 320 m.

These waters range have similar slightly basic pH (from pH 7.76 in Kulpin to pH 8.23 in Maglić). In terms of total NOM contents, the groundwaters in Kulpin, Bački Petrovac and Maglić are very similar (5.28, 5.59 and 6.50 mg C/l) whereas Gložan has just 3.00 mg C/l. As explained in Molnar et al. (2013) however, although the total NOM contents are similar, the character of NOM in each groundwater is different.

In terms of arsenic, all these waters have less severe water quality issues than the groundwater from Zrenjanin, with only Bački Petrovac and Maglić having arsenic concentrations which exceed the maximum allowable concentration of 10 µg/l (Official Gazette RS 42/98 and 44/99, 1998).

5.2 Investigating interactions between As and NOM

From the As speciation and NOM fractionation results presented above, it was decided that in this second phase of experiments, which investigates the interactions between As and

NOM, synthetic matrices would be prepared from commercially available As(V), As(III), and humic acid (HA) as a model NOM substance.

The groundwater in the region contain large amounts of both As and NOM. This means that any interactions between these two constituents can have a significant impact on the performance of the removal technologies applied. To investigate those interactions, the experiments in this phase of the investigation rely on the ability to analyse how much As has become complexed with HA, and how much is still free in solution. An arsenic speciation method (described in section 4.2.1) using solid phase extraction (SPE) resins was used to first separate the newly complexed As from the free As in solution, and then separate the free As(V) from the the free (III). The first step of the method uses C18, a hydrophilic resin used in reverse phase chromatography, to remove the HA, and therefore the As bound to the HA, from the solution. The second step uses LC-SAX, a strong anion exchange resin, to separate the As(III) from the As(V) at pH 5.6, where the As(V) present is deprotonated and the As(III) remains neutral.

Preliminary kinetics experiments were carried out for both As(V) and As(III), in order to ascertain the amount of time required for the As:HA system to reach equilibrium. In these experiments, As(V) or As(III) was spiked into HA solutions containing 5 mg C/l, in order to have initial arsenic concentrations of around 120 $\mu\text{g As/l}$. The samples were then passed through the ENVI-18 resin at regular time intervals, in order to separate the free arsenic in solution from the arsenic newly bound to the humic acid. In figure 14, the total inorganic arsenic results are plotted against time.

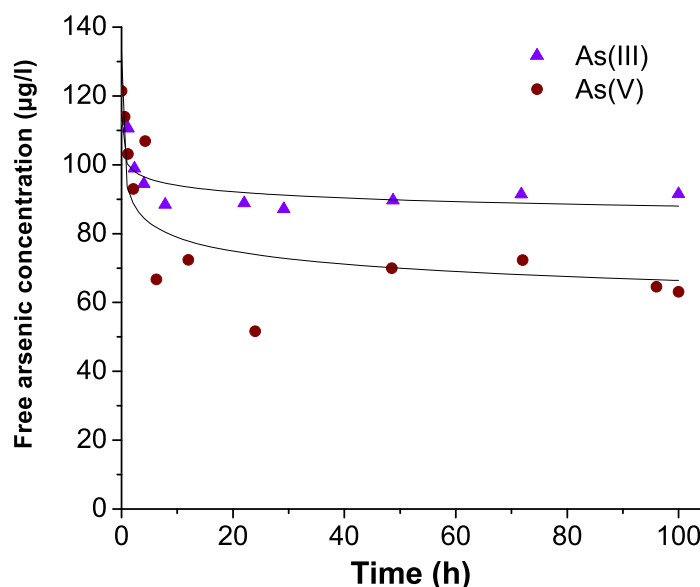


Figure 14. Preliminary kinetics experiments for interactions between humic acid and As(V) and As(III) (pH 7.5, 10 mM NaNO_3/l)

Slika 14. Preliminarni kinetički eksperimenti interakcija između huminskih kiselina i As(V) i As(III) (pH 7,5; 10 mM NaNO_3/l)

In figure 14, it appears that 22 hours was more than sufficient to be certain that an equilibrium had been reached between As(III) and HA, at which point the concentration of free inorganic arsenic in the solution had dropped to 89 µg/l, suggesting around 21% of the original As(III) is now complexed with the HA. The As(V):HA system took a similar amount of time to reach equilibrium, although based on the decay curve fit to the data in figure 14, it is possible that closer to 48 hours is required. At equilibrium, the concentration of free inorganic arsenic was as low as 62 µg/l, and 48% of the original As(V) was now bound with HA. These results are in agreement with the work of Ko et al. (2004) who also investigated interactions between arsenic and humic acid, and reported equilibrium times of around 48 h.

The amounts of complexed As(V) and As(III) were calculated from the difference between the initial arsenic concentrations and the free arsenic concentration at time t . Formation of the As:HA complex was then modelled with the pseudo-second order kinetics equation (Ho and Mckay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Eq. 12}$$

where q_e is the equilibrium amount of As complexed with HA (mg As/g HA), q_t the amount of As complexed with HA (mg As/g HA) at time t , and k_2 the second-order constant (g/mg h) which can be determined by plotting t/q_t versus t . The plots thus created are shown in figure 15, which shows the complexation between HA and both As(V) and As(III).

The superior fit of the kinetics data to the pseudo-second order model is in agreement with the findings of Ho and Mckay (1999), who reported that the majority of adsorption data given in the literature fits the pseudo-second order model better than the pseudo-first order model. Furthermore, Fakour and Lin (2014), in an investigation into ternary adsorption systems between As, HA and iron oxide based adsorbent, also reported pseudo-second order kinetics for complexation between As and HA, implying that chemisorption takes place, confirming the fact that HA and As are in fact forming complexes.

The pseudo-second order kinetics model gave a good fit for both sets of data, with coefficients of determination of 0.9848 and 0.9979 for As(V) and As(III) respectively (for comparison, the pseudo-first order model gave R^2 values of 0.55 and 0.12, plots not shown). The k_2 value calculated for As(V):HA complexation was 0.0224 g/mg h, and for As(III):HA complexation it was 0.139 g/mg h. The much larger k_2 value obtained for As(III):HA complexation indicates the complexation reaction proceeds considerably more slowly for As(III) than for As(V).

Note that the investigations with As(V) were carried out prior to the As(III) investigations. This is because the As(V):NOM interactions were expected to be less complicated than the As(III):NOM interactions due to the oxic conditions which favour the oxidation of As(III) to As(V) and strongly discourage the reduction of As(V). This means that of the two

interactions hypothesised in Objectives 2 and 3 in Chapter 3, only the complexation interaction is expected to occur in the As(V):NOM system, whereas the redox interaction is also expected to occur in the As(III):NOM system.

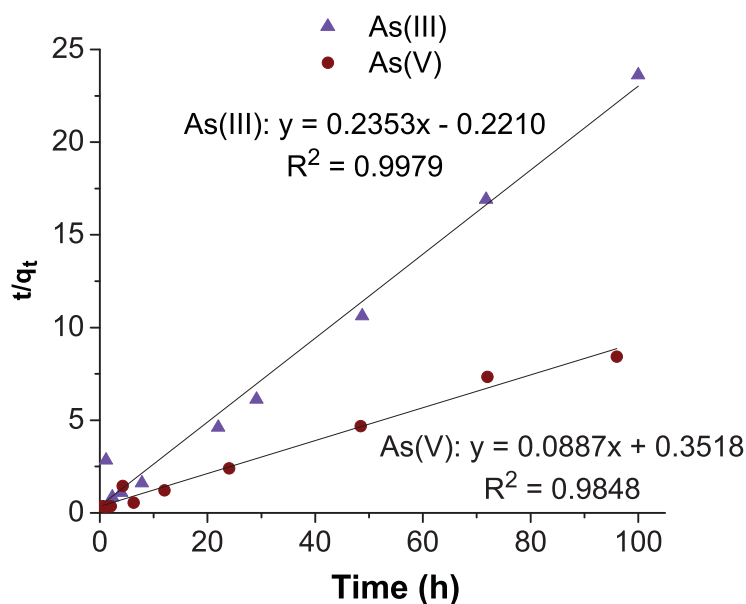


Figure 15. Pseudo-second order kinetics for the complexation between humic acid and As(V) and As(III) at room temperature.

Slika 15. Kinetika pseudo-drugog reda za kompleksiranje huminskih kiselina i As(V) i As(III) na sobnoj temperaturi.

On the basis of these preliminary results, it was concluded that interactions between both and As(III) and As(V) could be observed with this method, and that 48 h experiments would be necessary to be absolutely certain equilibrium was reached during the more in depth investigations. These experiments investigate interactions between arsenic and HA with different concentrations (10, 50 and 100 $\mu\text{g As/l}$) of As(III), As(V), and a combination of both, and two different concentrations of HA (5 and 10 mg C/l).

5.2.1 Interactions between As(V) and HA

The results of the investigations into the interactions between different concentrations of As(V) and 5 mg C/l and 10 mg C/l are shown in figures 16 and 17. Three different initial As(V) concentrations (C_0) were investigated (10, 50 and 100 $\mu\text{g/l}$), so in order to facilitate comparison between the experiments with different initial As(V) concentrations, the results are plotted as C/C_0 against time. In each experiment, as time passes, the amount of free As(V) observed in the solutions gradually decreases, leading to the assumption that As(V) is gradually complexing with the HA.

In the experiments with the lower HA concentration (5 mg HA/l), the following trend was observed: as the initial As(V) concentration increases, the proportion of As(V) bound to the HA also increases. Thus, for $C_0 = 10 \mu\text{g As/l}$, the final equilibrium concentration of

free As(V) was around 93%, such that only 7% of the As(V) was bound to the HA. In contrast, in the series where $C_0 = 50 \mu\text{g As/l}$, the final reduction in free As(V) (i.e., the percentage bound to the HA) after 48h was 25%, and in the series where $C_0 = 100 \mu\text{g As/l}$, that percentage was 27%.

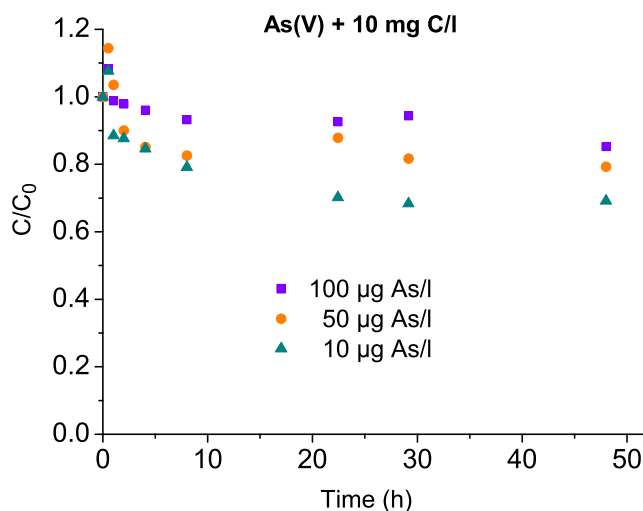


Figure 16. Change in free As(V) with time, in the presence of 5 mg C/l

Slika 16. Promena koncentracije slobodnog As(V) tokom vremena u prisustvu 5 mg C/l (pH 7.5; 10 mmol/l NaNO₃).

In the first five hours, there is very little change in the free As(V) concentration for the two series with lower initial arsenic concentrations. However, at $C_0 = 100 \mu\text{g As/l}$, 18% of the arsenic has already been complexed. Thus, the complexing of As(V) with HA proceeds more rapidly with increasing initial As(V) concentration, which is to be expected, as greater concentrations of As(V) mean more collisions per second between the arsenic and the humic acid, providing greater opportunity for a complexation reaction to occur.

In the series of experiments in figure 17, the concentration of humic acid was twice as high (10 mg C/l). It was therefore expected that the degree of complexing observed between the humic acid and the As(V) would also increase, relative to the series made with just 5 mg C/l. This expectation was met at the lowest initial As(V) concentration of 10 µg/l. In this series, the final equilibrium concentration was 69% of the original, such that 31% of the As(V) in solution was now bound to the HA, 4 times more than was complexed at the lower HA concentration. The degree of As(V) binding observed in the series with 50 µg As/l was also 31%, representing a less dramatic increase in comparison to the complexing achieved at 5 mg C/l. These results of these two series are in agreement with Ko et al. (2004), who also reported increased complexation of As(V) at higher HA concentrations.

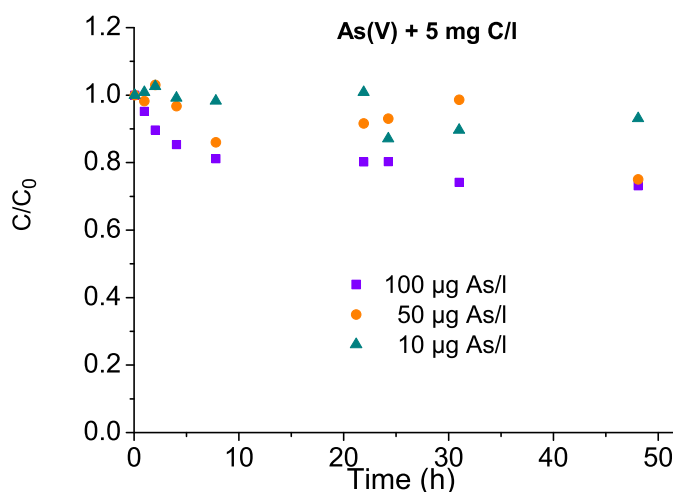


Figure 17. Change in free As(V) with time, in the presence of 10 mg C/l.

Slika 17. Promena slobodnog As(V) tokom vremena u prisustvu 10 mg C/l.
(pH 7.5; 10 mmol/l NaNO₃).

However, the expected increase in HA:As(V) complexing at increased humic acid concentrations was not observed in the series with 100 µg As/l. Instead, at this initial arsenate concentration, the amount of humic acid available did not have a significant impact on the degree of complexation observed. This suggests that the humic acid concentration is not the only factor which dictates the degree of complexation. Interestingly, at the higher humic acid concentration, the degree of As(V) complexation was approximately the same for all three series, regardless of the three different initial As(V) concentrations.

Taken altogether, the results in figures 16 and 17 are definite proof of the first interaction hypothesised in Objective 2 of Chapter 3. They suggest that in general, the degree of As(V):humic acid complexation which occurs is dependent of the concentration of As(V) present in solution. However, in the groundwaters of Vojvodina, both As(III) and As(V) are present (Tubić et al., 2010). For this reason, in the next section, the same set of experiments was repeated using As(III).

5.2.2 Interactions between As(III) and HA

5.2.2.1 Complexation interaction

If we assume that the only interaction between As(III) and HA results in complexation, then figures similar to those above may be plotted for the As(III) experiment (figure 18 below). In this figure, to provide a better comparison with the degree of complexation obtained with As(V), all the arsenic present is assumed to remain in its original oxidation state as As(III).

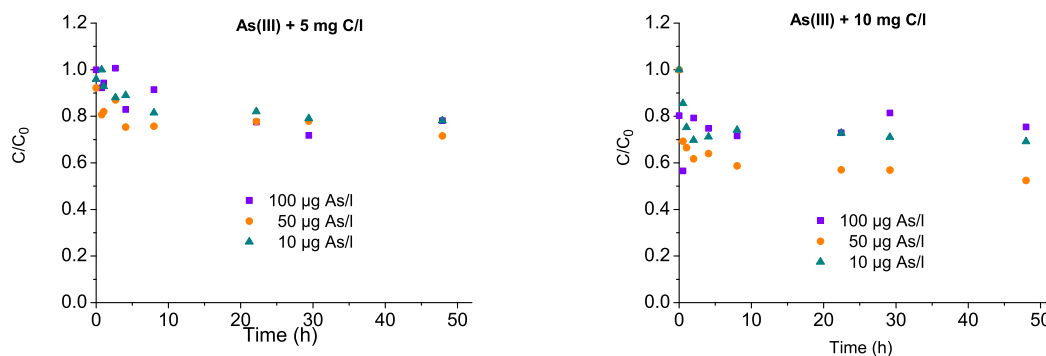


Figure 18. Change in free As(III) with time, in the presence of a) 5 and b) 10 mg C/l
Slika 18. Promena slobodnog As(III) tokom vremena u prisustvu a) 5 i b) 10 mg C/l
 ($C_0(\text{As(III)}) = 10, 50, 100 \mu\text{g/l}$; pH 7,5; 10 mmol/l NaNO₃).

At the lower HA concentration, the results for the complexation of As(III) are very similar for all three initial As(III) concentrations. The equilibrium concentrations of free arsenic are all around 70% of the initial concentration. Like the As(V) results, the greater the As(III) concentration, the faster the system approached equilibrium, after 10 hours when the initial arsenic concentration was 100 $\mu\text{g As/l}$, and after 48 hours when the initial arsenic concentration was 10 $\mu\text{g As/l}$.

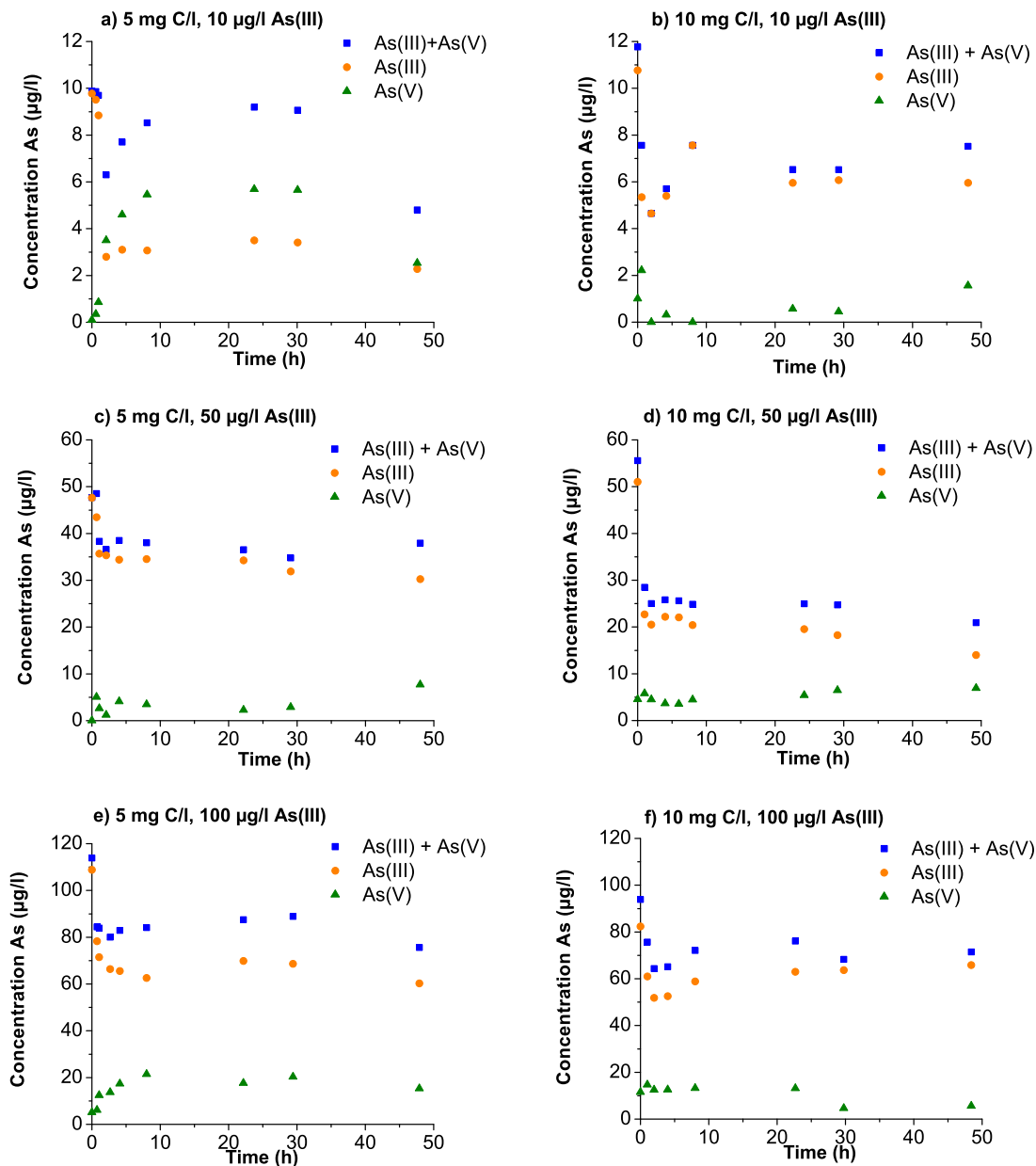
The results from the experiments with As(III) and the higher HA concentration of 10 mg C/l are more ambiguous. The 100 $\mu\text{g As/l}$ series reached equilibrium at a very similar concentration as it did in the presence of 5 mg C/l (71% of the initial arsenic concentration versus 66%). However, the equilibrium concentration for the 50 $\mu\text{g As/l}$ series was significantly lower (52% compared to 72%), and slightly higher for the 10 $\mu\text{g As/l}$ series (75% compared to 66%). It is unclear why the series with an initial concentration of 50 $\mu\text{g As/l}$ and 10 mg C/l should show the greatest degree of complexation out of all the experiments.

Comparison of the results for the complexation of As(V) and As(III) does however reveal a general trend: the amount of free arsenic remaining in solution after reaching equilibrium is about 10% lower for As(III) than As(V), suggesting that under the same conditions, approximately 10% more As(III) is complexed with HA than As(V). Redman et al. (2002) also investigated complexation between different species of As and HA, and reported that the overall degree of complexation observed with As(III):HA systems and As(V):HA systems was comparable.

5.2.2.2 Redox reaction interaction

The investigation into the interactions between arsenite and humic acid was expected to reveal an additional type of interaction, whereby As(III) would be oxidised by the HA to As(V) (as hypothesised in chapter 3, objective 3). To confirm the existence of this type of interaction, the free arsenic in solution at each time point was also analysed with the second stage of the arsenic speciation method given in section 4.2.1, whereby the sample is

acidified and passed through a column containing the LC-SAX resin. In this way, separation of As(V) and As(III) is achieved, allowing information about the changes in the distribution of As(V) and As(III) in the free arsenic over time to be obtained (Yu et al., 2003; Bednar et al., 2004).



(a) 5 mg C/l, 10 µg As(III)/l; b) 10 mg C/l, 10 µg As(III)/l; c) 5 mg C/l, 50 µg As(III)/l; d) 10 mg C/l, 50 µg As(III)/l; e) 5 mg C/l, 100 µg As(III)/l; f) 5 mg C/l; pH 7.5; 10 mmol/l NaNO₃)

Figure 19. Changes over time in the concentrations of total inorganic As, As(III) and As(V), in synthetic matrices containing different initial amounts of As(III) and HA.

Slika 19. Promena koncentracije ukupnog neorganskog As, As(III) i As(V) tokom vremena, u sintetičkom matriksu koji sadrži različiti početni koncentracije As(III) i HA.

Figure 19 shows all the results for the different combinations of initial As(III) and HA concentrations. Figures a), c) and e) show the experiments with initial arsenic

concentrations of 10, 50 and 100 $\mu\text{g/l}$ respectively, with a HA concentration of 5 mg C/l. Figures b), d) and f) show the same three initial As(III) concentrations with 10 mg C/l. In these figures, it is not possible to express the As(V) concentrations as C/C_0 values, as theoretically, the initial As(V) concentrations were all 0. The actual concentrations have therefore been plotted in figure 19.

Each graph shows the total free inorganic arsenic concentration measured in solution (As(III)+As(V)), and the separate values measured for As(III) and As(V). Note that the concentrations of inorganic arsenic shown are the sum of the As(V) and As(III) values measured by steps d) and e) of the speciation method given in 4.2.1, which occasionally differ slightly from the values directly measured during step c (see figure 8), due to the additional handling steps allowing additional opportunities for experimental error. It should also be noted that although the pH of 5.6 was chosen to maximise the dissociation of As(V) whilst maintaining the neutrality of As(III) (see figure 1 in chapter 2.2), the separation of the two arsenic species on the LC-SAX resin is never going to be perfect (Yu et al., 2003).

As was generally the case with the experiments with As(V), in these experiments, increasing the concentration of HA from 5 to 10 mg C/l results in greater overall complexation in each case (see section 5.2.2.1). However, the most significant thing to notice in the six graphs above is the presence of at least some As(V) in all of them. Although there was no As(V) present at the beginning of any of the experiments shown in figure 17, as time passes, increasing amounts of free As(V) were detected in the solutions. Oxidation of As(III) to As(V) in the absence of any other water constituents is very slow (Naidu et al., 2006). Therefore, the rapid oxidation of As(III) to As(V) observed here is due to the presence of HA, which is supported by Redman et al. (2002). They reported the rapid oxidation of As(III) to As(V) by NOM, and suggested that the oxidation was carried out by quinone groups in the NOM acting as electron acceptors. This result is also confirmed elsewhere in the literature, with Ko et al. (2004) reporting that under oxic conditions, HA is much more likely to oxidise than reduce arsenic.

Looking in more detail, a variety of interesting phenomena can be observed: In figure 19 a), the total concentration of free arsenic does not change significantly in the first 30 hours of the experiment. However, the concentration of As(III) drops very quickly, from an initial measured concentration of 9.8 $\mu\text{g As/l}$, down to about 3.1 $\mu\text{g As/l}$ after 5 hours. This change is also reflected in the changing As(V) concentration, which climbs up to 4.6 $\mu\text{g As/l}$ in the same time period. After 24 hours in total, the As(V) concentration has climbed to 5.7 $\mu\text{g As/l}$. After 30 h, the total free arsenic concentration begins to drop more significantly, down to 4.8 $\mu\text{g As/l}$ at the the end of the 48 h experiment. Both As(III) and As(V) concentrations drop in the final 24 hours, however the As(V) concentration drops more significantly (55% in comparison to the 35% drop in As(III)), confirming the results from the kinetics experiments whereby As(V) complexes with the HA more readily than As(III).

From figure 19 a), it would appear that the rate of oxidation of As(III) to As(V) by HA is considerably faster than the rate of complexation: In order to obtain a general idea of the initial rates of complexation, the results over the first 8 hours were fit with a linear regression (the coefficients of determination in all cases were > 0.7). The slope of the increase in As(V) concentrations is around $+0.70$, and the slope of the corresponding decrease in As(III) is -0.88 . The greater magnitude of the As(III) removal slope suggests that some As(III) is being complexed directly with the HA, but only a maximum of 20% of the removed As(III) (calculated from the difference in the slope magnitudes). This is definitely an overestimate, as it fails to take into account the other explanation for the difference in As(III) consumption and As(V) production: some of the As(V) produced is complexed with the HA before the speciation analysis. The slope for the removal of total inorganic arsenic in the first 8 hours is about -0.18 , which is almost 4 times slower than the observable rate of As(V) production.

The experiment in figure 19 b) has the same conditions as 19 a), but with the higher HA concentration of 10 mg C/l. The total arsenic concentration therefore drops more quickly – after 24 h, it is already down to about $6.5 \mu\text{g/l}$. Meanwhile, the As(III) concentration changes are similar to those in figure a) – the concentration drops by about 45%. However, there is a much smaller corresponding increase in the free As(V) concentration. Taking into account the greater reduction in total free arsenic, it seems that at the higher HA concentration, the rate of As(V) complexation is able to initially keep up with the rate of As(III) oxidation (the slope for the total inorganic arsenic removal in the first 8 hours is -0.28 , approximately twice as fast as the previous experiment with half the amount of HA).

Figures 19 c) and d) show the two $50 \mu\text{g As(III)/l}$ experiments, with HA concentrations of 5 and 10 mg C/l respectively. Taking Figure 19 d) into account first, it is initially very similar to 19 b), which also has 10 mg C/l. In the first two hours, 49% of the total arsenic is complexed. After this initial drop, the concentration of free arsenic in the solution then slowly declines until the end of the experiment. Interestingly, during this gradual reduction in the amount of total arsenic, from 4 h to 48 h, the concentration of As(V) increases gradually, whilst the As(III) concentration drops, so As(III) is still being oxidised to As(V). The rate of the As(III) removal after 4 h is about twice as fast as the removal of total free arsenic (-0.17 for As(III), -0.09 for total free arsenic) and the creation of As(V) ($+0.08$). The removal of As(V) under the same conditions (see figure 14) had a slope of -0.05 . If we assume a similar removal rate for As(V) in these experiments with As(III), then effectively all of the As(III) removal is accounted for by the oxidation of As(V), half of which is effectively complexed with the HA before analysis.

The results from the experiment with the lower HA concentration (figure 19 c)) show rapid complexation in the first 2 hours, followed by almost no change in the overall degree of As complexation for the remainder of the experiment. However, beyond the 2 h mark, the oxidation of As(III) to As(V) continues.

The results in figures 19 c) and d) are consistent with the supposition that the complexation sites on the HA and the sites responsible for acting as electron acceptors are not necessarily the same – humic acids are very complex aromatic molecules with amino acids, amino sugars and aliphatic compounds linked together, with phenolic OH groups, quinone structures and carboxylic groups (Redman et al., 2002; Buschmann et al., 2006).

Figures 19 e) and f), which depict the experiments carried out at an initial As(III) concentration of 100 µg/l, demonstrate the same behaviours observed at lower initial As(III) concentrations. In the first two hours of the experiment with 5 mg C/l, the overall concentration of free arsenic in solution dropped by 26%, but the concentration of free As(III) dropped by 33%, with the difference again being accounted for in the production of As(V), which climbed eventually to a maximum of 21.5 µg/l after 8 hours, at which point it represented 25% of the free total arsenic remaining in the solution. The experiment at the higher 10 mg C/l concentration (figure 19 f)) showed that for the final 40 h, the As(III) concentration did not change, with the remaining complexation occurring between the newly formed As(V) and the humic acid present.

At this point, one final observation about the complexation between As(III) and HA may be made. In general, the initial complexation which occurs within the first 2 hours seems to proceed considerably faster than would be expected in comparison with the complexation in the final 46 hours, such that a single decay curve is hard to fit: they underestimate the removal at the beginning of the experiment and overestimate it at the end. This could indicate two separate complexation mechanisms, one which is very fast, and one which is slower, occurring at different sites on the humic acid.

5.2.3 Interactions between a mixture of As(III) and As(V) and HA

Additional experiments with a mixture of both As(III) and As(V) were carried out under similar conditions: The HA concentrations were 5 and 10 mg C/l, and total arsenic concentrations were again 10, 50 and 100 µg/l, i.e. 5, 25 and 50 µg/l of both As(III) and As(V) were initially present in the samples. An example is given in figure 20, with a HA concentration of 5 mg C/l and As concentrations of 50 µg/l As(III) and 50 µg/l As(V).

This series of experiments largely confirmed the conclusions made when investigating As(V) and As(III) by themselves. At the beginning of the experiment, similar amounts of As(III) and As(V) were present. By the end of the 48 h experiment, the total free arsenic concentration in solution had decreased by around 20%. The observed simultaneous removal of As(III) and production of As(V) again suggests the continuous oxidation of As(III) to As(V).

The literature agrees that complexation between humic acid and arsenic occurs with both As(V) than As(III), and may be stronger with As(V). Redman et al (2002) reported the rapid oxidation of As(III) to As(V) by NOM, and suggested that the oxidation was carried out by quinone groups in the NOM acting as electron acceptors. Elsewhere, Buschmann et al (2006) found that As(V) binds more strongly to HA than As(III). They suggest that

As(III) binding to HA may proceed at phenolate functional groups via ligand exchange, and initially assumed that the negative charge of As(V) species at the pH investigated would lead to weaker binding. However, their finding that As(V) binding was stronger than As(III) binding was also reported by (Warwick et al. (2005), leading Buschmann et al. to propose an associative ligand exchange mechanism around the positively charged As(V) centre. Both authors also note that cationic bridging may also contribute significantly to the strong binding of As(V).

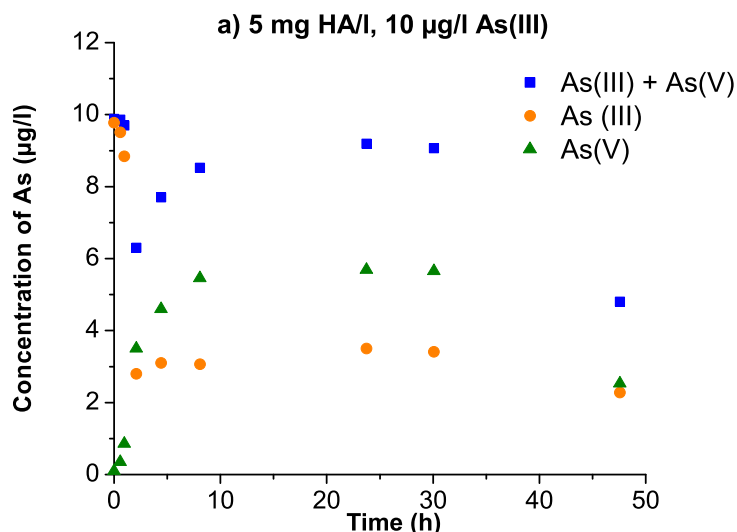


Figure 20. Changes in the free arsenic in solution, with a synthetic matrix (5 mg C/l, 50 µg/l As(III) and 50 µg/l As(V))

Slika 20. Promena koncentracije slobodnog arsena tokom vremena u sintetičkom matriksu (5 mg C/l, 50 µg/l As(III) i 50 µg/l As(V))

Redman et al. (2002) also note the difficulty of isolating the effects of the redox reaction from the effects of the binding reaction—an unfortunate limitation of this investigation is the inability to speciate the arsenic complexed with the HA, in order to definitively establish which species of arsenic has the strongest affinity for binding to HA in this system.

Summary of the arsenic:humic acid interactions identified

In the results presented in figures 16 – 20, the concentrations of both free As(V) and free As(III) in all the solutions investigated fell over time. Together with the good fit of the preliminary experimental data to the pseudo-second order model shown in figure 15, these results strongly suggest that both As species form complexes with HA. This is in agreement with Redman et al. (2002), and confirms the first interaction hypothesised in Objective 2, Chapter 3.

Furthermore, the existence of As(V) in each of the series of experiments given in figure 19 confirms that in the presence of HA, As(III) is readily oxidised to As(V). This is also in accordance with Redman et al (2002). and Buschmann et al. (2006), and is strong evidence for the redox interaction hypothesised in Objective 3.

Taken as a whole, the results from this research phase suggest the presence of up to three separate interactions between arsenic and humic acid, occurring at at least two different types of site on the surface of the humic acid molecules (Watson et al., 2012):

- a) A rapid complexation interaction, which reaches equilibrium within two hours, and which complexes both As(III) and As(V)
- b) A rapid redox interaction which oxidises As(III) to As(V). It is possible this interaction occurs at the same sites as the first complexation interaction, and.
- c) A slower complexation interaction, which takes closer to two days to reach equilibrium, and which has a greater affinity for As(V).

Note that the first two may in fact be the same interaction, with the oxidation step creating a chemical bond between the HA and As(V).

5.3 Development, characterisation and investigation of iron oxide based adsorbents




The first arsenic removal technology to be investigated by this dissertation is adsorption using iron oxide based adsorbents. Two iron oxide coated sands, prepared from iron chloride (IOCS1) and iron nitrate (IOCS2), were successfully developed in the laboratory (see chapter 4.3.1), and their general characteristics and capacity for arsenic adsorption were compared with a third iron oxide coated sand (IOCSW), which was sourced from a sand filter for the removal of iron and manganese at a local drinking water treatment plant.

5.3.1 Characterisation of the adsorbents (IOCS1, IOCS2, IOCSW)

Table 11 summarizes the results obtained during the physical characterisation of the three IOCS investigated, some of which were previously published (Watson, 2013; Watson et al., 2013b).

Table 11. Characterisation for the three iron oxide based adsorbents investigated.

Tabela 11. Karakterizacija ispitivanih adsorbenata na bazi gvožđe oksida

Parameter	IOCS1	IOCS2	IOCSW
Physical appearance			
Prepared from	FeCl ₃	Fe(NO ₃) ₃	Spent filter sand for removal of Fe + Mn
Granularity (mm)	0.8-1	0.8-1	1-1.6
Iron content (mg Fe/g)	4.45	6.14	4.82
Point of zero charge (pH _{pzc})	7	8	7
BET surface area (m ² /g)	7.887	6.928	33.83
SEM surface structure (nm)	55–75	24–35	30–55

Granularity: The two laboratory prepared IOCS have significantly smaller grains than the spent filter sand (table 11). This is to be expected due to the different qualities of materials they were prepared from. IOCS1 and IOCS2 were developed from fine quartz sand which had already been acid-washed, rinsed, dried and passed through a series of sieves to isolate the 0.5-0.8 mm fraction. The coating process thus increased the size of the granules by around 0.25 mm. In contrast, as explained in chapter 4.3.1.2, the sand generally used by water treatment plants is bought in bulk and has a wider initial particle size distribution (0.6–1.2 mm). The coating process of IOCSW is also considerably longer, as the sand filters are in operation for months at a time before the sand is fully spent, so that grain size

is larger (1–1.6 mm). In general, the difference in grain sizes was not expected to make a significant difference in the experiments planned in this dissertation, as they are all static, batch-type experiments. It is worth mentioning for future investigations however, as contact times between the water and the IOCS investigated in dynamic column experiments will be affected by the differences.

Iron contents: The iron contents of the three IOCS investigated were determined by acid digest followed by AAS analysis (table 11). Theoretically, the greater the iron content, the better the expected arsenic adsorption capacity of the sorbent, although the amount of iron on the external surface of the grains is a lot more relevant than the iron underneath. In this case, at 6.14 mg Fe/g, the coating of IOCS2 has the greatest iron content. These iron contents are similar to those reported for IOCS1 and IOCS2 by Thirunavukkarasu et al. (2001, 2003),

Point of zero charge: The point of zero charge (pzc) describes the condition when the electrical charge density on a surface of a sorbent is zero. Thus, the pzc is generally the pH value at which a solid submerged in a solution has a surface with a net electrical charge of zero.

As shown in figure 1, As(V) is anionic at all pH values greater than pH 2, whereas As(III) is largely neutral from pH 2 to pH 8, and only becomes significantly anionic above pH 9. The zero point charge of IOCS2 is 8, which means that at pH 7, the surface is positively charged, and therefore likely to attract As(V) anions, directly increasing the affinity of IOCS2 to adsorb As(V) (table 11) (McCafferty, 2010). The zero point charge of IOCS1 and IOCSW is 7, so at pH 7 their surfaces are neutral, so that electrostatic interactions between their surfaces and the As(V) anions do not occur, neither benefiting or adversely affecting adsorption.

None of the IOCS studied will attract or repel As(III) at any pH likely to be found in drinking water sources. The range of points of zero charge found for these three IOCS agrees with those reported in the literature, which are in the range pH 6.5–8.5 (Schwertmann and Cornell, 2000).

BET specific surface areas: The specific surface area of a sorbent is one of its most relevant physical characteristics. Larger surface areas lead to better contact between the sorbent and the liquid being filtered. In general, the specific surface areas of natural and synthetic iron oxides lie in the range of several to hundreds of m^2/g (Schwertmann and Cornell, 2000).

BET analysis determined that the specific surface areas of IOCS1, IOCS2 and IOCSW are 7.887, 6.928 and 33.83 m^2/g , respectively (table 11). The specific surface areas of IOCS1 and IOCS2 are in good agreement with the results of Thirunavukkarasu et al. (2001, 2003) who reported an area 5.1 m^2/g for similarly prepared IOCS. The difference in specific surface areas between IOCS1 and IOCS2 stem from differences in the preparation and

baking processes (see section 4.5.1), which is utilised in order to increase the expulsion of water molecules, leading to the development of porous structure.

The specific surface area of IOCSW is more than 4 times larger than either of the laboratory prepared IOCS, which can be explained by the long operation time of the sand filter for iron and manganese removal. It is also more than 10 times greater than the specific surface area of a similar material reported by Hsu et al. (2008), who investigated an IOCS reclaimed from a different technological process. The specific surface areas of all three IOCS suggest that the iron oxide is in fact hematite ($\alpha\text{-Fe}_2\text{O}_3$), the specific surface of which ranges from 2-90 m^2/g (Schwertmann and Cornell, 2000).

5.3.1.1 SEM and EDS analysis

In order to gain insight into the morphology of the IOCS surfaces and their elemental compositions, the three sorbents were analysed by SEM (Figure 21; Watson et al., 2013b).

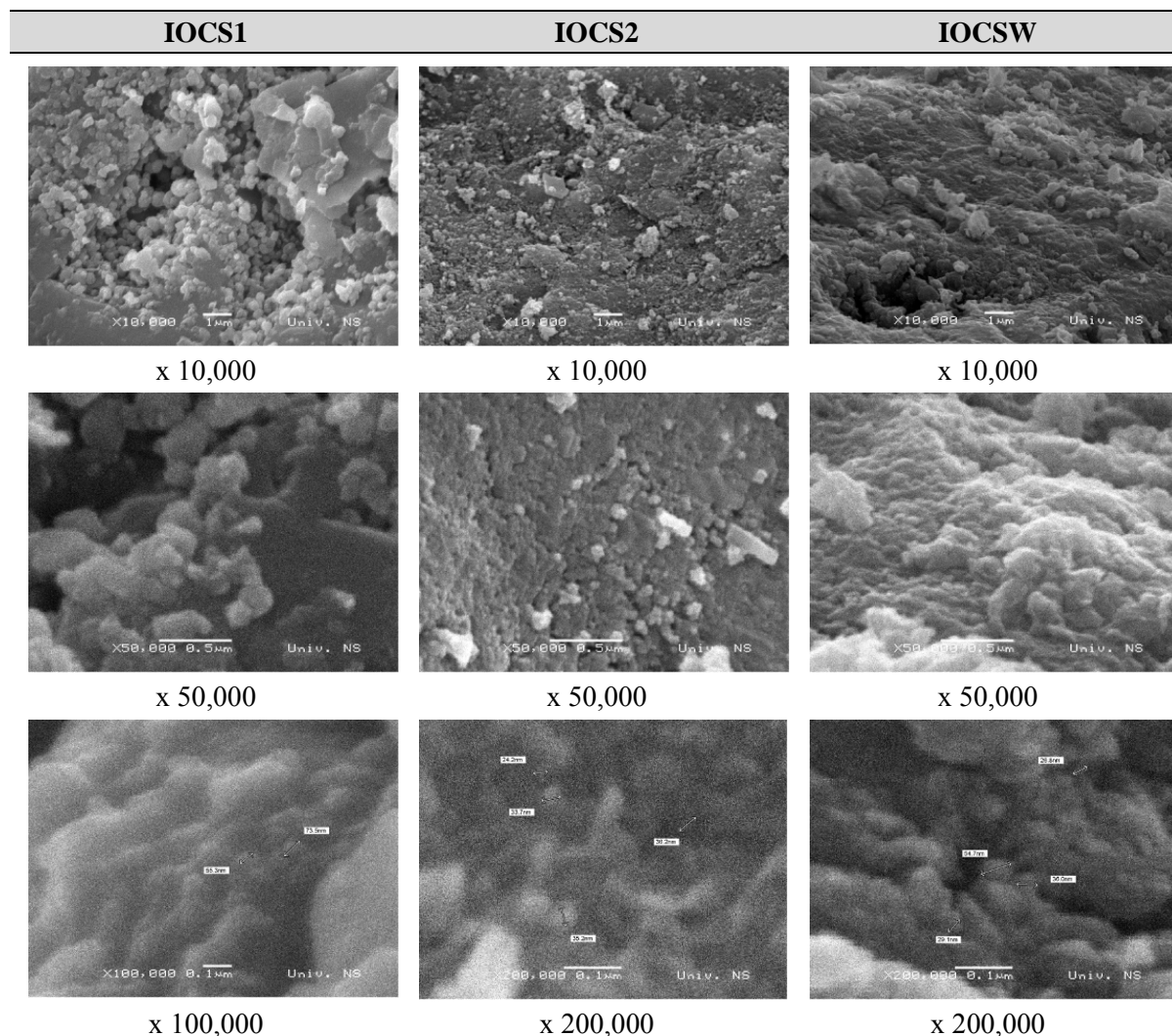


Figure 21. Results of SEM analyses for the three IOCS investigated.

Slika 21. Rezultati SEM analize tri ispitivana IOCS sorbenta.

The SEM images were taken at 10,000, 50,000 and 100,000 times magnification levels. At the first level of magnification, it appears as if IOCS1 has the roughest surface, with IOCS2 and IOCSW appearing relatively smooth, with infrequent small protrusions. However, at the highest level of magnification, the reason for the large specific surface area of IOCSW has become apparent. As shown in table 11, all three IOCS have visible nanostructures, which were measured by the SEM analysis and ranged from 55–75 nm for IOCS1, 24–35 nm for IOCS2, and 30–55 nm for IOCSW. However, at the 200,000 times magnification level, these structures are shown to have much better definition in the IOCSW image, with deep cavities and pores visible. The differences apparent in the three IOCS at the highest magnification level are therefore in very good agreement with the results of the BET specific surface area.

Naturally, it is not just the physical structure of the surface of an adsorbent which is important, the chemical make-up of the surface is also very significant. For this reason, EDS spectra were also taken of the IOCS investigated (examples shown in figure 22).

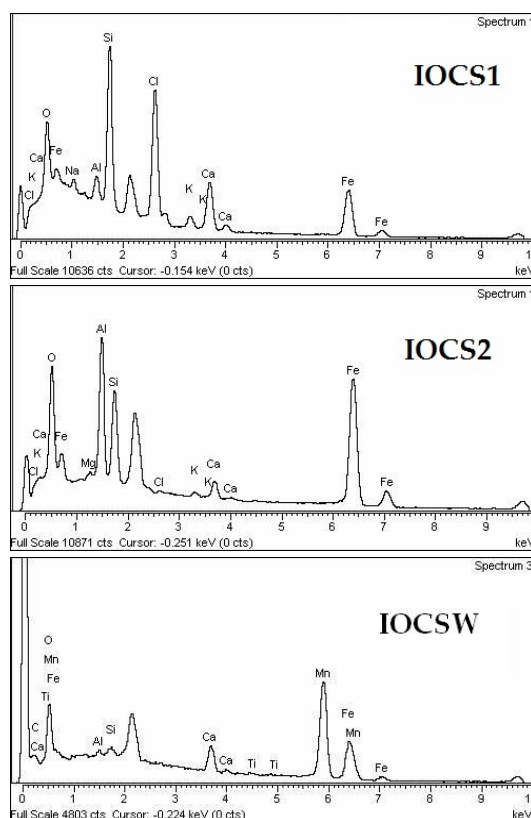


Figure 22. EDS spectra of IOCS1, IOCS2 and IOCSW.

Slika 22. EDS spektar IOCS1, IOCS2 i IOCSW

Note that the EDS spectra were in fact analysed at three different points on the surface of each IOCS, and the means of the elemental surface coverage calculated. The most interesting results are summarised in figure 23 (Watson et al., 2013).

IOCS1 was prepared from FeCl_3 , whereas IOCS2 was prepared from $\text{Fe}(\text{NO}_3)_3$. This difference is reflected by the large chlorine peak visible in the EDS spectra of IOCS1. The

chemicals and baking procedures used during their preparation also resulted in differences in iron coverage of IOCS1 and IOCS2. As can be seen in figure 23, the iron coverage for IOCS1 is just 16%, and the iron coverage for IOCS2 is 28%. This may be a

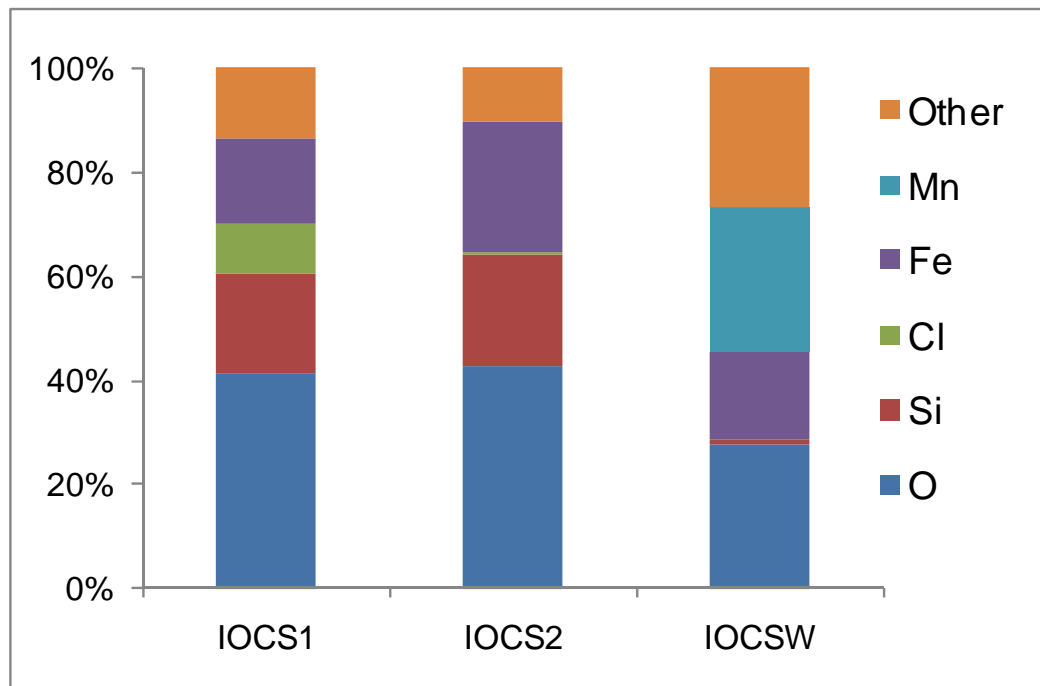


Figure 23. Summary of the EDS analyses of the three IOCS investigated, showing the percentage surface coverage of certain elements.

Slika 23. Rezultati EDS analize tri ispitivana IOCS sa procentom pokrivenosti površine određenim elementima.

The spectra also show two very significant differences between IOCSW and the two IOCS prepared in the laboratory: IOCSW has a very small silicon peak, and a very large manganese peak. The silicon peaks of IOCS1 and IOCS2 suggest that neither of the laboratory coating processes achieved complete coverage of the underlying quartz sand; the fact that IOCSW has no silicon peak shows that its coating is considerably more effective. The presence of manganese on the surface of IOCSW is also very interesting, because manganese also has a very good affinity for the adsorption of arsenic, and the application of iron-manganese binary oxides for arsenic removal has been a hot topic in the recent literature (Chakravarty et al., 2002; Zhang et al., 2007; Chang et al., 2011; Wu et al., 2012; Kong et al., 2013).

In fact, it turns out there is more manganese (28% coverage) than iron (17%) on the surface of IOCSW. This is a consequence of the quality of the raw water which enters the sand filter for iron and manganese removal from which the IOCSW originates. Waste filter sands from other water works will have different ratios of iron and manganese, depending on the ratio of iron and manganese in the water they treat. In this case, the total coverage of IOCSW which is available for As adsorption is 45% (iron plus manganese), suggesting that

in combination which its large surface specific area, it should be highly effective at removing arsenic from groundwater.

5.3.2 Investigating the arsenic removal capability of the adsorbents

In this section, the results of the initial arsenic adsorption experiments are presented. These experiments were carried out in synthetic matrices with a pH of 7 containing only arsenic, either as As(V) or as As(III), at initial arsenic concentrations of 200 $\mu\text{g/l}$.

5.3.2.1 Arsenic(V) removal capacities of IOCS

The As(V) removals achieved by the different doses of IOCS1, IOCS2 and IOCSW, in the absence of any competitive ions, are shown in figure 24 below.

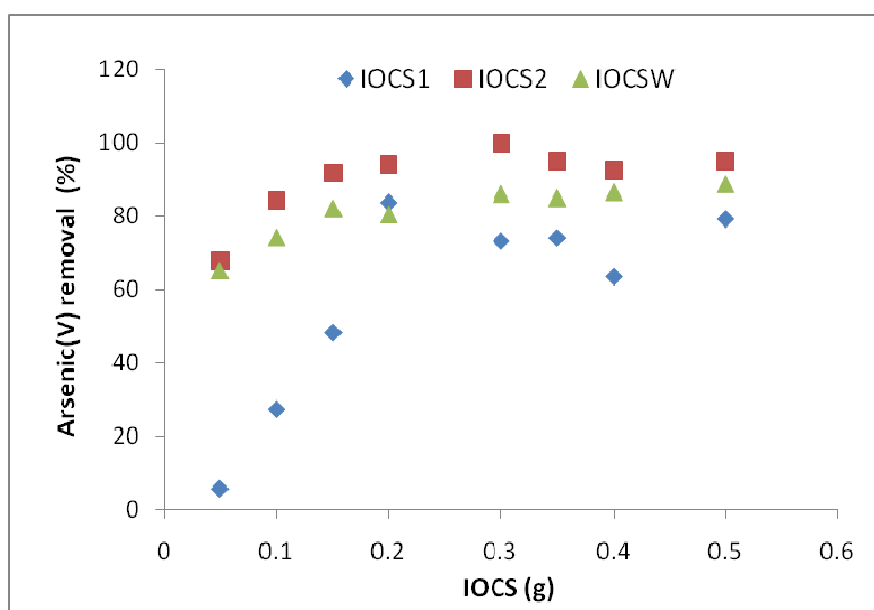


Figure 24. Arsenic(V) removals achieved after a 24 hour equilibration time by different doses of IOCS in a synthetic matrix initially containing 200 $\mu\text{g As/l}$.

Slika 24. Uklanjanje arsena(V) nakon ravnotežnog vremena od 24 sata primenom različitih doza IOCS u sintetičkom matriksu sa početnom koncentracijom od 200 $\mu\text{g As/l}$.

The greatest degree of As(V) removal achieved by IOCS1 was 83.7%, at a dose of 0.2 g. At this dose, the initial 200 $\mu\text{g As/l}$ was reduced to 32.5 $\mu\text{g/l}$. Increasing the dose beyond this point did not improve the removal efficacy. At doses less than 0.2 g, the effective As(V) removal increased steadily with increasing IOCS1 dose. The lowest dose of 0.05 g removed only 5.75% of the initial arsenic. Lower doses of IOCS2 and IOCSW were much more effective. 0.05 g of IOCS2 and IOCSW were sufficient to remove 65.2 and 67.8% of the initial As(V) respectively. Increasing the doses of IOCS2 and IOCSW beyond 0.3 g did not result in improved As(V) removal, and resulted in better than 90% removals for both IOCS2 and IOCSW at a dose of 0.3 g.

Comparing the actual arsenic concentrations after treatment by IOCS with the MAC of 10 µg/l (Official Gazette RS 42/98 and 44/99, 1998) shows that the results for IOCS1 are not particularly encouraging. However, both IOCS2 and IOCSW successfully brought the arsenic concentrations in the synthetic matrix down from an initial concentration of 200 µg/l arsenate to below 10 µg/l at all doses greater than 0.3 g for IOCS2 and at a dose of 0.5 g for IOCSW. The IOCS2 results are very similar to the results of Gupta et al (2005). The fact that IOCS2 proved to be more effective than IOCSW, despite having a considerably smaller surface area, is best explained by the differences in their points of zero charge. As already mentioned, IOCS2 has a pzc of 8, whereas IOCS1 and IOCSW both have a pzc of 7. This means that at pH 7, IOCS2 has a positively charged surface, and therefore attracts the As(V) anions, greatly favouring adsorption.

Elsewhere, Hsu et al., (2008) performed similar experiments with a different reclaimed IOCS. In their case, the IOCS was taken from a fluidized and air-aerated bed reactor for the removal of ferrous ions from a nitrate removal system. The efficacy of IOCSW in this investigation compares favourably to the results Hsu et al. (2008) achieved under the same initial conditions (200 µg As(V)/l, pH 7), whereby they report 1 g of their reclaimed IOCS removing about 65% of the arsenic. The improved performance of IOCSW relative to IOCS1 and the IOCS of Hsu et al. (2008) is likely due to its much larger surface area.

According to Catalano et al. (2008), the adsorption of arsenic onto hematite occurs with the simultaneous formation of inner (specific adsorption) and outer sphere complexes (external adsorption). The outer sphere complexes are formed by ligand exchange between the oxyanions of arsenate and arsenite and the hydroxyl groups on the surface of the IOCS (Thirunavukkarasu et al., 2003). Non-specific adsorption (spherical outer surface complexation) involves electrostatic attractions between oppositely charged surfaces and the ions in solution, wherein the ions is adsorbed at a certain distance from the specific surface area. The bonds in the inner sphere complexes are stronger and more difficult to break, providing strong adsorption of ions, unlike the outer spherical complexes where the bonds are much weaker. The formation of external spherical complexes is therefore sensitive to changes in the ionic strength of a solution and is limited to pH values lower than the pH_{pzc} of the adsorbent (Cheng et al., 2009; Zhang et al., 2009).

On the basis of these results, it seems clear that for the removal of As(V), IOCS2 and IOCSW have considerably more potential than IOCS1. This is due to the increased coverage of iron and manganese on their surfaces. Note that although IOCS2 proved to be the most effective at the doses investigated, the fact that IOCSW is a waste material already generated by water treatment plants in Vojvodina makes it highly likely to be the most economically efficient IOCS to implement in full-scale treatment plants.

5.3.2.2 Arsenic(III) removal capacities of IOCS

The results for the As(III) removals achieved by the same IOCS in the absence of any competitive ions are given in figure 25. As explained above, the high performance of

IOCS2 for the removal of As(V) was due to its elevated point of zero charge allowing for electrostatic attraction between the arsenate anions and the IOCS surface at pH 7. However, at this pH, the vast majority of As(III) present in solution is neutral (see table 2), and the higher point of zero charge of IOCS2 does not yield an advantage, so that its removal of As(III) does not significantly differ from that of IOCS1. For all the investigated IOCS, there is not a large difference in the As(III) removals achieved. However, at doses ≥ 0.4 g, IOCSW displayed better performance than IOCS1 and IOCS2. The percentage removals of As(III) achieved at a dose of 0.5 g were 70.9% for IOCS1, 76.2% for IOCS2, and 93.4% for IOCSW.

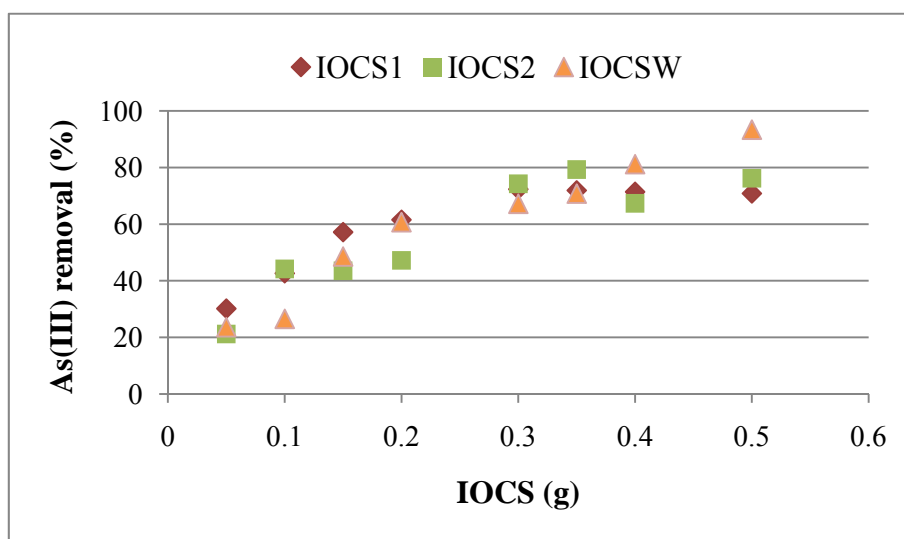


Figure 25. Arsenic(III) removals achieved in 24 hours by different amounts of IOCS in a synthetic matrix initially containing 200 $\mu\text{g/l}$ As.

Slika 25. Uklanjanje arsena(III) nakon ravnotežnog vremena od 24 sata primenom različitih doza IOCS u sintetičkom matriksu sa početom koncentracijom od 200 $\mu\text{g/l}$ As.

Meanwhile, the greatly improved removal of As(III) by IOCSW compared to its removal of As(V), can be satisfactorily explained by the manganese on its surface. As mentioned above, iron:manganese binary oxides have been widely investigated for arsenic removal, and have been particularly successful at removing As(III) (Chakravarty et al., 2002; Chen et al., 2006; An and Zhao, 2012; Kong et al., 2013). According to these sources, manganese oxide is not only capable of adsorbing As(V), it is also capable of oxidising and/or adsorbing As(III), indicating the existence of more than one removal mechanism. Although it was originally sourced due to its expected iron oxide coating, as explained in section 5.3.1.5 above, IOCSW actually has more manganese on its surface than iron. Its strong affinity for As(III) adsorption is therefore completely in agreement with the literature.

In general, IOCS1 and IOCS2 were less effective at removing As(III) than As(V), whereas IOCSW was actually more effective.

5.3.2.3 Modelling the arsenic removal capacities of IOCS with the Langmuir and Freundlich isotherms

In order to simplify comparison of results between the different IOCS investigated in this work and in the literature, whilst also obtaining additional information about the adsorption mechanisms at work, each of the above As(V) and As(III) adsorption experiments were modelled using the Freundlich and Langmuir isotherms, as shown in figures 26 and 27.

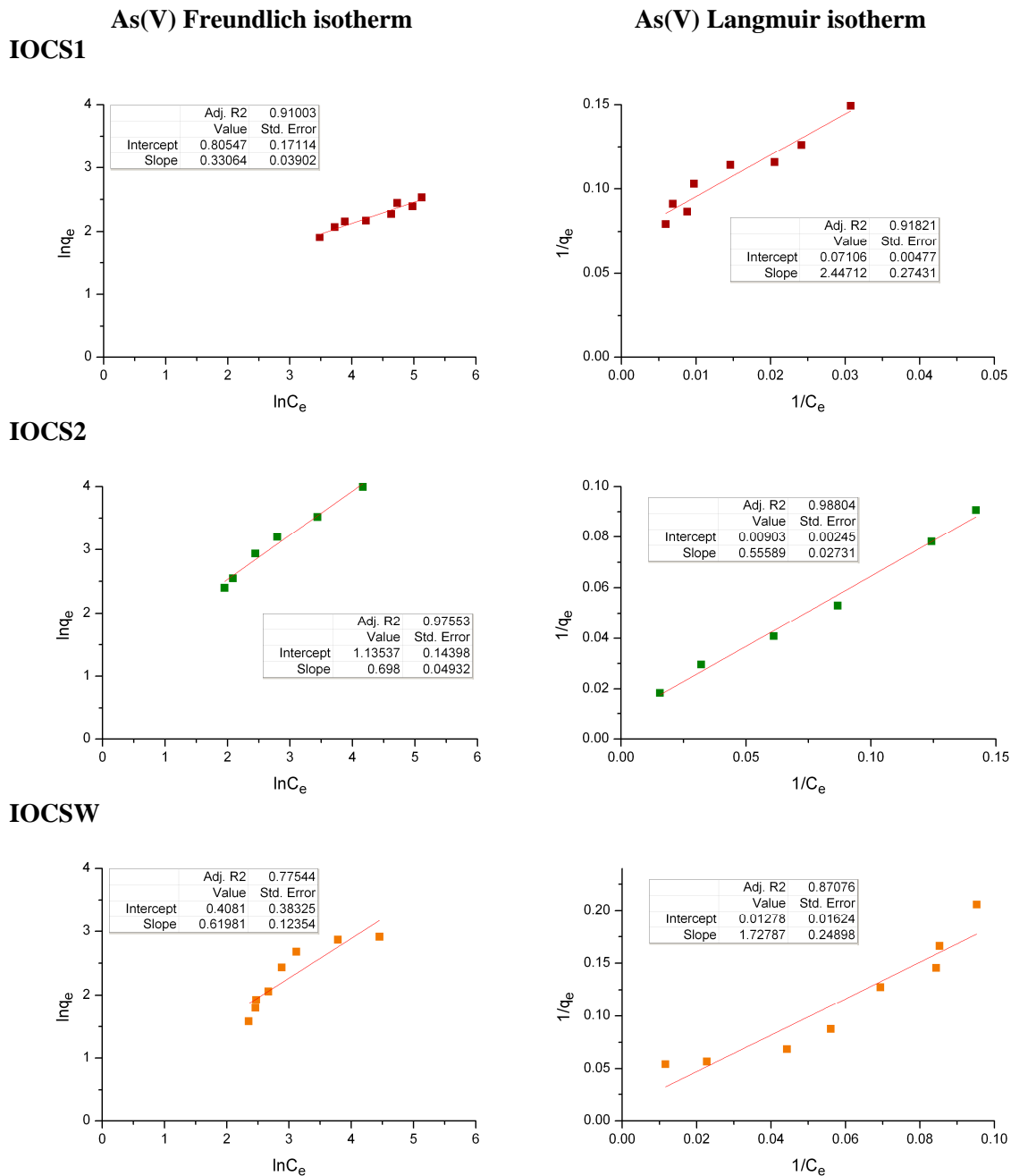


Figure 26. Freundlich and Langmuir isotherms for the adsorption of As(V) onto IOCS1, IOCS2 and IOCSW.

Slika 26. Freundlich i Langmuir adsorpcione izoterme As(V) na IOCS1, IOCS2 i IOCSW.

The Freundlich isotherm assumes multilayer adsorption onto a heterogeneous surface. The Freundlich constant K_F relates to the adsorption capacity, with larger K_F values indicating

larger overall capacities, and n is a dimensionless constant indicating the adsorption intensity – how rapidly adsorption is expected to occur. The Langmuir isotherm assumes a homogenous surface whereby all adsorption sites are equivalent. It also assumes monolayer coverage only, which allows for the definition of q_{max} , the maximum adsorption capacity of the sorbent. The Langmuir constant K_L relates to the energy of adsorption.

As explained in section 2.3.2, in order to obtain linear plots, the Freundlich isotherms were plotted as $\ln q_e$ versus $\ln C_e$, and the coefficients calculated:

$$K_F = e^{(intercept)}; b = (slope)^{-1}. \quad \text{Eq. 13}$$

In a similar vein, Langmuir isotherms were plotted as $1/q_e$ versus $1/C_e$, and the coefficients calculated as shown below:

$$K_L = \frac{intercept}{slope} \quad \text{Eq. 14}$$

$$q_{max} = (slope)^{-1} \quad \text{Eq. 15}$$

The separation factor R_L was also calculated, as given in Eq 5 in section 2.3.2. The separation factor is effectively defined by the shape of the isotherm, and yields information about the nature of the adsorption process. For $R_L > 1$ adsorption is unfavourable; for $0 < R_L < 1$ adsorption is favourable; for $R_L = 1$ adsorption is linear; and for $R_L = 0$, adsorption is irreversible.

Based on the adjusted R^2 values, As(V) adsorption by all three IOCS is better described by the Langmuir isotherm, although in the case of IOCS1 and IOCS2, the difference in the goodness of fit is very small. With the exception of IOCS1, the situation is the same with adsorption of As(III), with the Langmuir isotherm having very marginally better adjusted R^2 values than the Freundlich isotherm.

The very small adsorption affinity obtained for As(III) adsorption onto IOCS1 ($K_F = 0.0040$, table 10) by the Freundlich isotherm is evidence that the concentrations investigated (initial As(III) concentration = 200 $\mu\text{g/l}$, 0.05 to 0.5 g IOCS1) are too high to accurately model this system with the Langmuir isotherm: the difference between C_0 and C_e values are generally small, increasing the impact of analytical error on the model. Given the fact that negative values of the Langmuir constant have no physical meaning, it can therefore be concluded that the Freundlich isotherm is more appropriate for this system within the concentration range investigated.

Table 12 summarises the goodness of fit for each experiment, and provides the corresponding K_F , n , K_L , q_{max} and R_L values. Looking at the Freundlich isotherm, for all three IOCS investigated, K_F values obtained for the As(V) adsorption are about an order of magnitude larger than the values obtained for As(III), indicating that As(V) is adsorbed considerably more effectively than As(III). The largest K_F values for As(III) and As(V) were 0.3096 and 3.112 (mg/g)(l/mg)^{1/n} respectively, and were observed for IOCS2. The lowest K_F value for As(III) was 0.0040 (mg/g)(l/mg)^{1/n} for IOCS1, and the lowest K_F value

for As(V) was $1.504 \text{ (mg/g)(l/mg)}^{1/n}$. In general, the high K_F values compare favourably to a similar investigation into iron oxide coated granulated activated carbons, which were 0.647 and 0.140 $(\mu\text{g/g})(\text{l}/\mu\text{g})^{1/n}$ for As(V) and As(III) respectively (Jovanović and Ljubisavljević, 2011).

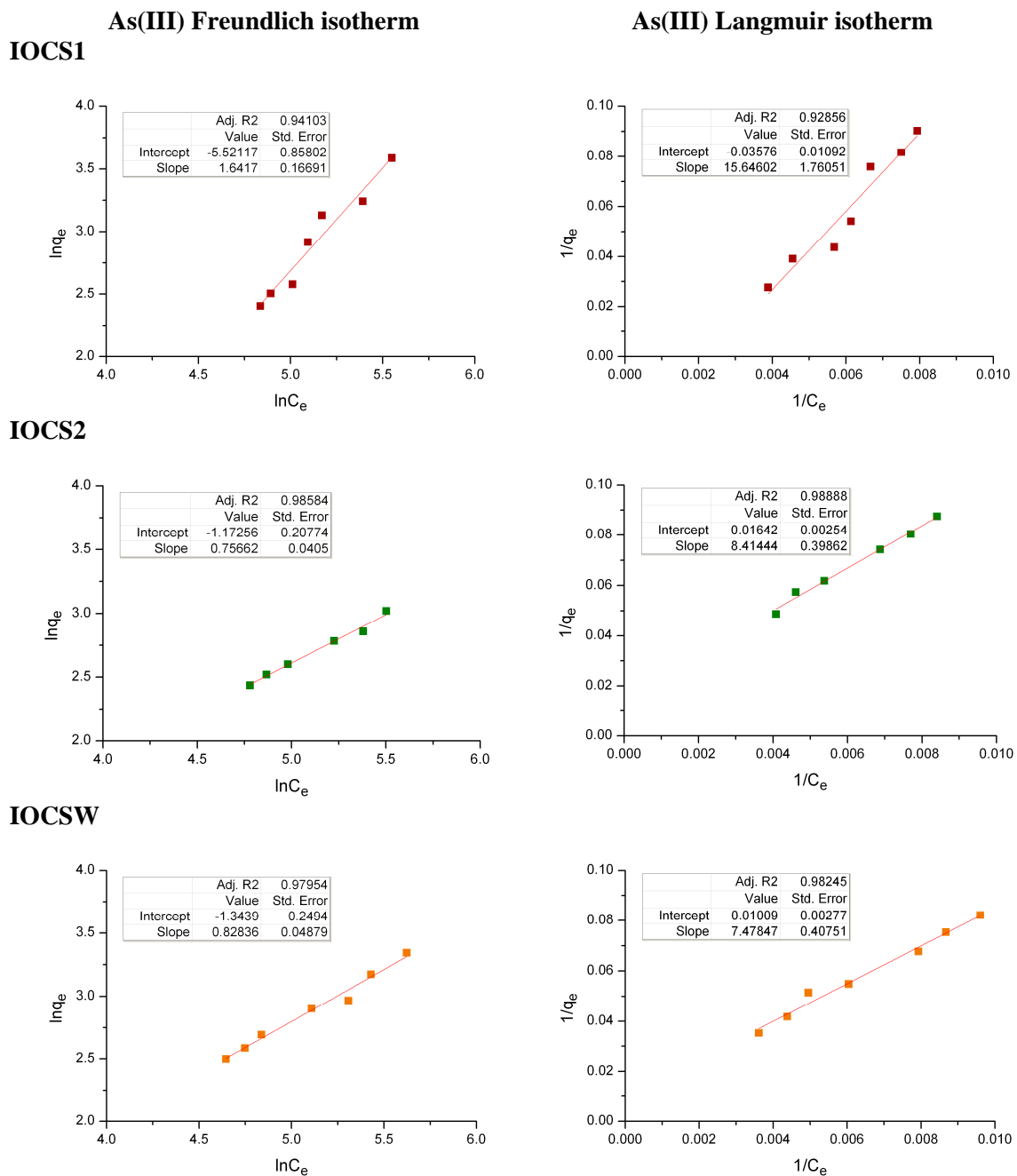


Figure 27. Freundlich and Langmuir isotherms for the adsorption of As(III) onto IOCS1, IOCS2 and IOCSW.

Slika 27. Freundlich i Langmuir adsorpcione izoterme As(III) na IOCS1, IOCS2 i IOCSW.

From the Langmuir isotherms, the values of R_L are all between zero and one, indicating favourable adsorption in all cases. The largest As(V) q_{max} was the 111 $\mu\text{g/g}$ achieved by IOCS2, 1.4 times larger than the 78.3 $\mu\text{g As(V)/g}$ adsorption capacity of IOCSW, and

almost 8 times larger than the 14.1 $\mu\text{g As(V)/g}$ obtained for IOCS1. For As(III), IOCSW has the largest q_{max} of 99 $\mu\text{g As(III)/g}$, 1.6 times larger than the q_{max} obtained for IOCS2.

Table 12. Summary of parameters obtained for the Freundlich and Langmuir isotherms, for the adsorption of As(III) and As(V) on IOCS1, IOCS2 and IOCSW.

Tabela 12. Parametri Freundlich i Langmuir adsorpcione izoterme As(III) i As(V) na IOCS1, IOCS2 i IOCSW.

Isotherm	IOCS1		IOCS2		IOCSW	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Freundlich						
$Adj. R^2$	0.9410	0.9100	0.9858	0.9755	0.9795	0.7754
$K_F (\mu\text{g/g})(l/\mu\text{g})^{1/n}$	0.0040	2.238	0.3096	3.112	0.2608	1.504
n	0.6091	3.024	1.3217	1.433	1.2072	1.613
Langmuir						
$Adj. R^2$	0.9286	0.9182	0.9889	0.9880	0.9824	0.8708
$K_L (l/\mu\text{g})$	n/a	0.0290	0.0020	0.0162	0.0013	0.0074
$q_{max} (\mu\text{g/g})$	n/a	14.07	60.90	110.7	99.11	78.25
R_L	n/a	0.147	0.590	0.236	0.689	0.506

The Freundlich and Langmuir isotherms therefore revealed broadly similar trends, with the As(V) adsorption capacity being greater than the As(III) adsorption capacity, with one notable exception: in the Langmuir isotherm, the q_{max} for adsorption of As(III) onto IOCSW is 99.1 $\mu\text{g/g}$, and only 78.3 $\mu\text{g/g}$ for As(V). As explained in section 5.3.2.2 above, the significantly better adsorption of As(III) by IOCSW is due to it having a large percentage of manganese on its surface as well as iron. As such, it is therefore actually a Fe-Mn binary oxide due to the ability of manganese oxide to oxidise arsenite to arsenate (Zhang et al., 2007; Ruiping et al., 2009; Chang et al., 2010; Wu et al., 2011). These authors have all reported that Fe-Mn binary oxides are therefore capable of removing large amounts of As(III) as well as As(V). The results for IOCS1 and IOCS2, which do not include manganese on their surface, and where As(V) is adsorbed better than As(III), are in agreement with the findings of Hsu et al. (2008a).

5.3.3 The effect of certain competitive ions on arsenic removal by IOCS

Naturally, in real groundwaters, arsenic is never found alone – there is always a wide variety of other water constituents, all of which have the potential to interfere with the adsorption process, most often by competing for adsorption sites on the surface of the sorbent. This section presents the results of an investigation into the effects of three different ions which are commonly found in arsenic-bearing groundwaters and which have the potential to act as competitive ions during the adsorption process: phosphate (PO_4^{3-}), silicate (SiO_3^{2-}) and humic acid (HA). The effect of these competitive ions on the adsorption of both As(V) and As(III) by IOCS1, IOCS2 and IOCSW was investigated.

5.3.3.1 Arsenic removal by IOCS in the presence of phosphate

Figure 28 shows the arsenic removal achieved by different doses of the three IOCS investigated at initial As concentrations of 200 $\mu\text{g/l}$, in the absence of phosphates, and in the presence of 1, 5 and 9 mg $\text{PO}_4^{3-}/\text{l}$ (concentrations based on typical environmental concentrations in the groundwaters of Vojvodina).

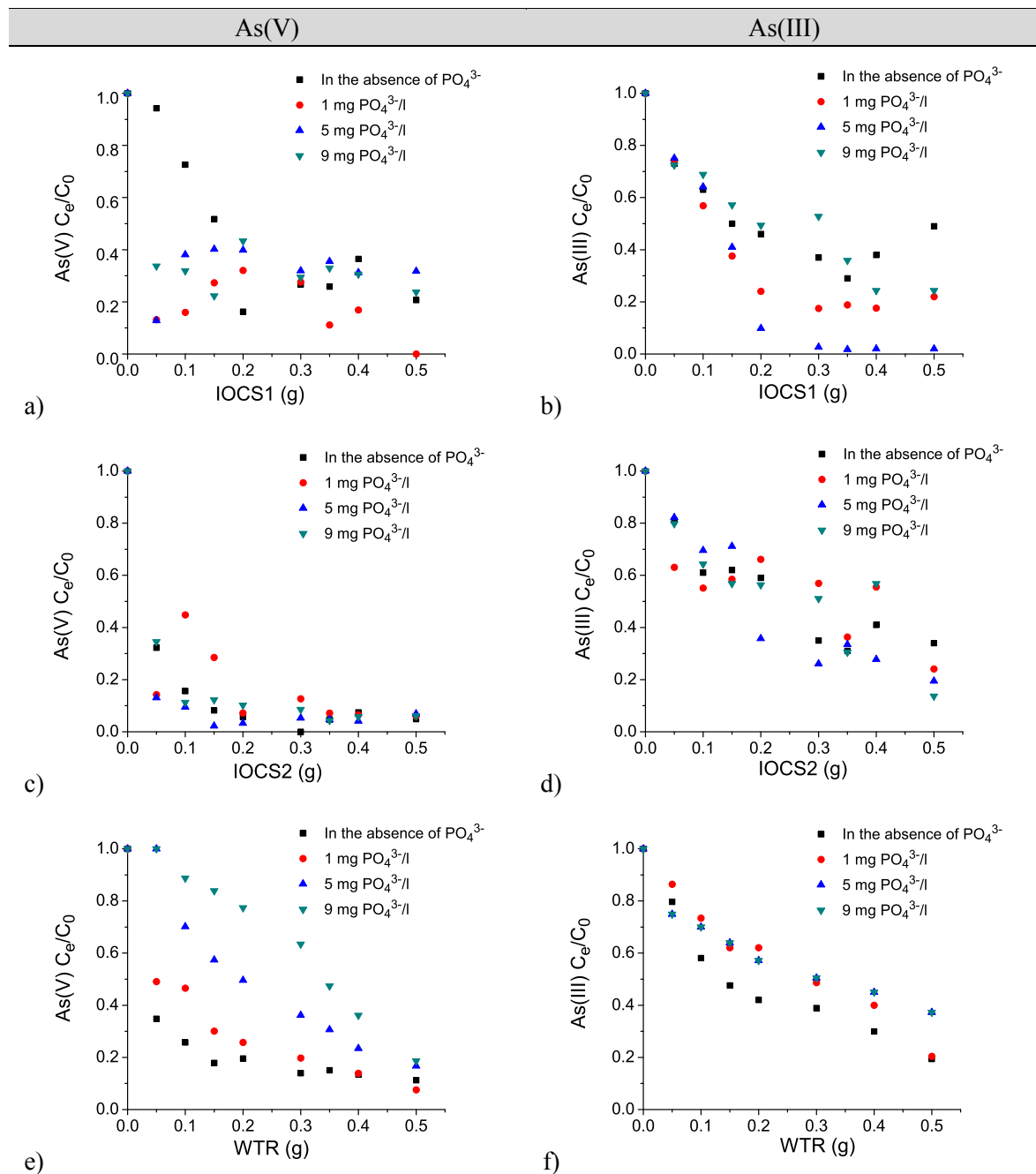


Figure 28. Effect of phosphates on the removal of arsenic by IOCS (initial concentration 200 $\mu\text{g As/l}$).

Slika 28. Uticaj fosfata na uklanjanje arsena primenom IOCS pri početnoj koncentracija od 200 $\mu\text{g As/l}$.

Boujelben et al. (2008) investigated the adsorption of phosphate ions on IOCS and iron oxide coated brick, and after fitting their data to the Langmuir isotherm, reported phosphate adsorption capacities of the order of 1 mg PO₄³⁻/g sorbent. Elsewhere, Youngran et al. (2007) concluded that phosphate ions directly competed with arsenic for adsorption sites on the surface of IOCS, and thus reduced the arsenic removal efficacy of their adsorbent. The presence of phosphate was therefore expected to interfere with the removal of arsenic in this experiment.

The IOCS1 results in figures 28 a) and b) are therefore very interesting, whereby the presence of low amounts of phosphate enhanced the removal of both As(V) and As(III). This effect was particularly noticeable at low IOCS1 doses, when the loading (the amount of arsenic adsorbed per gram of adsorbent) is greatest. At doses of 0.05 and 0.1 g IOCS1, 1 mg PO₄³⁻/l increased As(V) adsorption from 15.8% and 27.4% respectively, to around 58% for both doses. The increase in As(III) adsorption at these lower IOCS1 doses (0.05 and 0.1 g) was much less significant, but at greater doses, up to 0.5 g, the presence of 1 mg/l phosphate improved As(III) adsorption from around 60% to 80% at 1 mg PO₄³⁻/l, and almost 100% at 5 mg PO₄³⁻/l.

The impact of phosphates on the adsorption of arsenic on IOCS2 is considerably less pronounced. At the lower IOCS2 doses, 1 mg PO₄³⁻/l reduces the efficacy of the As(V) removal process, whereas the higher concentrations of phosphate improve As(V) removal. However, any negative effect from the phosphate concentrations investigated was not enough to impair the removal of As(V) at IOCS2 doses above 0.2 g. Broadly speaking, As(III) removals were not as significantly impacted as the As(V) removals, with almost no change in As(III) removal observed at IOCS2 doses of less than 0.2 g. However, at the maximum applied dose of 0.5 g IOCS2, As(III) removals were slightly improved, from about 65% removal in the absence of phosphate to around 80% removal with phosphate. The literature does not have a satisfactory explanation for this observation, so the mechanism behind this increase in As(III) removal should be the subject of future research.

The impact of phosphates on the arsenic removal by IOCSW is considerably clearer. As shown in figures 28 e) and f), As(V) adsorption is hindered by phosphates, and As(III) adsorption is not. With just 1 mg PO₄³⁻/l, the effect was less obvious, reducing As(V) adsorption by around 10% at low doses of IOCSW (< 0.1 g). However, at those same low doses, higher phosphate concentrations resulted in the adsorption of considerably less As(V), dropping from 74% with a dose of 0.1 g IOCSW in the absence of phosphates, down to 30% and 11% As(V) removal at 5 and 9 mg PO₄³⁻/l respectively. Even at greater IOCSW doses, the competitive effect of high phosphate concentrations is readily apparent, such that whereas in the absence of phosphates 0.5 g IOCSW removed 89% of the As(V), the presence of 5 and 9 mg PO₄³⁻/l lead to As(V) removals of just 77% and 64%.

The competition between As(V) and phosphate anions is attributed to their similar chemical behaviour and dissociation constants. In aqueous solutions phosphates and arsenates are oxyanions with the following dissociation constants. Phosphates: pK₁ = 2.13,

$pK_2 = 21.7$, $pK_3 = 12.44$ and H_3AsO_4 : $pK_1 = 3.60$, $pK_2 = 7.25$, and $pK_3 = 12.52$ (Whitten, Gailey and Davis, 1992). Like arsenates, phosphates form internal spherical complexes with the hydroxyl groups on the surface of iron oxide (Manning and Goldberg, 1996; Jackson and Miller, 2000).

In contrast, the removal of As(III) by IOCSW was almost entirely unaffected by the presence of phosphates, with just a very slight suggestion at the higher IOCS doses (> 0.3 g) of a competitive effect. This very significant difference between the adsorption behaviours of As(III) and As(V) in the presence of phosphates is unique to IOCSW. This difference is therefore likely due to the iron-manganese binary oxide nature of IOCSW. If the findings of Zhang et al (2007) are taken into consideration, who confirm that As(III) removal by iron-manganese binary-oxides is considerably better than As(V) removal, it would appear from the results in figure 28 that although the phosphates definitely interact in different ways with the iron oxide adsorption sites on the three IOCS investigated, they do not interact with the manganese oxide sites, and therefore do not have such a negative impact on the adsorption of As(III) on IOCSW.

In summary, phosphates significantly decreased the adsorption of arsenic onto IOCSW. As(V) removal efficacies were lowered by 20-80% by 9 mg PO_4^{3-} , depending upon the applied IOCSW dose. As(III) removal efficacies were less affected, and were less than 20% lower at all doses with the same phosphate concentration. Phosphates also slightly reduced the removal of As(V) onto IOCS2, but had no significant effect on As(III) removals. The negative effect of phosphates on arsenic adsorption is in general agreement with the literature (Youngran et al., 2007; Hsu et al., 2008b; Li et al., 2012). In contrast, the removal of both As(V) and As(III) by IOCS1 was actually improved by the presence of phosphates, an effect which was particularly notable at low IOCS1 doses, when the phosphate to IOCS ratios were the greatest. Further investigation of other possible interactions between phosphates, arsenic and iron oxides are necessary to explain the results observed for IOCS1.

5.3.3.2 Arsenic removal by IOCS in the presence of silicate

Figure 29 shows the arsenic removal achieved by different doses of the three IOCS investigated at initial As concentrations of $200 \mu\text{g/l}$, in the absence of silicates, and in the presence of 4, 8 and $12 \text{ mg SiO}_3^{2-}/\text{l}$.

For IOCS1, the effect of the presence of silicates was similar as the effect observed for phosphates, with improvements observed in the As(V) adsorption at low IOCS1 doses: with $12 \text{ mg SiO}_3^{2-}/\text{l}$, the adsorption of the 0.05 g dose increased from 6 to 25%, and of the 0.1 g dose from 27 to 41%. Even more significant increases were observed at these IOCS1 doses in the presence of the lower $4 \text{ mg SiO}_3^{2-}/\text{l}$, with the As(V) removal by 0.05 g IOCS1 increasing from 6 to 60%. On the other hand, at these same low IOCS1 doses, $8 \text{ mg SiO}_3^{2-}/\text{l}$ tended to hinder As(V) adsorption. At higher IOCS1 doses (> 0.3 g), the presence of silicates has less of an impact. The As(III) adsorption results are rather

different: The lowest silicate dose had no real effect, but at 8 and 12 mg $\text{SiO}_3^{2-}/\text{l}$, the adsorption of As(III) is significantly worse. In fact, at the lowest IOCS1 dose of 0.05 g, the presence of 12 mg $\text{SiO}_3^{2-}/\text{l}$ lowers the amount of As(III) adsorbed by a factor of more than 3, whereas at the highest dose, the As(III) adsorption is lowered by about a factor of 2.

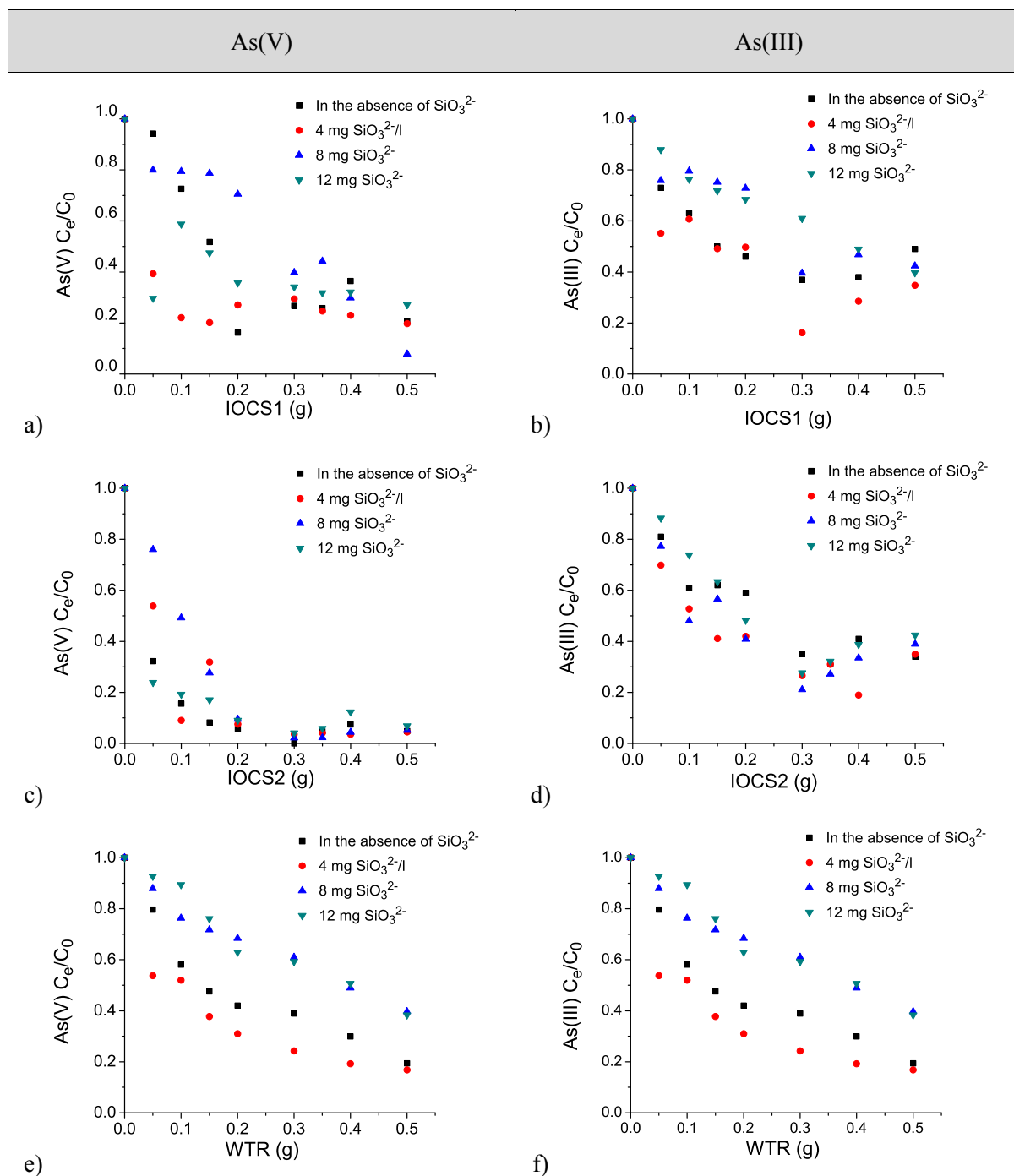


Figure 29. Effect of silicates on the removal of arsenic by IOCS (initial concentration of arsenic 200 $\mu\text{g}/\text{l}$).

Slika 29. Uticaj silikata na uklanjanje arsena primenom IOCS pri početnoj koncentracija arsena od 200 $\mu\text{g}/\text{l}$.

Vaishya and Gupta (2003) also reported the negative effect of silicates on the removal of As(III) by IOCS1, suggesting the silicate adsorbs on the surface hydroxyl groups, blocking adsorption sites and also increasing electrostatic repulsion between the As and the IOCS1 surface. As Möller and Sylvester (2008) suggest, the negative effects of silicates on the removal of As are more significant above pH 7.5.

The results of the experiments into the adsorption of As(V) onto IOCS2 in the presence of silicates are not very clear. At IOCS2 doses above 0.2 g, more than 90% of the As(V) was adsorbed in each experiment, independent of the amount of silicates present. At lower IOCS2 doses, the presence of 4 and 8 mg $\text{SiO}_3^{2-}/\text{l}$ clearly hinders the adsorption of As(III), reducing adsorption by around 20 and 40% respectively at an IOCS2 dose of 0.05 g. However, the results for the run with 12 mg $\text{SiO}_3^{2-}/\text{l}$ do not deviate significantly from the results without silicates. The As(III) results are in direct contradiction, with 12 mg $\text{SiO}_3^{2-}/\text{l}$ reducing the removal of As(III) slightly (by not more than 10% at most doses), and the presence of smaller amounts of silicates slightly improving As(III) removal. Meng et al. (2002) also reported that As(III) adsorption onto ferric hydroxide was even more sensitive to the presence of silicates than As(V), which is in good agreement with the results observed for IOCS1 and IOCS2.

The results from the experiments with IOCSW are also fairly straightforward. In all but one of the experimental runs, the addition of silicates definitely hindered the removal of both As(V) and As(III) by IOCSW, and in general, the higher the silicate concentration, the more obvious the effect. 4 mg/l silicates was enough to reduce the As(V) adsorption from 65 to 23%, from 74 to 40%, and from 89 to 76% at doses of 0.05, 0.1 and 0.5 g respectively. In contrast, the highest concentration of 12 mg/l silicates was required to reduce the As(III) adsorption at all applied IOCSW doses, whereby the effect was very uniform, consistently reducing the adsorption of As(III) by around 20%. The only exception to the observation that silicates hinder the adsorption of arsenic onto IOCSW was seen during the experiment with As(III) and 4 mg $\text{SiO}_3^{2-}/\text{l}$. In this case, at all but the highest IOCSW dose of 0.5 g, the presence of a small amount of silicates slightly improved As(III) adsorption, with the biggest improvement (18% more As(III) adsorbed) observed at the lowest dose of 0.05 g, and the increase steadily decreasing as the IOCSW dose increases, until at 0.5 g IOCSW, the As(III) adsorption results are not significantly different.

The results for IOCSW are in good agreement with the literature. Youngran et al (2007) reported that 5 mg silicates was enough to reduce As(V) removal by iron oxide by about half. Similar findings were given also given by Hsu et al. (2008b) and Meng et al. (2002), who proposed silicates strongly associated with ferric hydroxide, reducing the surface sites available for As(V) adsorption and increasing the electrostatic repulsion between As(V) and the negatively charged surface. They reported that silicate concentrations less than 1.4 mg/l did not have an impact, but anything above this concentration was likely to reduce arsenate removal.

5.3.3.3 Arsenic removal by IOCS in the presence of humic acid

The final competitive species investigated in this phase of the dissertation was humic acid. The results obtained, with initial arsenic concentrations of 200 $\mu\text{g/l}$, and humic acid concentrations of 4, 8 and 12 mg HA/l, are presented in figure 30.

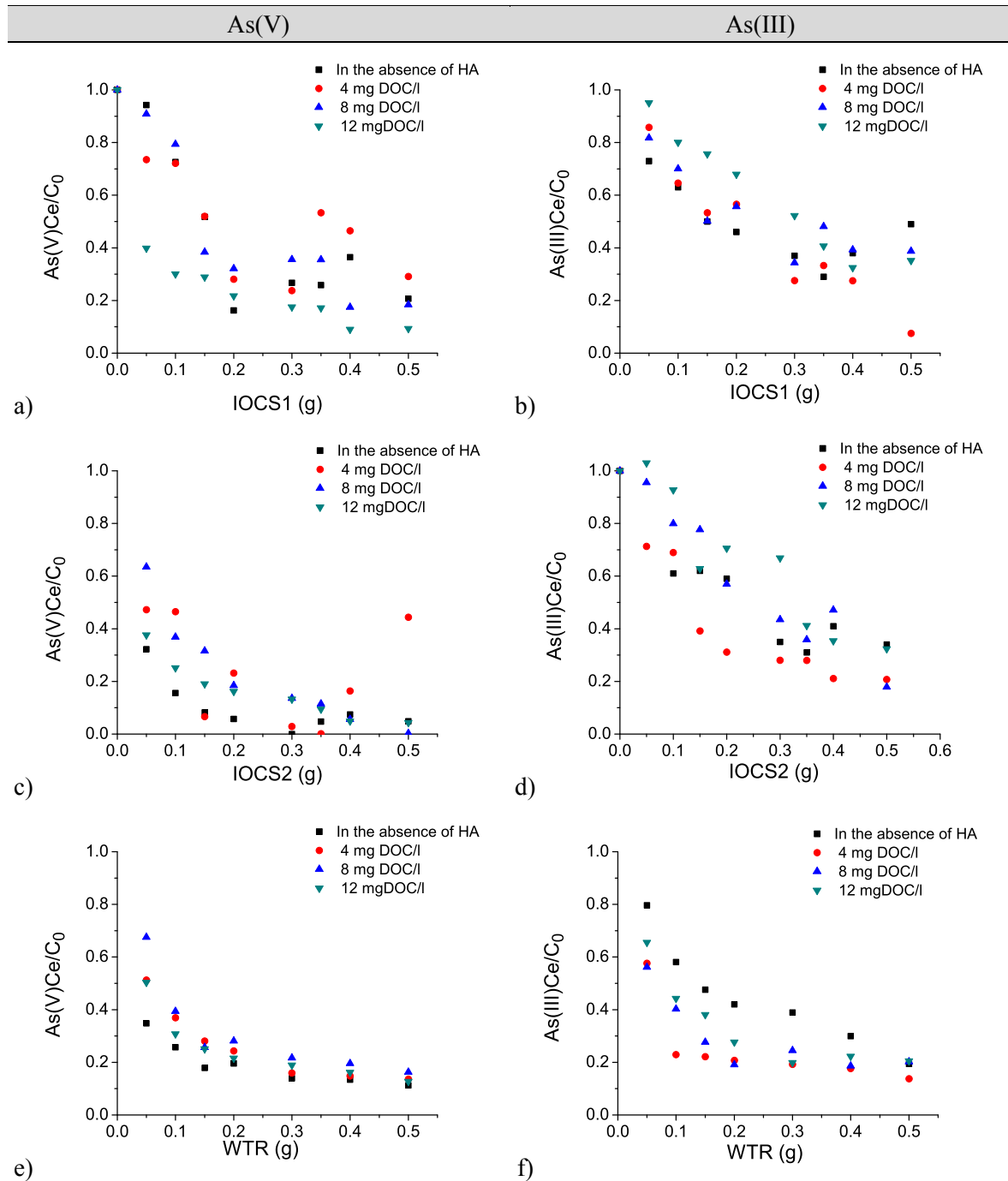


Figure 30. Effect of humic acid on the removal of arsenic by IOCS (initial concentration of 200 $\mu\text{g As/l}$).

Slika 30. Uticaj huminskih kiselina na uklanjanje arsena primenom IOCS pri početnoj koncentracija 200 $\mu\text{g As/l}$.

During the adsorption of As(V) onto IOCS1, the presence of 4 and 8 mg HA did not have a very significant effect. However, at the highest HA concentration of 12 mg HA/l, As(V) adsorption was greatly improved, increasing from 6% to 60% at the lowest IOCS1 dose, and steadily decreasing in impact as the dose increases. At the greatest IOCS1 dose (0.5 g), As(V) adsorption increased from 80% to 90% in the presence of 12 mg HA/l. The results for the adsorption of As(III) onto IOCS1 tell a different story: whereas the lower concentrations of HA again have little impact on the As(III) adsorptions achieved, the presence of 12 mg HA/l slightly reduced the efficacy of As(III) removal, with As(III) adsorptions falling by around 20% at the lower doses (< 0.3 g IOCS1). At larger IOCS1 doses, this effect was not observed.

In general, the reduction of arsenic removal efficiency by IOCS in the presence of HA is to be expected, due to the formation of complexes in which the iron cations (Fe^{3+}) mediate between the NOM functional groups and the arsenic oxyanions, preventing the adsorption of arsenic (Sun et al., 2006; Hsu et al., 2008b). A large number of NOM functional groups, including carboxylic and phenolic groups are able form complexes with other cations such as Ca^{2+} and Fe^{2+} (Tipping and Rey-Castro, 2002; Benedetti et al., 2003). Complexation of the arsenic oxyanions with NOM can prevent its removal by complexation on the surface of Fe^{3+} .

The adsorption of As(V) onto IOCS2 is definitely hindered by the presence of HA. The experiment with 8 mg HA gave the most consistent results, reducing the amount of As(V) adsorbed by around 30% at low IOCS2 doses: at a dose of 0.1 g IOCS2, in the absence of competitive anions, 84% of As(V) was adsorbed, whereas in the presence of 4, 8 and 12 mg HA/l, As(V) removals were 54, 63 and 61% respectively. The As(III) adsorption onto IOCS2 results are similar, with the presence of 8 and 12 mg HA/l reducing the efficacy of As(III) removal at all doses less than 0.35 g IOCS2. This is probably because the large HA molecules block the adsorption sites on the surface of IOCS2. Interestingly, at the lowest HA concentration, As(III) removal was improved. This is likely to be due to the interactions investigated in phase 1 of this dissertation: it is possible that in the presence of HA, some of the As(III) is rapidly oxidised to As(V). As shown in table 12, the adsorption of As(V) onto IOCS2 is considerably more favourable than the adsorption of As(III), so at the lowest HA concentrations, the steric hindrance of the HA is countered by the redox interaction allowing for the more favourable adsorption of As(V), resulting in better overall removal of arsenic.

Of the three IOCS investigated, IOCSW proved to be the most resilient to the presence of HA. Although HA definitely hindered the adsorption of As(V), the effect was much less noticeable than the effect observed for IOCS1 or IOCS2. At doses of 0.1 g IOCSW or greater, the presence of 12 mg HA/l only reduced the As(V) removal by less than 15%. Furthermore, the presence of HA actually improved the adsorption of As(III) at all three HA concentrations investigated, although the improvement decreased with increasing HA concentration. The reason for this is not immediately obvious, as from the isotherm data in

table 12, IOCSW is the only IOCS which performs better during the adsorption of As(III) than As(V). The redox interactions between As(III) and HA would therefore be expected to decrease overall arsenic adsorption rather than improve it. The explanation likely lies in an unexplored interaction between the manganese oxide on the surface of IOCSW and the HA, and remains a topic for future investigation.

Summary of the investigation into the adsorption of arsenic onto IOCS

In general, the adsorption isotherms for the adsorption of As(V) and As(III) onto IOCS were best fit with the Langmuir isotherm, suggesting monolayer adsorption. The greatest q_{max} value for As(V) adsorption, and thus the highest As(V) adsorption potential, was 111 $\mu\text{g/g}$, and was obtained for IOCS2. The best As(III) removal was exhibited by IOCSW, with a q_{max} of 99.1 $\mu\text{g/l}$. IOCSW was the only IOCS which achieved better removal of As(III) than As(V), doubtless the result of the manganese oxide which is also present on its surface (Zhang et al., 2007). In the absence of significant amounts of other anions competing for adsorption sites, the choice of the most effective IOCS for arsenic removal will therefore be dependent on the distribution of As(III) and As(V) in the source water, although given the status of IOCSW as a waste material already generated in water treatment plants in Vojvodina, its use is likely to be much more efficient irrespective of this distribution.

Of course, arsenic will rarely be found in drinking water sources by itself, and the effect of three common competitive anions, phosphates, silicates and humic acid, was therefore investigated. Significant differences between the arsenic adsorption behaviours of the three IOCS investigated were observed in the presence of these anions.

Under real water treatment conditions, whereby as well as a redox-conditions-dependent mixture of As(III) and As(V), many other competing anions are also expected to be present, the results presented above suggest that overall, high concentrations of phosphates and silicates favour the application of IOCS2 over IOCSW. If NOM is one of the dominant competitive anions present, IOCSW performs the best, being the only IOCS to show better As removal in the presence of HA.. Even in the presence of phosphates and silicates, the performance of IOCSW was impressive, for although it was less effective in the presence of both of these anions, given its status as a waste-product of current drinking water treatment processes in Vojvodina, its application in the real world is considerably more attractive than that of IOCS1 or IOCS2. In future, further research should therefore look to apply IOCSW to real arsenic removal systems, focus on identifying other competitive anions which may limit its application in water treatment plants, and endeavour to investigate which competitive anions interact synergistically or antagonistically to the removal of arsenic, when arsenic is present in complex mixtures.

5.4 Removing arsenic from groundwater by applying coagulation and enhanced coagulation with pH correction and pre-oxidation

In order to provide a point of comparison for the adsorption results given in the previous section, coagulation technology was also investigated, another technology on the USEPA list of BAT for arsenic removal (USEPA, 2005). Various combinations of different coagulation and oxidation processes were investigated, to explore how they effect the distribution of arsenic species in groundwaters, and how effective they are at removing arsenic and natural organic matter. The majority of the experiments were carried out in groundwater from Zrenjanin, due to its high arsenic content, but groundwaters from Kulpin, Bački Petrovac, Maglić and Gložan were also investigated. The coagulation processes investigated included coagulation with ferric chloride (FeCl_3), polyaluminium chloride (PACl) and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), enhanced with combinations of pH correction and/or preoxidation with hydrogen peroxide or ozonation. The doses investigated are given in table 5 in section 4.4.

5.4.1 Coagulation of groundwaters with elevated As and NOM concentrations

A preliminary investigation was carried out on the Zrenjanin groundwater to establish the arsenic removal efficacy of coagulation with three different coagulants: FeCl_3 , PACl and $\text{Al}_2(\text{SO}_4)_3$. These experiments were carried out at the natural water pH of 7.70 (figure 31).

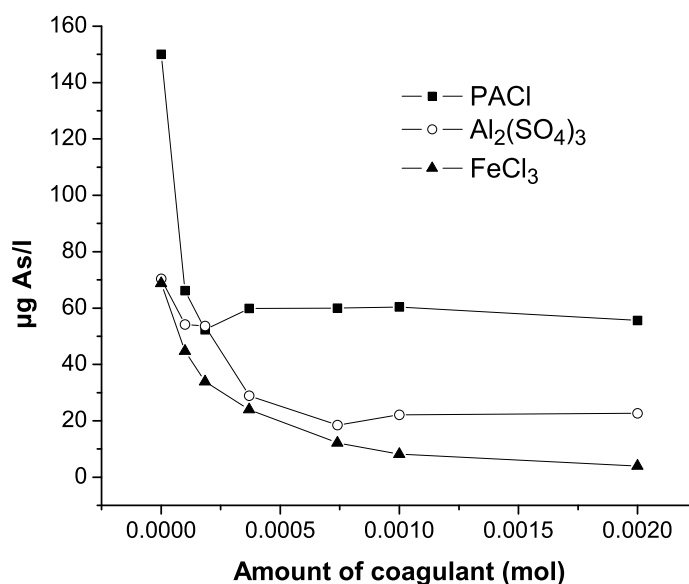


Figure 31. Change in As concentration after coagulation with FeCl_3 , PACl and $\text{Al}_2(\text{SO}_4)_3$.
Slika 31. Promena koncentracije As nakon koagulacije primenom FeCl_3 , PACl i $\text{Al}_2(\text{SO}_4)_3$.

FeCl_3 showed the best efficacy for arsenic removal, which is supported by the literature which also reports effective arsenic removal at the pH range investigated (Jiang, 2001;

Baskan and Pala, 2009). A maximum arsenic removal of 90% was obtained with the highest coagulant dose of 2.0 mM (300 mg FeCl_3/l). At this dose, the residual arsenic concentration was less than 5 $\mu\text{g}/\text{l}$. The aluminium-based coagulants were less effective. Approximately 31–75% arsenic was removed by $\text{Al}_2(\text{SO}_4)_3$ in doses of 3–50 mg Al/l , with the best results achieved at 0.74 mM Al (20 mg Al/l). PACl was the least effective coagulation process, achieving arsenic removals of 19–66%.

The final efficiency of the coagulation and flocculation processes depends not just on the processes themselves but also on the performance of the floc separation. Floc settleability is therefore also an important factor in determining how effective coagulation processes are when implemented during drinking water treatment. An experiment was therefore carried out to establish which coagulant resulted in the best settled sludge. Ferric chloride, which showed the best performance for arsenic removal, and PACl, which showed the best performance for DOC removal (Tubić et al., 2010a), were chosen for investigation, with the arsenic removals of those coagulation processes analysed before and after filtration. The arsenic removals achieved during this experiment are given in figure 32.

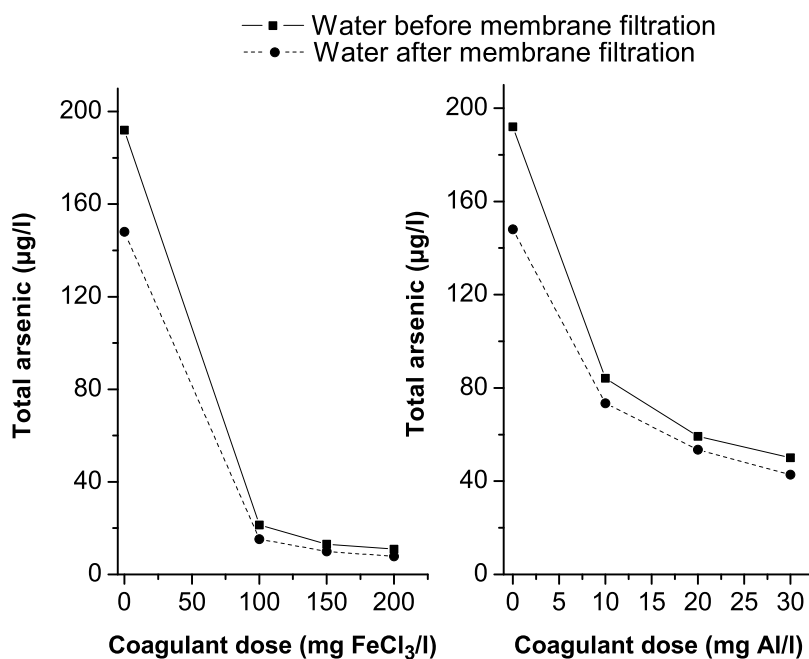


Figure 32. Total arsenic removals with different doses of ferric chloride and polyaluminium chloride coagulant, before and after membrane filtration.

Slika 32. Sadržaj arsena u vodi koagulisanoj gvožđe-hloridom i polialuminijum-hloridom pre i nakon membranske filtracije.

In the raw water, the total arsenic concentration was 196 $\mu\text{g As}/\text{l}$, of which 134 $\mu\text{g}/\text{l}$, or 68%, is dissolved in solution. During the 30 minute settling period after coagulation, virtually all of the ferric chloride flocs were fully settled, with membrane filtration removing very little additional arsenic from solution. The settling was slightly less effective during coagulation by polyaluminium chloride, with membrane filtration

removing twice as much arsenic from solution. After membrane filtration, a dose of 100 mg FeCl₃/l was sufficient to remove 92% of the arsenic from the groundwater, from an original 192 µg As/l to 15.3 µg As/l. Further increasing the coagulant dose to 150 and 200 mg FeCl₃/l yielded only marginal gains, resulting in 95 and 96% removals respectively. Roughly equivalent doses of PACl (20 and 30 mg Al/l) were considerably less effective, with arsenic removals ranging from 62 to 78% after membrane filtration.

The DOC removal behaved rather differently, with coagulation by PACl proving to be considerably more effective at removing organic compounds from the water than FeCl₃, as shown in table 13.

Table 13. DOC removals achieved by different doses of FeCl₃ and PACl.

Tabela 13. Uklanjanje DOC primenom različitih doza FeCl₃ i PACl.

Coagulant	Dose	DOC (mg/l)	% removal
Raw water	-	9.45	-
FeCl ₃	100 mg FeCl ₃ /l	8.83	6.56
FeCl ₃	150 mg FeCl ₃ /l	7.81	17.4
FeCl ₃	200 mg FeCl ₃ /l	7.56	20.0
PACl	10 mg Al/l	7.42	21.5
PACl	20 mg Al/l	6.47	31.5
PACl	30 mg Al/l	5.86	38.0

For DOC removal, in the presence of 192 µg As/l, the lowest PACl dose of 10 mg Al/l and the ferric chloride dose of 200 mg FeCl₃/l showed the same efficacy. 38% was the best DOC removal achieved with the highest PACl dose, which nonetheless resulted in a relatively high residual DOC value of 5.86 mg C/l. The results show that careful choice of the type of coagulant as well as the coagulant dose can lead to high removal efficiencies of one of the parameters of interest - either As or DOC, but not both. In order to try and achieve good removals of both of these parameters, it is necessary to investigate further combinations of treatment techniques, as discussed in section 5.4.3 and beyond.

5.4.2 Effect of coagulation on the speciation of arsenic

Having established during the preliminary phase of research the effect simple pH adjustment has on the arsenic speciation in the raw groundwater (section 5.1.2), the impact of coagulation may be investigated. Arsenic speciation analyses were carried out after coagulation by FeCl₃ and PACl. The speciation analyses are shown in figures 33 and 34.

After iron chloride coagulation, the majority of the residual arsenic present in the water samples was As(III), the share of which increased from 35% in the raw water to 75, 69 and 59% in the coagulated waters, at doses of 100, 150 and 200 mg FeCl₃/l. The fact that the lower the dose of coagulant, the greater the share of As(III) in the residual arsenic, suggests that coagulation with iron chloride strongly favours the removal of As(V) over As(III) (figure 33). This result can be explained by the fact that at the natural pH of the

water (7.8), almost all of the As(III) is in a neutral form, whereas the As(V) is partially deprotonated and therefore negatively charged, so that it is strongly attracted to the cationic ferric hydroxide flocs (Sharma and Sohn, 2009).

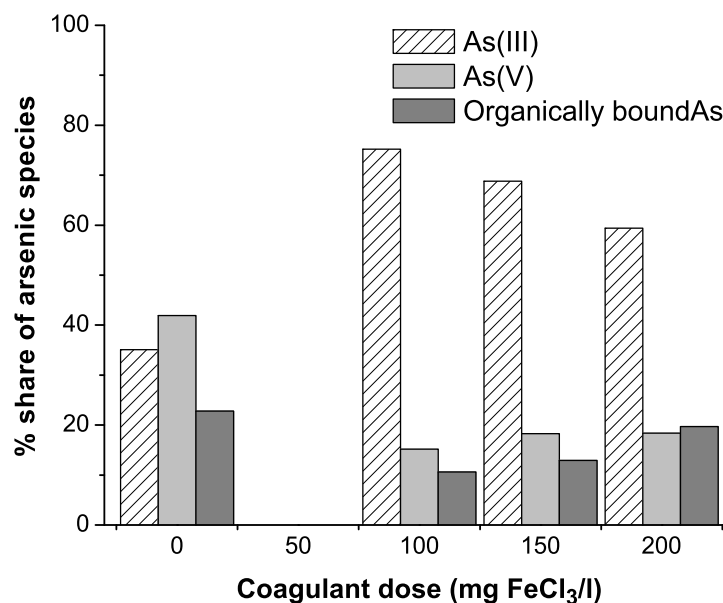


Figure 33. Changes in arsenic speciation during FeCl₃ coagulation.

Slika 33. Promena sadržaja pojedinih oblika arsena u vodi koagulisanoj FeCl₃.

Coagulation with polyaluminium chloride performs slightly differently. The share of As(III) in the residual arsenic again increases, but only slightly, from 35% to 42, 51 and 54% at doses of 10, 20 and 30 mg Al/l. In general, PACl has less affinity for As(V) than FeCl₃ where its share decreases much more. In contrast, the obvious growth in the share of As(III) after coagulation indicates that As(III) is less efficiently removed by coagulation in comparison to As(V). It is also notable that as the dose of PACl increases, the share of organically bound As steadily decreases, suggesting better removal of organic arsenic by PACl than by FeCl₃. This result is in agreement with observations from previous investigations into the removal of DOC by coagulation, whereby PACl has been found to be considerably more effective at removing NOM than FeCl₃ (Tubić et al., 2010a). Nonetheless, the organic As fraction is the smallest fraction in the raw water, so it should be borne in mind that in terms of overall As removal, FeCl₃ is the more effective coagulant.

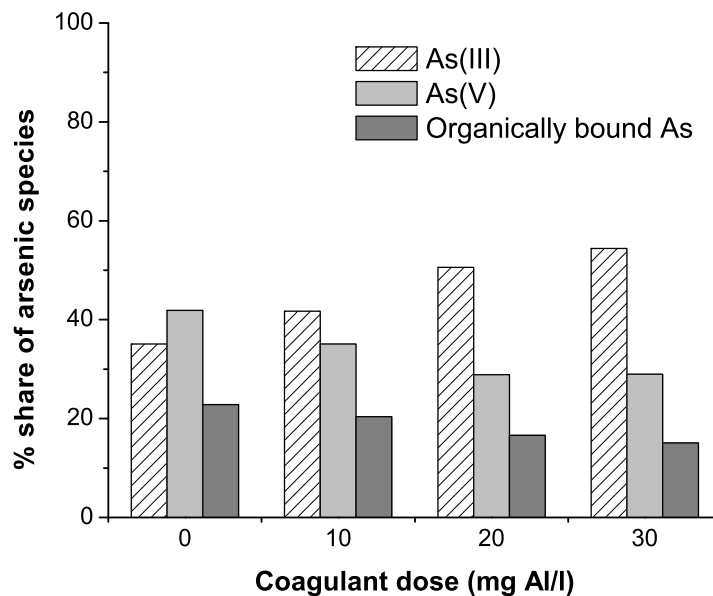


Figure 34. Changes in arsenic speciation during PACl coagulation.

Slika 34. Promena sadržaja pojedinih oblika arsena u vodi koaguliranoj PACl.

5.4.3 Enhanced coagulation using pH correction

More in-depth investigations were conducted into the effect of pH correction on the arsenic and NOM removals achieved at different coagulant doses of ferric chloride. Water pH was adjusted from pH 7.8 to pH 7.0 and 6.5, and arsenic and DOC contents analysed before and after coagulation with different FeCl_3 doses, ranging from 100–200 mg FeCl_3/l . The overall arsenic and NOM removal results obtained are given in figure 35.

As can be seen in the figure below, when the pH of the water is lowered, the coagulation efficacy for As removal increases slightly. For example, at the highest dose of 200 mg FeCl_3/l , decreasing the pH of the water from 7.8 to 6.5 increases the dissolved arsenic removal from 94% to 96%. This improvement in ferric chloride coagulation efficiency is in line with the findings of other authors (Baskan and Pala, 2009; Pallier et al., 2010), who also report better arsenic removals at lower pH values.

DOC removals during ferric chloride coagulation were significantly more sensitive to pH correction than the arsenic removals, although the trends observed are similar. In comparison with the raw water, pH correction improved the removal of DOC by 33–44%. This result is in agreement with Uyak and Toroz (2005) who investigated the relation between FeCl_3 dose and water pH, and concluded that the most effective removal of NOM at coagulant doses of 100–200 mg FeCl_3/l occurred in the pH range pH=5.0–6.0. Kipton et al. (1992) suggested that at normal water pH values (pH 6–8), all the carboxyl groups are dissociated, causing them to repel one another, spreading out the molecule. Hydrogen bonding makes these polymeric structures more stable, altering their solubility, depending upon the pH, ionic strength and the nature of the electrolyte.

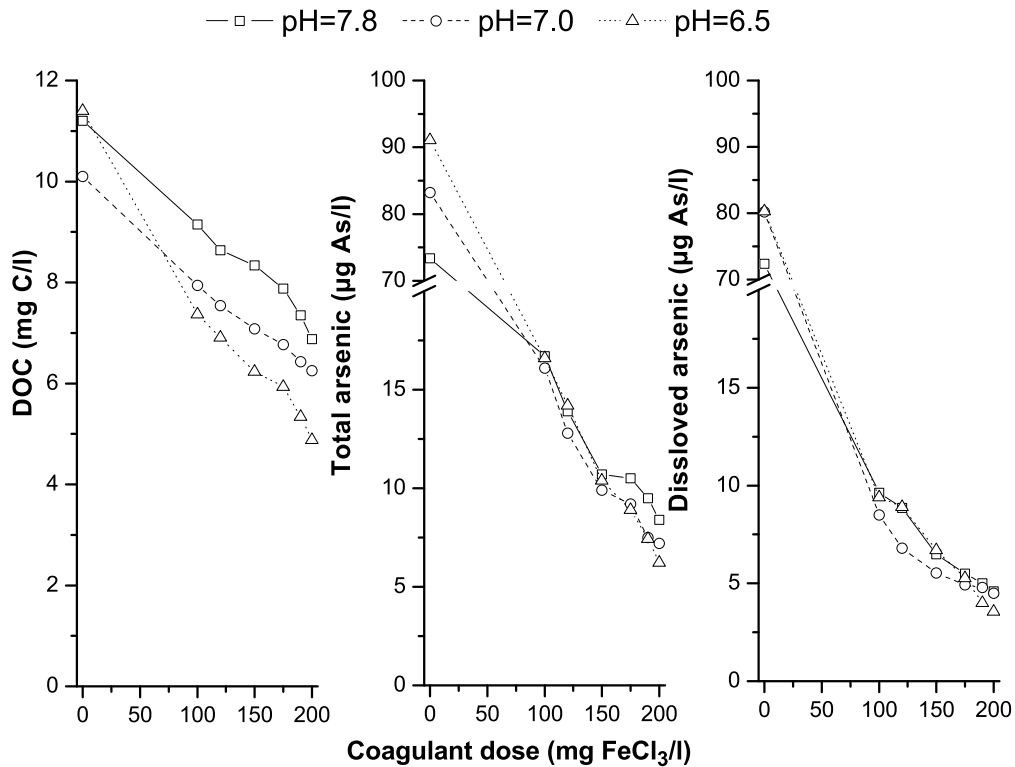


Figure 35. pH dependence of DOC and total and dissolved arsenic removal by ferric chloride coagulation. Some results previously published (Tubić et al., 2010a).

Slika 35. Uticaj pH na uklanjanje DOC, ukupnog i rastvorenog arsena koagulacijom sa gvožđe hloridom. Deo rezultati već objavljen (Tubić et al., 2010a).

5.4.3.1 Effect of pH on the residual arsenic speciation after coagulation

This next section investigates how adjusting the pH from pH 7.8 to 7.0 or 6.5 affects the speciation of the residual arsenic after coagulation by FeCl_3 . Arsenic speciation analysis was also performed before and after coagulation with different coagulant doses, ranging from 100–200 $\text{mg FeCl}_3/\text{l}$.

The speciation results are given in figure 36, and clearly show how the gains in total arsenic removal achieved by pH correction result from the shift in the $\text{As(III)}:\text{As(V)}$ equilibrium towards As(III) , as As(III) is harder to remove by ferric chloride coagulation. The same shift was observed by Pawlak et al. (2003), who also reported preferential removal of As(V) in comparison to As(III) . At pH 7.8, the ranges of percentage removals for As(III) and As(V) achieved at all doses (100–200 $\text{mg FeCl}_3/\text{l}$) were 84–91% for As(III) and 92–96% for As(V) . At pH 6.5, the ranges achieved were 24–66% and 97–99%. Given the evidence for redox interactions between As and HA reported in section 5.2.2.2, it can be assumed that the significant amounts of NOM present in the water are oxidising the As(III) , assisting in its removal by the coagulation process.

From these results, it can be concluded that the total arsenic removal efficiency by coagulation depends on the dose of coagulant, the pH of the raw water, and also the species

of arsenic present in the raw water (as As (III), As (V) or As bound to organic components). DOC removal was considerably more sensitive to changes in coagulant dose than arsenic removal, and the best removals by FeCl_3 were achieved by applying a dose of 200 mg FeCl_3/l (figure 35).

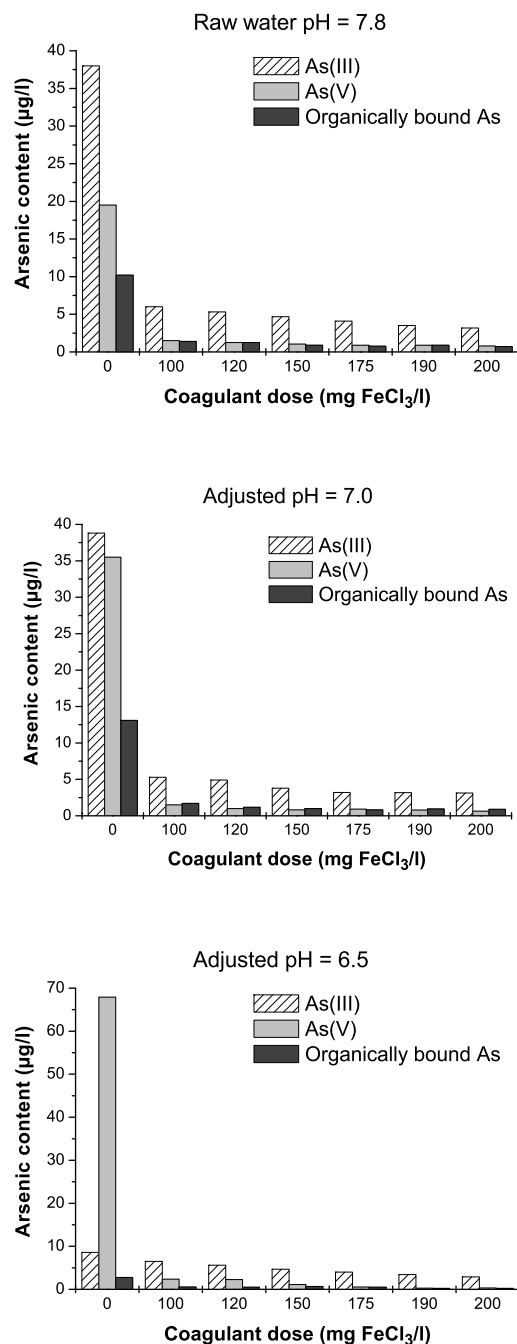


Figure 36. pH dependence of changes in the arsenic speciation during ferric chloride coagulation.

Slika 36. Uticaj pH na specijaciju arsena tokom koagulacije sa gvožđe hloridom.

Reducing the pH value of the water prior to coagulation improved the coagulation effect, improving the removal of both DOC and arsenic. The dissolved arsenic concentrations

after coagulation at all applied doses satisfy the MAC for arsenic (Official Gazette RS 42/98 and 44/99). However, some arsenic remains in colloidal form in solution, so to achieve satisfactory water quality, it is necessary to apply ≥ 150 mg FeCl₃/l, depending upon the water pH. The results of the speciation analysis show that the majority of the residual arsenic after coagulation is in the form As(III). In order to better remove residual As(III) from the water, it should be oxidised to As(V) prior to coagulation, via application of an oxidative pretreatment such as ozone, hydrogen peroxide or other oxidizing agent.

5.4.4 Enhanced coagulation using preoxidation

This next series of experiments explores options for enhancing groundwater coagulation (by FeCl₃, PACl, Al₂(SO₄)₃ and their combinations) by introducing a preoxidation step utilising hydrogen peroxide or ozone. Hydrogen peroxide is one of the cheapest water oxidation technologies available, whereas ozone is considerably more expensive, but is broadly applied due to its efficacy (Bissen and Frimmel, 2003). This research builds in part on the work of Tubić (2010), who demonstrated the improved efficacy of combined treatments dosing different coagulants together, such as dosing PACl followed by a relatively low dose of FeCl₃. This approach harnesses the advantages of both coagulants, whereby PACl effectively removes DOC and FeCl₃ effectively removes As.

5.4.4.1 Enhanced coagulation with preoxidation using hydrogen peroxide

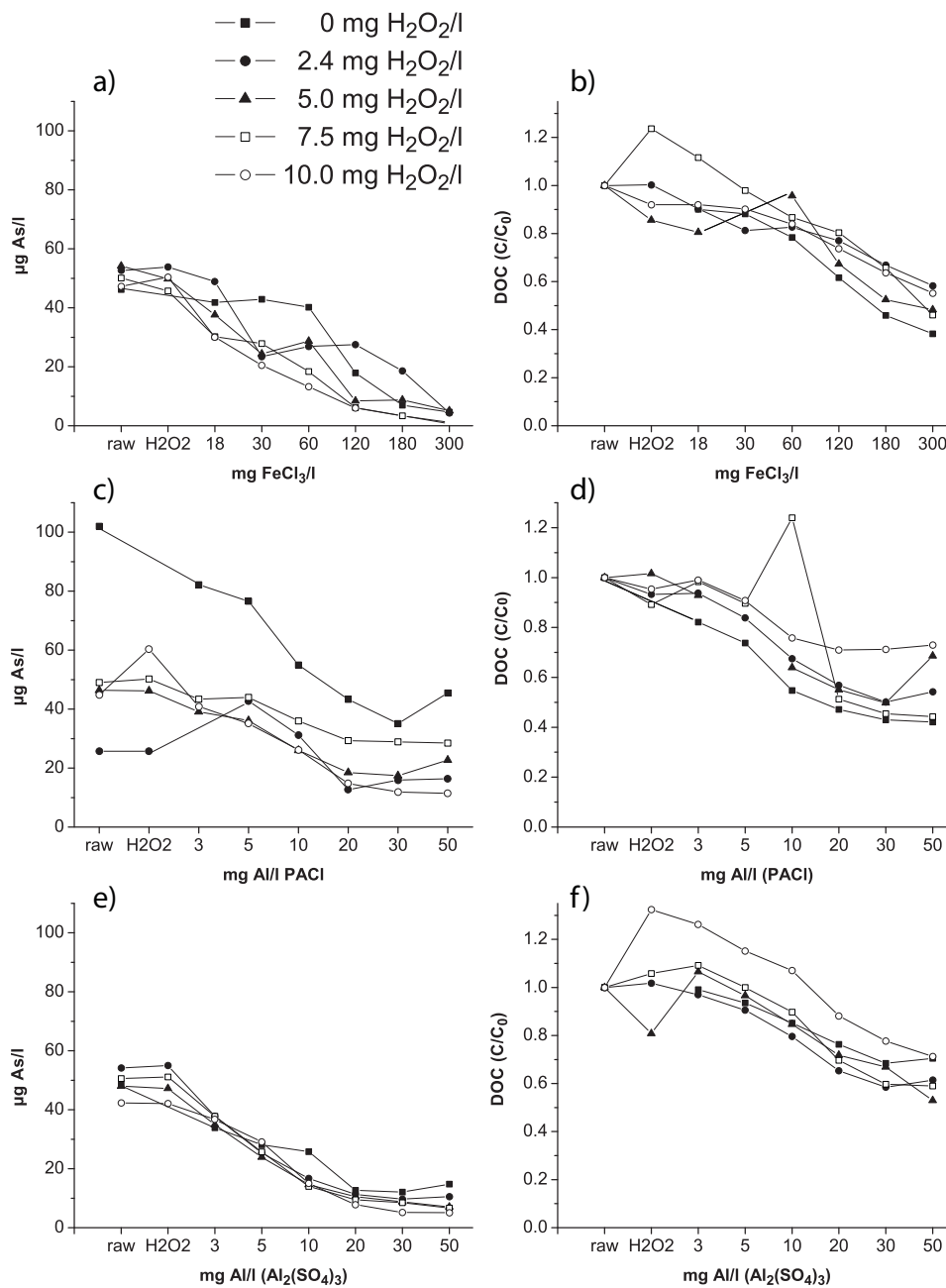
In this experiment, hydrogen peroxide doses of 2.0–10 mg H₂O₂/l were applied prior to coagulation with FeCl₃, PACl, Al(SO₄)₃ and their combinations (PACl/FeCl₃ and Al(SO₄)₃/FeCl₃). The arsenic and NOM removal results for the coagulants are shown in figure 37(a–f). Note that the water was sampled at different times for this experiment, resulting in differences in the initial water qualities, particularly in the DOC values.

A large number of dose combinations were investigated. In order to focus the discussion on the most critical information, the results for arsenic removal are compared below with the 10 µg As/l MAC (Official Gazette RS 42/98 and 44/99). There is no regulatory limit set for NOM, which showed quite a lot of variation in the initial concentrations. For the sake of comparison, the DOC removals were therefore plotted as C/C_0 .

For FeCl₃ coagulation, to satisfy the MAC criteria for As without preoxidation, it is necessary to apply a coagulant dose of 180 mg FeCl₃/l (figure 37(a)). Introducing the preoxidation step with 5 mg H₂O₂/l decreases the coagulant demand to 120 mg FeCl₃/l. Further increasing the dose of hydrogen peroxide does not significantly increase the arsenic removal efficacy of the process. In contrast, there is no benefit to applying preoxidation for the DOC removal, especially at doses above 5 mg H₂O₂/l (figure 37(b)).

In the PACl coagulation experiments, the introduction of the hydrogen peroxide preoxidation step improved the efficacy of the As removal process. However, although the residual As concentrations approached the MAC, even with preoxidation, they did not satisfy the drinking water criteria (figure 37(c)). The best As removal was achieved at

doses of 20 mg Al/l and 2.4 mg H₂O₂/l. The DOC removals were worse at all doses. The optimal DOC removal was achieved with 30 mg Al/l. Increasing the PACl dose from 30 to 50 mg Al/l did not result in an improvement in DOC removal (figure 37(d)).



FeCl₃ coagulant: a) As and b) DOC; PACl coagulant: c) As and d) DOC;
Al₂(SO₄)₃ coagulant: e) As and f) DOC.

Figure 37. Effect of hydrogen peroxide oxidation on the removal of As and DOC by coagulation.

Slika 37. Uticaj predoksidacije sa vodonik-peroksidom na uklanjanje arsena i DOC koagulacijom.

Coagulation with Al₂(SO₄)₃ showed a high efficacy for As removal, with an optimal dose of 20 mg Al/l removing 79% of the arsenic present (figure 37 (e)). Introducing peroxide

doses greater than 5 mg H₂O₂ with this coagulant dose is sufficient to achieve As levels below the MAC. In the case of DOC, the best removals were only around 40%, and were achieved by applying 2.4 mg H₂O₂ with a 30 mg Al/l dose of coagulant.

The preoxidation step with hydrogen peroxide did not overcome the weak affinity of PACl for arsenic sufficiently enough for this technique to be a practical solution for arsenic removal, as the MAC for As was not satisfied. However, significant gains were made in the As removal efficacy of FeCl₃, while coagulation by Al₂(SO₄)₃ was also improved. These gains were expected, as the results of the speciation study show that As(V) is more readily removed by coagulation than As(III), a conclusion supported by many authors (Bissen and Frimmel, 2003; Sancha, 2006; Cui et al., 2015; Terracciano, Ge and Meng, 2015).

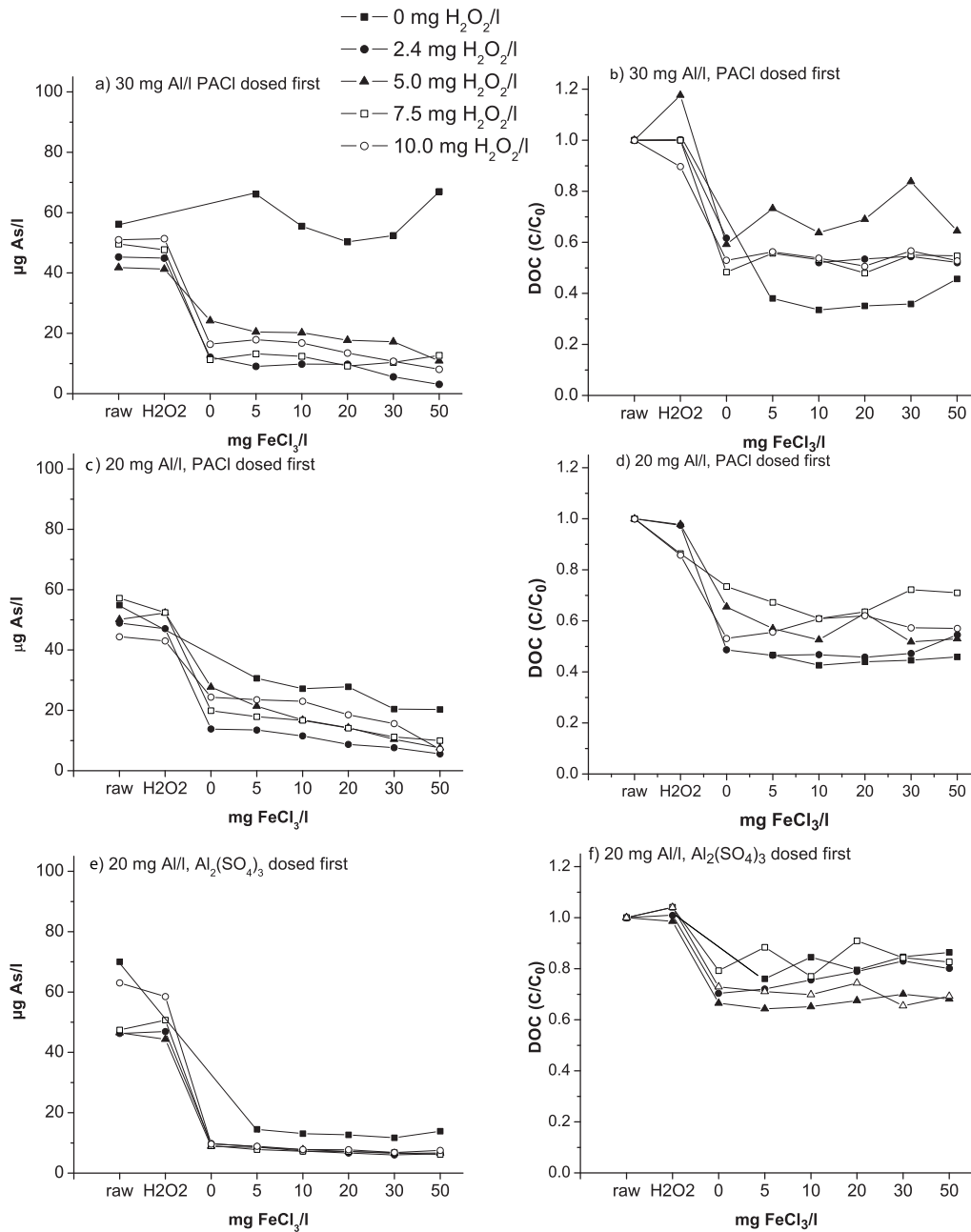
In the next set of experiments, preoxidation with hydrogen peroxide was applied to a combined coagulation technique. Two doses of PACl (30 and 20 mg Al/l) and one dose of Al₂(SO₄)₃ (20 mg Al/l) were investigated, in combination with different FeCl₃ doses, and the results given in figure 38.

The PACl–FeCl₃ combination which applied 30 mg Al/l needs doses of 5 mg FeCl₃/l and 2.4 mg H₂O₂/l in order to achieve As levels below the 10 µg As/l MAC (figure 38(a)). The best removal was achieved with the same conditions but with a 30 mg FeCl₃/l dose. However, the As removal gains made in comparison to the 5 mg FeCl₃/l dose are not significant enough to justify application of the increased dose from an economic standpoint, especially considering the considerably larger volume of waste sludge that would be produced. The best DOC removals made by the PACl–FeCl₃ combination were achieved without the preoxidation step (figure 38(b)). This result was to be expected, because hydrogen peroxide preoxidation did not improve the DOC removals achieved by either of these two coagulants by themselves (see section 5.4.4.1). The negative impact of the preoxidation step implies that H₂O₂ is too weak an oxidant to achieve a microfloculation effect. Instead, it is just strong enough to oxidise some of the functional groups on the surface of the NOM, increasing the polarity of the NOM and thus increasing the coagulant demand.

As could be expected, the PACl–FeCl₃ combination with the lower Al dose (20 mg Al/l) was less effective than the 30 mg Al/l dose (figure 38(c)). Reducing the PACl dose from 30 mg Al/l to 20 mg Al/l meant that 4 times more FeCl₃ was required, with the same 2.4 mg H₂O₂/l dose, to reduce As below 10 µg/l. As before, the preoxidation step did not benefit the DOC removals by this technique (figure 38(d)).

Finally, none of the Al₂(SO₄)₃–FeCl₃ doses investigated were able to achieve arsenic concentrations of less than 10 µg/l without preoxidation (figure 38(e)). However, 2.4 mg H₂O₂/l sufficiently enhanced coagulation with 20 mg Al/l and 5 mg FeCl₃ to achieve satisfactory water quality, with the preoxidation step increasing coagulation efficacy by almost 10%. Further increasing the FeCl₃ and H₂O₂ doses did not result in

improvements in the arsenic removal. The $Al_2(SO_4)_3$ - $FeCl_3$ combination was ineffective at removing DOC (figure 38(e)), with or without peroxide preoxidation.



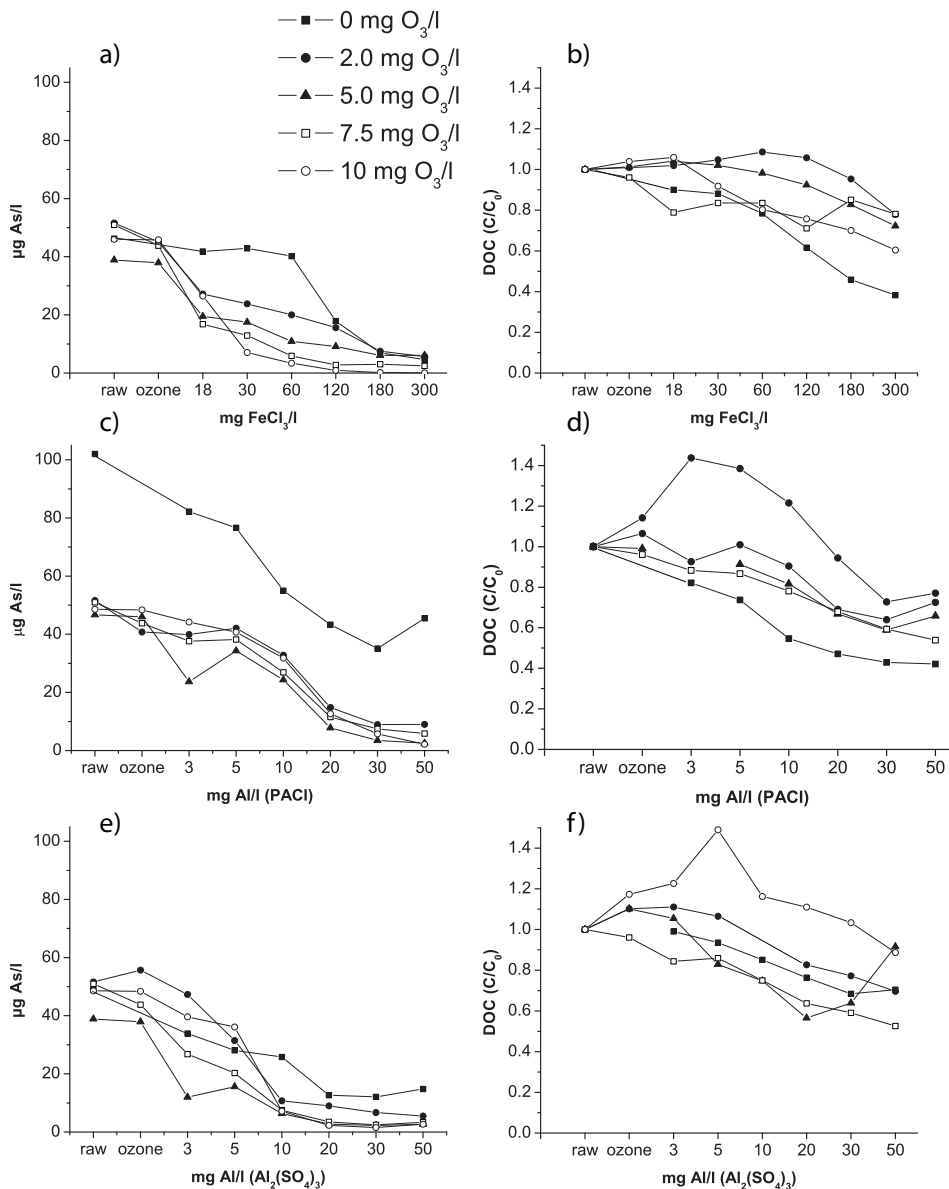
PACl- $FeCl_3$ (30 mg Al/l): a) As and b) DOC; PACl- $FeCl_3$ (20 mg Al/l): c) As and d) DOC; $Al_2(SO_4)_3$ - $FeCl_3$ (20 mg Al/l): e) As and f) DOC.

Figure 38. Effect of hydrogen peroxide oxidation on the removal of As and DOC by combinations of coagulants.

Slika 38. Uticaj predoksidacije sa vodonik-peroksidom na uklanjanje arsena i DOC koagulacijom primenom kombinacije koagulanata.

5.4.4.2 Enhanced coagulation with preoxidation using ozone.

Globally, despite its relatively expensive investment and operation costs, ozone is the most commonly applied drinking water oxidation technique. Ozone doses of 2.0–10 mg O₃/l (0.2-1.0 mg O₃/mg DOC) were chosen for investigation, based on previous research (Tubić et al., 2010b). The results of the experiments with preozonation prior to coagulation with PACl, Al₂(SO₄)₃ and FeCl₃, as well as the PACl–FeCl₃ combination, are shown in figures 39 and 40.



FeCl₃ coagulant: a) As and b) DOC; PACl coagulant: c) As and d) DOC;
Al₂(SO₄)₃ coagulant: e) As and f) DOC.

Figure 39. Effect of applying ozonation prior to coagulation on As and DOC removals.

Slika 39. Uticaj predozonizacije na uklanjanje arsena i DOC koagulacijom.

For FeCl₃ coagulation, application of ozone as the preoxidation step affords us a choice of dosing combinations. Without preozonation, a 180 mg FeCl₃ dose is required to satisfy the

MAC for arsenic. With preozonation, arsenic concentrations of less than 10 µg/l were obtained by either i) dosing 10 mg O₃/l prior to just 30 mg FeCl₃/l, or ii) dosing 5 mg O₃/l with 120 mg FeCl₃ (figure 39(a)). The second option is likely cheaper in terms of chemical consumption. However, it should be noted that the first option will produce approximately four times less sludge, which may make it the more viable solution, depending on local regulations concerning waste disposal and the concentrations of As in the sludges produced. It may also be interesting to note that although it is unlikely to be economically viable, preozonation with 10 mg O₃/l prior to 180 mg FeCl₃/l coagulant dose resulted in effectively complete arsenic removal, with the arsenic concentration falling below the 0.5 µg/l method detection limit. Interestingly, preozonation improved DOC removals at coagulant doses ≤ 30 mg FeCl₃/l, but at doses ≥ 60 mg FeCl₃/l it had a negative effect. (figure 39(b)). In the absence of As, one would normally expect preozonation to have a beneficial effect on DOC removal due to the microfloculation effect.

In the case of PACl, preozonation with a dose of 5 mg O₃/l increased the percentage removal of As at a dose of 20 mg Al/l by 25%, sufficient to bring the concentration to less than 10 µg As/l (figure 39(c)). At this same ozone dose, increasing the PACl dose to 30 mg Al/l resulted in a further reduction in the arsenic concentration, from 7.8 to 3.5 µg/l. Despite the generally better performance of PACl in removing DOC, once again preozonation did not improve DOC removal (figure 39(d)).

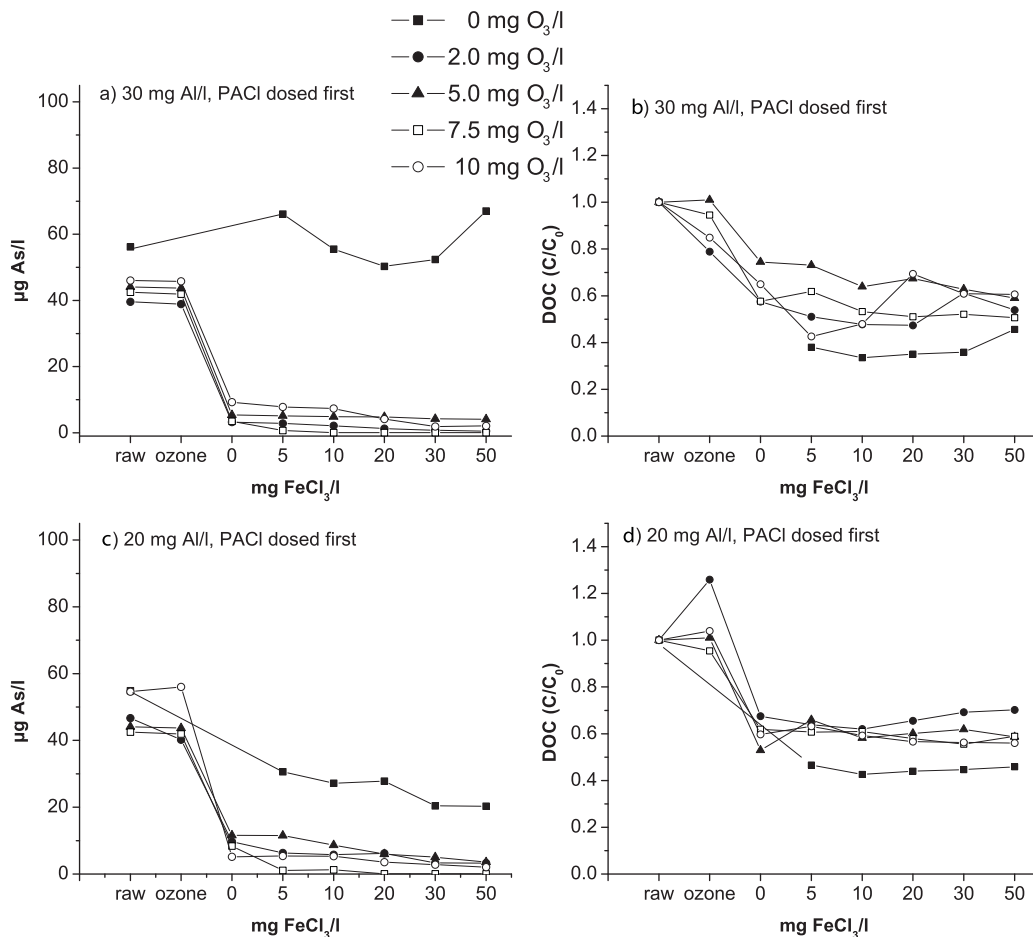
Preozonation dramatically improved the performance of Al₂(SO₄)₃ coagulation for As removal. In this set of experiments, none of the doses of Al₂(SO₄)₃ resulted in As concentrations of less than 10 µg/l without the preoxidation step. With the preoxidation step, applying a 5 mg O₃/l dose together with 10 mg Al₂(SO₄)₃/l was sufficient to remove As down to 6.4 from 38.9 µg/l (figure 39(e)). This 5 mg O₃/l dose also increased DOC removal by 10 mg Al₂(SO₄)₃/l, for around 25% (figure 39 (e)).

Given its superior impact on the removal of arsenic, it can be concluded that ozone, which is a strong oxidising agent which reacts faster than H₂O₂, is the most effective agent for oxidising arsenic containing molecules, and is therefore a very good choice for implementation together with single-coagulant coagulation during the water treatment process. This conclusion is supported by the literature, which states that of all the oxidation techniques commonly applied, ozone tends to be the fastest (Jiang, 2001; Ghurye and Clifford, 2004; Sharma and Sohn, 2009).

The final set of treatments investigated was preozonation prior to different PACl–FeCl₃ combined coagulant doses (30 and 20 mg Al/l). At 30 mg Al/l, preozonation at 2 mg O₃/l already reduces As concentrations below 10 µg/l without the addition of FeCl₃ (figure 40 (a)). Addition of 5 mg FeCl₃/l did not improve As removal without also increasing the preozonation dose to 7.5 mg O₃/l. Working under the assumption that enhanced As removal is necessary and that preozonation will therefore be applied, the best compromise to additionally maximise DOC removal would be to apply 2 mg O₃/l and 30 mg Al/l in combination with 20 mg FeCl₃/l (figure 40(a,b)).

At the lower 20 mg Al/l dose, a higher dose of 10 mg O₃/l was required to achieve satisfactory drinking water quality without the addition of FeCl₃ (figure 40(c)). Addition of 5 mg FeCl₃/l allows the ozone dose to be reduced to 2 mg O₃/l, whilst still maintaining satisfactory water quality. Applying preozonation to the combined doses of 20 mg Al/l and 5 mg FeCl₃/l does not benefit the removal of DOC (figure 40(d)).

Of the combined coagulation treatments investigated (figure 40), the most effective coagulation treatment for the removal of arsenic applied preozonation at a dose of 7.5 mg O₃/l, with subsequent combined coagulation with PACl–FeCl₃ at doses of 30 mg Al/l and 10 mg FeCl₃/l. However, DOC removals by the combined treatment were not improved by preozonation. This may be due the ozone application changing the structure of NOM, whereby increasing the dose of ozone increases the formation of smaller molecules that are more difficult to remove by coagulation.



PACl–FeCl₃ (30 mg Al/l): a) As and b) DOC; PACl–FeCl₃ (20 mg Al/l): c) As and d) DOC.

Figure 40. Effect of applying ozonation preoxidation prior to combined coagulation on As and DOC removals.

Slika 40. Uticaj predoksidacije ozonom na uklanjanje arsena i DOC primenom kombinacije koagulanata.

The results obtained for the effects of preozonation on the coagulation techniques investigated highlights the difficulty in optimising water treatment processes for the removal of more than one constituent at a time. The final phase of research (section 5.5) demonstrates how response surface methodology may be employed to solve optimisation problems involving multiple water constituents. However, if clear priority is given to the removal of arsenic, then preozonation at a dose of 7.5 mg O₃/l, with subsequent combined coagulation with PACl–FeCl₃ at doses of 30 mg Al/l and 5 mg FeCl₃/l results in the best quality of treated water (arsenic content < 2 µg/l), whilst simultaneously satisfying treatment techno-economic aspects, whereby the process is efficient, low cost, and produces a relatively small amount of waste sludge, in comparison to coagulation alone.

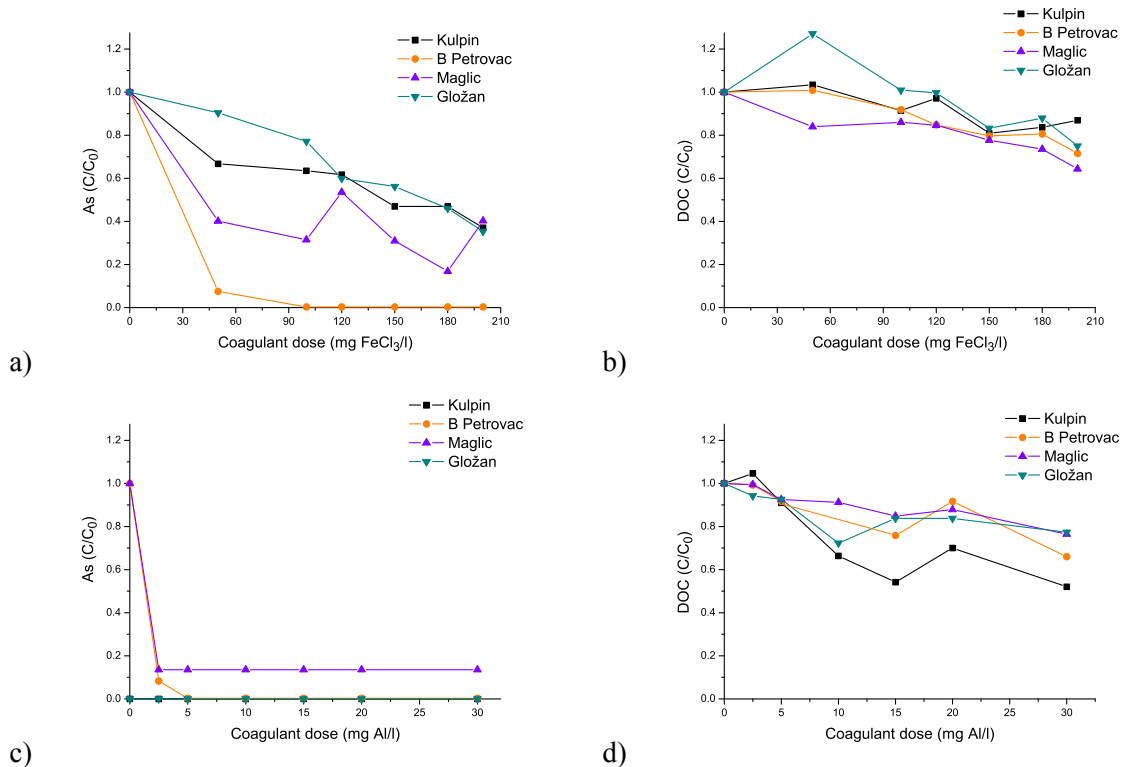
5.4.5 Enhanced coagulation of other groundwaters

In order to assess the wider applicability of the conclusions drawn from the above investigation into the treatment of groundwater from Zrenjanin by coagulation in combination with preoxidation, similar experiments were carried out on waters from Kulpin, Bački Petrovac, Maglić and Gložan, using FeCl₃ and PACl as the coagulants and preozonation. The arsenic and NOM removal results in this section are again presented as C/C₀ ratios, and applied ozone doses are normalised and expressed as mg O₃/mg DOC, in order to facilitate comparison between the different raw waters, which all have differing initial NOM and As concentrations (see section 5.1 above).

The DOC concentrations and especially the arsenic concentrations in these groundwaters are all considerably lower than those found in the Zrenjanin water supply blend. It was therefore anticipated that lower coagulation doses would be adequate to achieve satisfactory arsenic removals. The coagulation results shown in figure 41(a–d) bear this out (Watson et al., 2013). The groundwater from Bački Petrovac had the highest initial arsenic concentration (18 µg As/l), and doses of 100 mg FeCl₃/l or 10 mg Al/l were sufficient to completely remove the arsenic to levels below the method detection limit (< 0.5 µg As/l).

It is also clear from figure 41(a) that in the groundwaters investigated, the greater the initial arsenic concentration, the greater the percentage removal achieved. The water quality of the samples again varies with time, such that during the PACl coagulation experiments (figure 41(c)), no arsenic was detected in either of the initial raw groundwaters from Kulpin or Gložan.

The greater the coagulant dose, the greater were the DOC removals observed, with PACl generally performing better than FeCl₃. The best DOC removal was observed during coagulation of the Kulpin water by PACl, whereby removals achieved ranged up to 48% at a dose of 30 mg Al/l. In contrast, the best DOC removal by FeCl₃ was 36%, applying a 200 mg FeCl₃/l dose to the Maglić groundwater. The better DOC removals by PACl in comparison with FeCl₃ (figures 41(b,d)) are in agreement with previous findings (Tubić et al., 2010a).



FeCl₃ coagulant: a) As and b) DOC; PACl coagulant: c) As and d) DOC.

Figure 41. Arsenic and DOC removals by different doses of FeCl₃ and PACl.

Slika 41. Uklanjanje arsena i DOC primenom različitih doza koagulanata FeCl₃ i PACl.

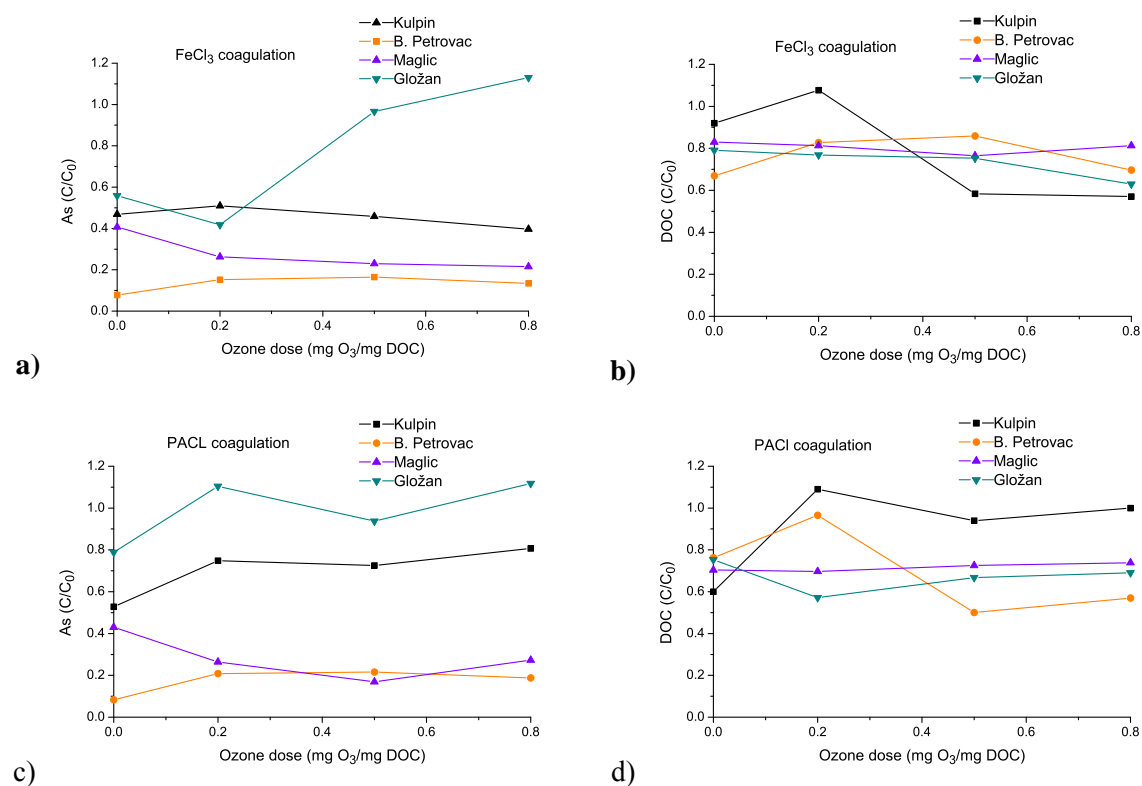
The preozonation experiments were carried out for both FeCl₃ and PACl coagulation, at the previously determined optimal doses for the individual water matrices:

- Kulpin: FeCl₃ dose = 150 mg FeCl₃/l; PACl dose = 15 mg Al/l,
- B. Petrovac: FeCl₃ dose = 200 mg FeCl₃/l; PACl dose = 30 mg Al/l,
- Maglič: FeCl₃ dose = 200 mg FeCl₃/l; PACl dose = 30 mg Al/l,
- Gložan: FeCl₃ dose = 150 mg FeCl₃/l; PACl dose = 10 mg Al/l.

In the majority of cases (figure 42) preozonation did not significantly improve the removal of arsenic by either of the coagulants applied. In the Kulpin groundwater, in the case of FeCl₃, ozonation with 0.8 mg O₃/mg DOC marginally improved the coagulation process for arsenic removal from 53 to 60% (figure 42(a)). In contrast, polyaluminium chloride coagulation efficacy for arsenic removal was reduced from 47 to 25% with the addition of a 0.2 mg O₃/mg DOC dose (figure 42(c)). Preozonation at all ozone doses of the Bački Petrovac water made the process less effective for both coagulants investigated, nor did it make any significant differences in the removal of arsenic from the water of Gložan, which already had a very low initial arsenic concentration of 3.7 µg As/l. Finally, in the Maglič water, where the initial arsenic concentration was 11.8 µg As/l, preozonation definitely improved both coagulation processes, with an ozone dose of 0.5 mg O₃/mg DOC sufficient

to increase As removal by FeCl_3 from 59% to 77% and by PACl from 57% to 83% (figures 42(a,c)).

The explanation of why the behaviour of the arsenic removals observed was inconsistent, is likely due to the variations in the other water constituents. The results for preozonation before the PACl treatment were considerably more varied (figure 42(d)). Preozonation of the Kulpin and Maglić waters made no significant difference to coagulation efficiency for DOC removal, whereas coagulation of the Gložan water after preozonation was slightly improved depending on the ozone dose, and coagulation of the Bački Petrovac water after preozonation was significantly improved at doses > 0.5 mg O_3 /mg DOC, with the best DOC removal of 50%. The corresponding As removal achieved at these doses was 78% (figure 42(c)).



(Kulpin: 15 mg Al/l or 150 mg FeCl_3 /l; B. Petrovac: 30 mg Al/l or 200 mg FeCl_3 /l;
Maglić: 30 mg Al/l or 200 mg FeCl_3 /l; Gložan: 10 mg Al/l or 150 mg FeCl_3 /l.)

Figure 42. Arsenic and DOC removals by different doses of FeCl_3 and PACl in combination with ozonation.

Slika 42. Uticaj predozonizacije na uklanjanje arsena i DOC koagulacijom sa FeCl_3 i PACl.

Examination of the way in which the differing character of the NOM present in the groundwater effects their removal by coagulation processes is beyond the scope of this work, although more information may be found in Tubić et al. (2013).

Summary of investigation into coagulation combined with preoxidation

It can be concluded that the contrasting results observed in the five different water matrices investigated suggest complicated interactions exist between the NOM and As which exist together in the groundwaters of Vojvodina. In the case of Zrenjanin, preoxidation, and in particular preozonation, had a positive effect on the removal of arsenic by coagulation, meaningfully decreasing the coagulant demand of the water. Nonetheless, preoxidation failed to improve NOM removal. In contrast, preozonation improved As and NOM removals in water from Bački Petrovac for all the combinations of coagulant investigated.

During efforts to improve coagulation process efficiency for the removal of arsenic from such waters, it is therefore very important to take into consideration the content, and also the structure of the NOM present. Furthermore, efforts to optimise coagulation processes to maximise removals of arsenic and NOM may require an element of compromise, as the best conditions for arsenic removal will rarely also be the best conditions for the removal of NOM. For this reason, the final phase of this research demonstrates the use of response surface methodology to investigate the interactions between As and NOM in the coagulation process, whilst optimising their simultaneous removals.

5.5 RSM investigation into the interactions between As and NOM during iron chloride coagulation

The final stage of this investigation utilises response surface methodology to focus on the interactions between arsenic and natural organic matter during the ferric chloride coagulation process. The results of this investigation were reported in Watson et al. (2016). RSM was used to model the experimental data created from a 3-factor Box-Behnken design which used the initial concentration of As(V), the initial concentration of HA and FeCl₃ dose as the process variables. The experimental conditions of each run, which were carried out in the randomised order shown, and the results obtained, are given in table 14.

Table 14. *The Box-Behnken design applied, showing the uncoded values of the three independent variables investigated and the experimental results obtained.*

Tabela 14. *Primena Box-Behnken dizajna – prikaz nekodiranih vrednosti tri nezavisno promenljive i eksperimentalno dobijenih rezultata.*

Run	A: As µg/l	B: HA mg/l	C: FeCl ₃ mg/l	As removal %	HA removal %	Combined removal %
1	110	7	150	82.4	16.3	49.4
2	20	7	250	95.4	67.9	81.7
3	110	2	250	35.2	17.0	26.1
4	110	12	50	1.65	5.19	3.42
5	110	7	150	78.9	22.2	50.6
6	200	7	250	96.6	7.60	52.1
7	200	12	150	78.1	20.0	49.1
8	20	12	150	85.5	75.0	80.3
9	200	7	50	4.04	15.6	9.81
10	110	7	50	84.3	24.0	54.2
11	110	2	50	4.05	17.3	10.7
12	110	7	150	85.8	14.4	50.1
13	110	7	150	79.6	17.5	48.5
14	20	7	50	22.6	6.14	14.4
15	110	7	150	72.1	19.0	45.5
16	200	2	150	78.5	86.9	82.7
17	110	12	250	96.7	73.5	85.1
18	20	2	150	99.8	57.3	78.6

In order to reveal as much information as possible about the extent of the interactions between arsenic and HA, three different responses were analysed: RemAs, the percentage removal of As(V); RemHA, the percentage removal of HA; and RemComb, a multiple response generated from the following desirability function, which combines the first two responses using the arithmetic mean:

$$RemComb = \frac{RemAs + RemHA}{2} \quad \text{Eq. 16}$$

As explained in section 2.3.1, the presence of too much NOM can cause many problems for the distribution of safe drinking water. Therefore, the equal desirabilities of As(V) and HA removals in the *RemComb* response, reflect the fact that they must be given equal priority within local water supply systems here in Vojvodina, where it is often necessary to significantly remove both arsenic and NOM in order to achieve satisfactory water quality at the tap. Use of this simple multiple response makes it possible to optimise the coagulation process for the best simultaneous removal of both parameters, and in comparison with the other two responses, allows for the identification of any additional interactions between experimental factors which may not be apparent when examining one response at a time.

As shown in table 14, depending upon the experimental conditions, arsenic removals ranged from 1.65 to 99.8%, humic acid removals ranged from 5.19 to 86.9%, and the combined response varied from 3.42 to 85.1%.

5.5.1 Identifying the best response function for the data

The different response functions were generated and correlated with the experimental data to obtain a regression equation. The relative quality of the regressions found were based upon the sequential sum of the squares and lack of fit tests. The model summary statistics are given in table 15.

Table 15. Model summary statistics for the three responses investigated.

Tabela 15. Sumarni statistički model za tri ispitivana odgovora.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
As removal					
Linear	0.3387	< 0.0001	0.0376	-0.5681	
2FI	0.0966	0.0001	0.2951	-0.9971	
Quadratic	0.0056	0.0012	0.7831	-0.5551	Suggested
Cubic	0.0012		0.9819		Aliased
HA removal					
Linear	0.0105	0.0003	0.4419	0.1142	
2FI	0.6799	0.0002	0.3773	-0.7620	
Quadratic	0.0005	0.0097	0.8959	0.3014	Suggested
Cubic	0.0097		0.9800		Aliased
Combined removal					
Linear	0.0240	< 0.0001	0.3679	-0.0756	
2FI	0.3549	< 0.0001	0.3939	-0.9695	
Quadratic	0.0034	0.0007	0.8361	-0.1866	Suggested
Cubic	0.0007		0.9889		Aliased

These statistics indicate that for each of the three responses investigated, the quadratic model should be chosen for further analysis, as it provides the best fit to the experimental data with the lowest standard deviations, the highest correlation coefficients and the lowest p values, and without the aliasing which occurs in the cubic model, where the higher order

terms are confounded behind lower order ones. The responses were therefore modelled as second-order polynomial equations in the form presented in **equation 17**:

$$Y = f(x) = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 \quad \text{Eq. 17}$$

where Y is the predicted response (As removal $RemAs$, HA removal $RemHA$ or the combined removal function $RemComb$); k the number of factors; x_i and x_j the factors which influence the predicted response Y ; β_0 is the constant coefficient; and β_i , β_{ij} and β_{ii} are the coefficients of the linear, interaction and quadratic terms, respectively.

5.5.2 Fitting the models

The second order polynomial functions thus fitted for the three responses are given in equations 18-20. Each response was analysed as a function of the sum of a constant, three linear effects, three interaction effects and three quadratic effects, as shown in equation 17. A, B and C are the initial As(V) concentration in $\mu\text{g/l}$, the initial HA concentration in mg/l and the FeCl_3 dose in mg/l , respectively.

$$\begin{aligned} &RemAs \\ &= 18.54925 + 0.012022A - 12.6573B + 0.517239C - 0.04706AB \\ &- 0.00197AC + 0.034344BC + 0.002284A^2 + 0.897327B^2 - 0.00131C^2 \end{aligned} \quad \text{Eq. 18}$$

$$\begin{aligned} &RemHA \\ &= -9.01944 - 0.54321A - 0.25793B + 1.234911C + 0.007773AB \\ &+ 0.000548AC + 0.03196BC + 0.001557A^2 - 0.30571B^2 - 0.00385C^2 \end{aligned} \quad \text{Eq. 19}$$

$$\begin{aligned} &RemComb \\ &= 4.764906 - 0.26559A - 6.45763B + 0.876075C - 0.01964AB \\ &- 0.00069AC + 0.033152BC + 0.00192A^2 + 0.295809B^2 - 0.00258C^2 \end{aligned} \quad \text{Eq. 20}$$

ANOVA results for the three quadratic models, as well as values for the coefficient of determination R^2 and adjusted R^2 , are presented in table 16. It is evident from this table that the modelled responses fit well with the experimental data. The coefficients of determination for the second order polynomial equations for the As, HA and combined removal responses are 0.8979, 0.9510 and 0.9229 respectively, showing that the equations are reliable. The p-values are less than 0.05, indicating that each of the three models is statistically significant.

Figure 43 depicts the normal probability plot of residuals for each of the three responses modelled. The residuals are the difference between the observed values obtained experimentally and the values predicted by the model.

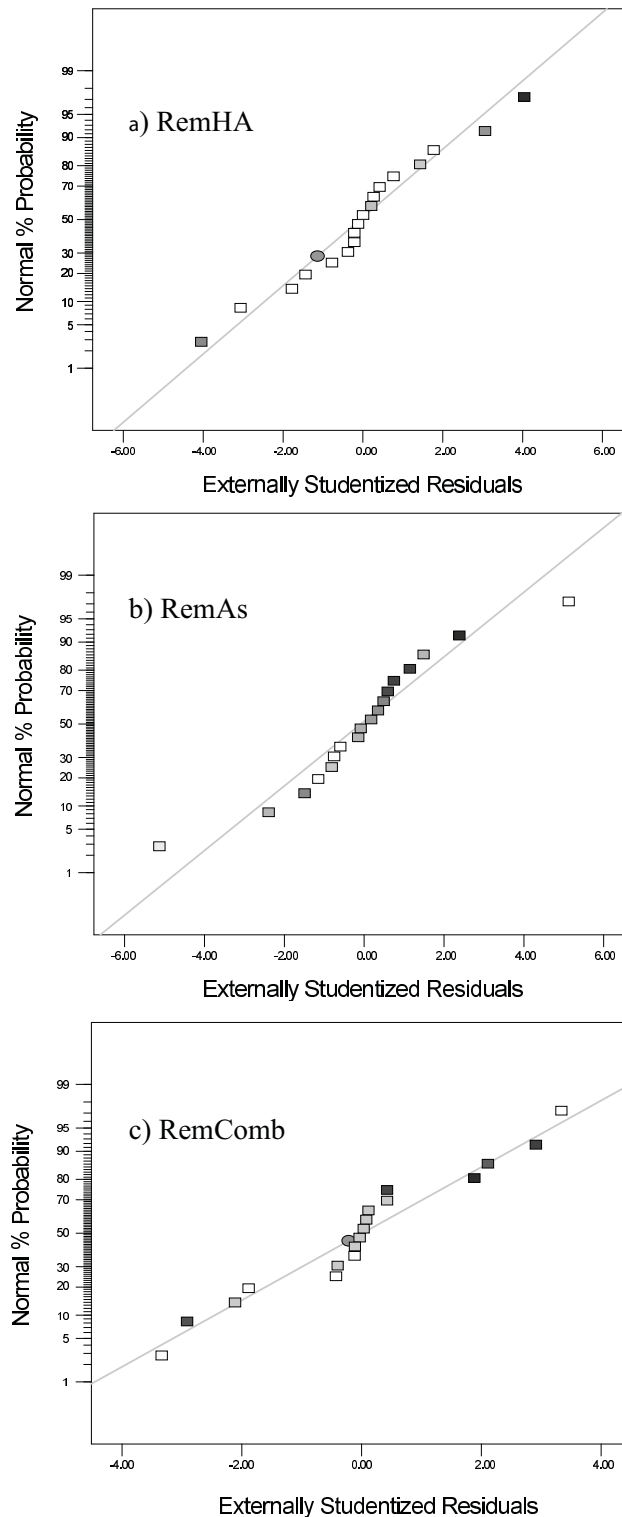


Figure 43. Normal probability plots of the residuals for each of the three responses modelled (greyscale shading indicates percentage removal: white = 0%, black = 100%).

Slika 43. Normalna verovatnoća raspodele reziduala za svaki modelovani odziv (boje ukazuju na procenat uklanjanja: bela boja=0%, crna boja= 100%).

One of the assumptions of the regression applied is that the data is normally distributed, and that therefore, a plot of the theoretical (model) percentiles of the normal distribution and the observed sample distribution should be approximately linear. In this case, the

residuals have been externally studentized: the residuals have been divided by an estimate of their standard deviation, in order to account for the fact that the residuals are not true errors, but are instead estimates of the errors based on observable data, and therefore may have different variances. Although the normal probability plot for response *RemHA* does display a slight S-shape, suggesting the data is slightly more uniformly distributed than the normal distribution, any deviation from linearity in the three plots is sufficiently minor to justify the conclusion that they do not deviate significantly from normality, and the regression applied is therefore appropriate.

Table 16. ANOVA results for the three second order responses modelled: *As(V)*, *HA* and combined removals.

Tablea 16. ANOVA rezultati za modelirane odzive drugog reda za uklanjanje *As(V)*, *HA* i njihove kombinacije.

	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
As removal					
Model	11183.28	9	1242.59	7.82	0.0041*
Lack of Fit	1204.52	3	401.51	30.21	0.0012*
Pure Error	66.45	5	13.29		
			$R^2 = 0.8979, R^2_{adj} = 0.7831$		
HA removal					
Model	19597.91	9	2177.55	17.25	0.0003*
Lack of Fit	888.86	3	296.29	12.23	0.0097*
Pure Error	121.17	5	24.23		
			$R^2 = 0.9510, R^2_{adj} = 0.8959$		
Combined removal					
Model	11272.25	9	1252.47	10.64	0.0014*
Lack of Fit	902.30	3	300.77	37.80	0.0007*
Pure Error	39.78	5	7.96		
			$R^2 = 0.9229, R^2_{adj} = 0.8361$		

* Significant ($p < 0.05$)

Table 17 gives an insight into the linear, interaction and quadratic effects of the factors for the three responses investigated, and the statistical significance of the response functions generated, which was checked by F-test. The p-value was used to check the significance of each term in the polynomial equations. The greater the F-value, and therefore the lower the p-value, the more significant the terms of the models.

For the *As* removal response, the statistical analysis in the table above shows that the FeCl_3 dose is the only significant linear term, with three significant interaction terms (*As* x *HA*, *As* x FeCl_3 , *HA* x FeCl_3), and two quadratic terms: *As* x *As* and *HA* x *HA*. The most significant terms are the *HA* x *HA* term, the FeCl_3 dose and the *As* x *HA* interaction. Only four terms were significant in the *HA* removal response, with by far the most significant terms being the linear and quadratic terms for the FeCl_3 dose, but with the interaction

between HA x FeCl₃ and the quadratic As x As term also contributing. The same four terms are significant for the combined response, although the significance of the HA x FeCl₃ interaction term and the quadratic As x As term is greater.

Table 17. ANOVA results for the terms of the second-order polynomial equations for As(V), HA and combined removals.

Tabela 17. ANOVA rezultati za polinomijalne jednačine drugog reda za uklanjanje As(V), HA i njihove kombinacije

	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
As removal					
As	724.41	1	724.41	4.56	0.0652
HA	2.85	1	2.85	0.018	0.8967
FeCl ₃	1855.73	1	1855.73	11.68	0.0091*
As.HA	1793.67	1	1793.67	11.29	0.0099*
As.FeCl ₃	1217.18	1	1217.18	7.66	0.0244*
HA.FeCl ₃	1179.54	1	1179.54	7.42	0.0261*
As ²	1492.94	1	1492.94	9.40	0.0155*
HA ²	2195.99	1	2195.99	13.82	0.0059*
FeCl ₃ ²	745.57	1	745.57	4.69	0.0622
HA removal					
As	265.34	1	265.34	2.10	0.1852
HA	246.92	1	246.92	1.96	0.1995
FeCl ₃	10624.79	1	10624.79	84.15	< 0.0001*
As.HA	48.93	1	48.93	0.39	0.5509
As.FeCl ₃	97.39	1	97.39	0.77	0.4054
HA.FeCl ₃	1021.44	1	1021.44	8.09	0.0217*
As ²	694.18	1	694.18	5.50	0.0471*
HA ²	254.88	1	254.88	2.02	0.1931
FeCl ₃ ²	6462.48	1	6462.48	51.19	< 0.0001*
Combined removal					
As	466.65	1	466.65	3.96	0.0817
HA	49.18	1	49.18	0.42	0.5362
FeCl ₃	5340.31	1	5340.31	45.35	0.0001*
As.HA	312.52	1	312.52	2.65	0.1419
As.FeCl ₃	156.50	1	156.50	1.33	0.2823
HA.FeCl ₃	1099.07	1	1099.07	9.33	0.0157*
As ²	1055.79	1	1055.79	8.97	0.0172*
HA ²	238.64	1	238.64	2.03	0.1924
FeCl ₃ ²	2899.53	1	2899.53	24.62	0.0011*

* Significant (p<0.05)

The fact that the same four terms are significant for HA removal and the combined removal indicates that in systems where both are present, the initial HA concentration has a greater influence in defining the removal efficiencies achieved than the initial As

concentration. This is supported by the fact that two As containing interaction effects (As x HA and As x FeCl₃) which are significant for the As removal response are not significant for the combined response. The dominance of HA in this system is in agreement with previous results, in which a real water containing a large amount of NOM (DOC = 9.33±1.92 mg C/L; HA fraction 14% of total DOC) was investigated, and where large amounts of coagulant were required to achieve good HA and As removals (Tubić et al., 2010a).

5.5.3 Effects of the initial HA and As concentrations and coagulant dose on the modelled responses

Figures 44–46 illustrate the 3D response surfaces for the three second-order polynomial models generated, for the removals of As and HA and the combined response. In these experiments, at any one time three factors were varied and a single response modelled. Four dimensions would be required in order to display the relation of the response to all three factors simultaneously. It is therefore usual practice to hold one factor constant and plot the response in relation to the other two factors. By plotting three graphs, holding the third factor constant at the three different levels investigated, the full scope of the experiment may be displayed.

The ANOVA results (table 17) were used to choose which two factors would be best displayed and which would be held constant: the interaction between the initial HA concentration and the FeCl₃ dose is one of the most significant factors for all three responses. The responses are therefore all depicted in relation to these two factors, with the third factor, the initial arsenic concentration, held at each of the levels investigated: 20 µg/l, 110 µg/l and 200 µg/l. In each of the figures, the experimental data is also plotted as a circle for each design point, with the dark grey circles depicting experimental data points above and the light grey circles depicting data points below the modelled response surface.

The 3D surface plots for HA removal show in figure 44 that as the initial HA concentration increases, the coagulant dose required to achieve maximum HA removal also increases. At an initial HA concentration of 2 mg/l, a dose of 175 mg/l FeCl₃ is sufficient to achieve a maximum HA removal of 70%. However, at an initial HA concentration of 12 mg/l, 220 mg/l FeCl₃ is required to achieve a maximum removal of 96%. The good removal of HA at optimal coagulant doses is in agreement with the findings of other authors (Sharp et al., 2006). These modelled doses agree with the results obtained in an earlier investigation, in which a dose of 180 mg/l FeCl₃ gave the best results for removing NOM (54% removal relative to raw water) from groundwater with an initial average DOC concentration of 9.33 ± 1.92 mg C/l (Tubić et al., 2010a).

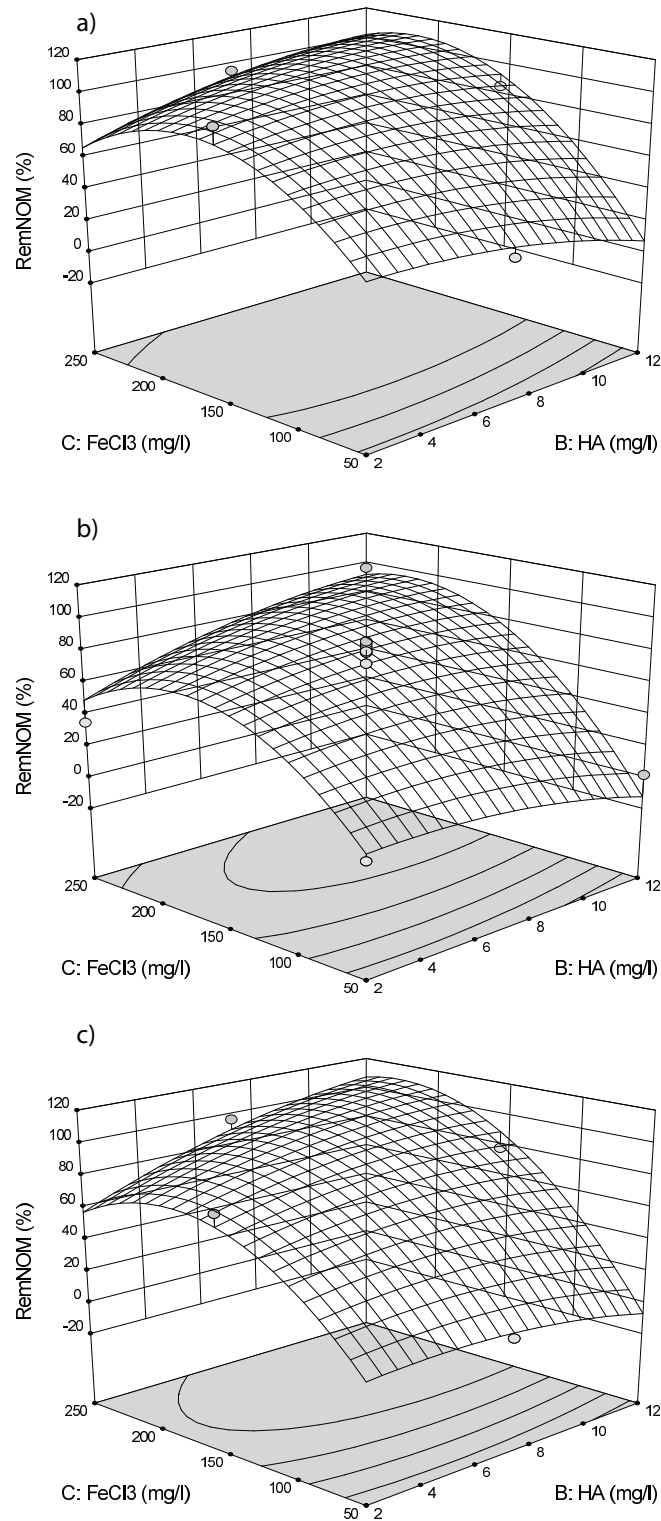


Figure 44. 3D surface plots for HA removal showing the effects of initial HA concentration and FeCl₃ dose for initial As concentrations of (a) 20 µg As/l; (b) 110 µg As /l; and (c) 200 µg As/l.

Slika 44. Primena RSM u ispitivanju uticaja početne koncentracije HA i doze FeCl₃ u prisustvu arsena, pri početnim koncentracijama od (a) 20 µg As/l; (b) 110 µg As/l; i (c) 200 µg As/l na uklanjanje HA.

The model shows that increasing the coagulant dose beyond this range is counterproductive, negatively impacting HA removal efficacy. This is agreement with the findings of Trinh and Kang (2011) who investigated DOC removal by coagulation using RSM, and also found that increasing the coagulant dose beyond the optimum range modelled, resulted in a reduction in DOC removal. The plots in figure 44 also indicate that the percentage of HA removal achieved at a particular coagulant dose is not directly impacted by the initial HA concentration. It is also clear from the similarity of figures 44 a), b) and c), that the initial arsenic concentration also plays no significant role in determining the removal of HA, hence its omission from the discussion above.

The As removal response shown in figure 45 displays more subtle variation in response to the factors investigated. Figure 45 a) depicts the As removals achieved at the lowest initial As(V) concentration investigated. At increasing initial HA concentrations, the sensitivity of the As removal response to the changes in the coagulant dose also increases. The model shows that at lower initial HA concentrations, As coagulation performs poorly, achieving 53% As removal at a dose of 200 mg/l FeCl₃. At higher HA concentrations, the same high dose achieved up to 87% As removals. This is due to the occurrence of complexation between the HA and the As(V) (see section 5.2). Fakour and Lin (2014) showed that when the ratio between HA and As concentrations is high, the proportion of complexed arsenic increases, with 45% of As(V) bound to HA when the concentration of HA is 100 times greater than that of As. Therefore, in this case, with HA concentrations up to 600 times higher than those of As, it can be assumed that the majority of As is complexed to HA. This explains the great impact of the initial HA dose on the removal of As at low initial As concentrations.

At the higher initial As concentrations (figure 45 b) and c)), the role of HA as a competing anion on the floc surface becomes more pronounced. At the lowest HA concentration, a greater proportion of the floc surface is available for As adsorption and complexation with ferrous hydroxide (Baskan and Pala, 2009), and up to 78% removal efficacy is achieved. However, at high HA concentrations, As removal falls as low as 30% at the highest coagulant dose. It is likely that only the smaller proportion of As which is complexed with the HA (Buschmann et al., 2006; Fakour and Lin, 2014) is then removed by coagulation, while the rest of the As remains in water as a consequence of steric hindrance and the much stronger interactions between HA and coagulant flocs. This is supported by the findings of Sharp et al. (2006) who reported 84% removal of HAF by coagulation, which does not leave free space for the adsorption (Pallier et al., 2010) and formation of Fe(AsO₄) complexes (Baskan and Pala, 2009), which is main mechanism proposed for As removal during coagulation.

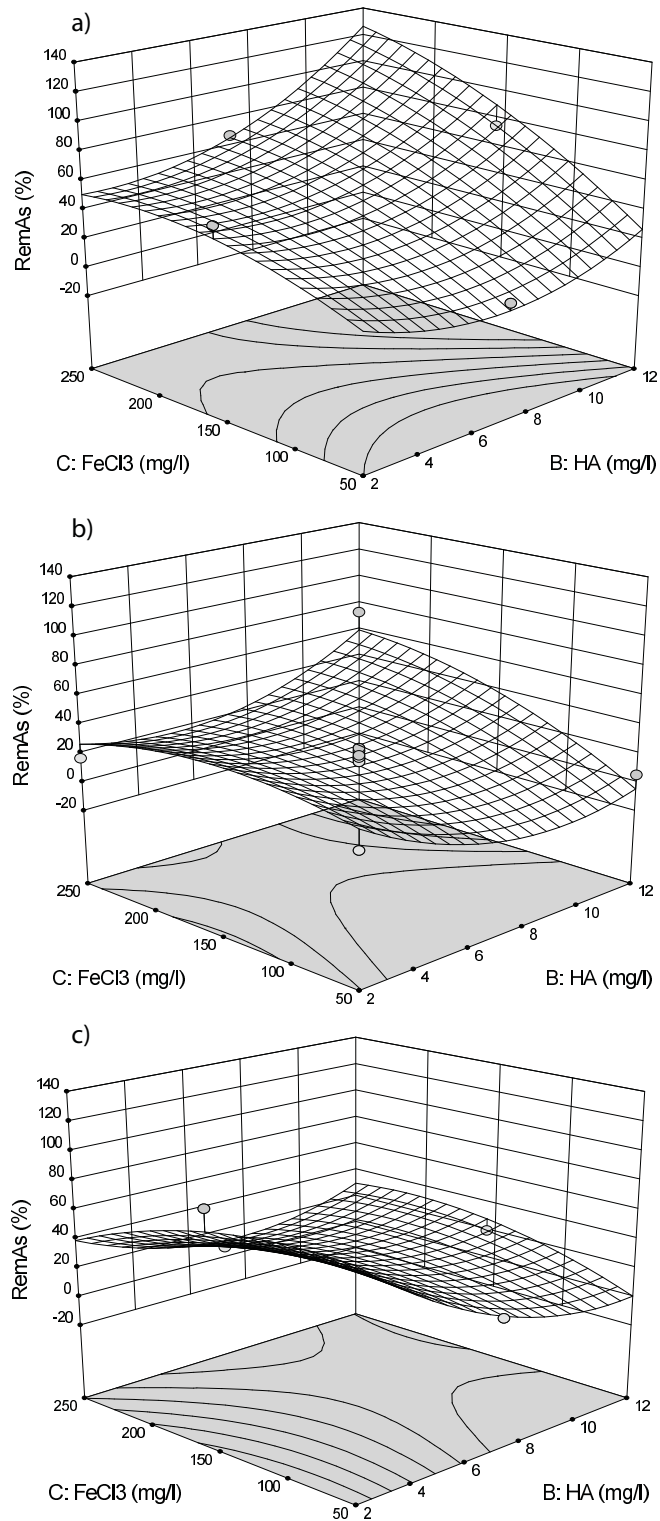


Figure 45. 3D surface plots for the As removal response showing the effects of initial HA concentration and FeCl_3 dose, held at the initial As(V) concentrations of (a) $20 \mu\text{g As/l}$; (b) $110 \mu\text{g As/l}$; and (c) $200 \mu\text{g As/l}$.

Slika 45. Primena RSM u ispitivanju uticaja početne koncentracije HA i doze FeCl_3 u prisustvu arsena, pri početnim koncentracijama od (a) $20 \mu\text{g As/l}$; (b) $110 \mu\text{g As/l}$; i (c) $200 \mu\text{g As/l}$ na uklanjanje arsena.

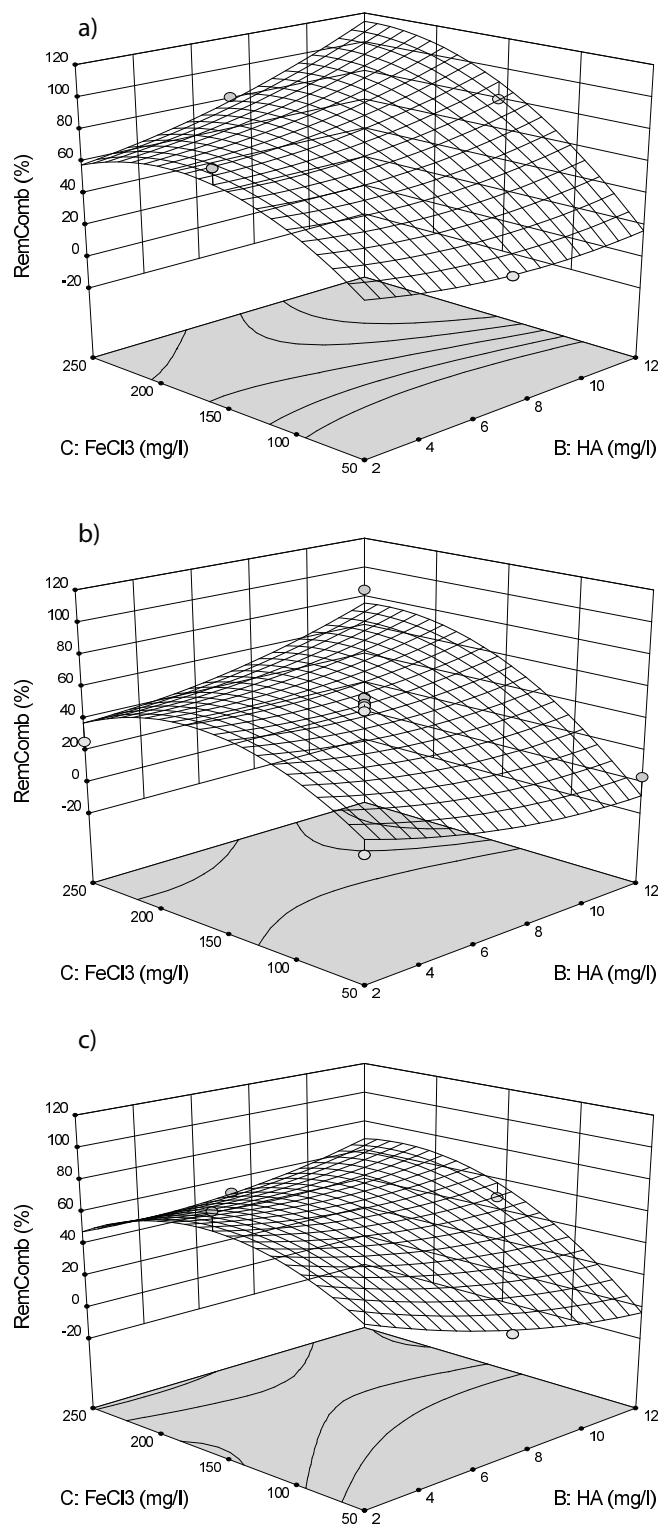


Figure 46. 3D surface plots for the combined response encompassing both HA and As removal, showing the effects of coagulant dose and initial HA concentration, held at the initial As(V) concentrations of (a) 20 µg As/l; (b) 110 µg As/l; (c) 200 µg As/l.

Slika 46. Primena RSM u ispitivanju uticaja početne koncentracije HA i doze FeCl₃ u prisustvu arsena, pri početnim koncentracijama od (a) 20 µg As/l; (b) 110 µg As/l; i (c) 200 µg As/l na kombinovan odziv.

The separate As and HA removal responses (figures 44 and 45) show that their optimal removals occur under different conditions. However, in many areas of the world, as well as here in Vojvodina, it is necessary to remove both arsenic and natural organic matter during the preparation of drinking water. That is why the desirability function defined in equation 16 treats the removal of both As and HA as having equal significance. The final combined removal response modelled is shown in figure 46. At low initial As concentrations (20 µg/l, figure 46 a)), the combined removal efficiency increases with increasing coagulant dose. This effect is particularly pronounced as the initial HA concentration increases. At higher initial As concentrations (figures 46 b) and c)), the combined response surface flattens out somewhat, suggesting that the coagulation performance gains which can be achieved by increasing the coagulant dose are less significant. The optimum FeCl₃ coagulant dose for the simultaneous removal of both As and HA varies between 175 to 250 mg FeCl₃/l depending upon the initial HA concentration, but does not change greatly as the initial As concentration increases, although the overall efficacy of the coagulation process does decrease. The interactions between the initial HA and As concentrations, and their effect on the resulting combined removal response, have interesting consequences for larger water treatment plants. Although the concentrations of HA and As may not vary significantly over time within a single well, in plants with multiple wells, particularly where those wells take water from different aquifer layers, careful blending can allow control over the HA and As concentrations entering the plant. The interactions displayed by the combined response suggest that optimising the simultaneous removal of HA and As in such cases is far from trivial, but may be achieved on a case by case basis with good experimental design.

5.5.4 Comparison of the model with independent experimental data

In order to obtain independent verification of the performance of the combined removal model (equation 20), data was taken from a prior investigation, in which the experimental conditions were similar: groundwaters from the cities of Zrenjanin and Kikinda were investigated, as they contain both arsenic and natural organic matter. These waters were adjusted to pH 7 and coagulated with a range of doses from 60 to 200 mg/l FeCl₃. The factors were thus all within the range of the independent variables in the model, but with different values than the design points. The initial arsenic and DOC concentrations were used to predict the combined removal of arsenic and DOC at the different coagulant doses applied, and the results were correlated with the actual combined removals, as shown in figure 47.

The R^2 values are high for both data sets, although it is notable that in contrast to the Zrenjanin data, the correlation between the modelled and experimental data from Kikinda does not go through the origin. In the case of Kikinda, the model shows a tendency to overestimate the combined removal at low coagulant doses and overestimate the removal at high doses. This is likely to be a consequence of the fact that the natural organic matter in the Kikinda groundwater does not contain humic acid (Agbaba et al., 2015), and as such,

probably interacts with arsenic differently. However, the very good agreement between the experimental and predicted data from Zrenjanin indicates that as long as the experimental conditions are held within the design limits, the model developed utilising the Box-Behnken design can be an effective tool for predicting the combined removal of arsenic and NOM by FeCl_3 coagulation.

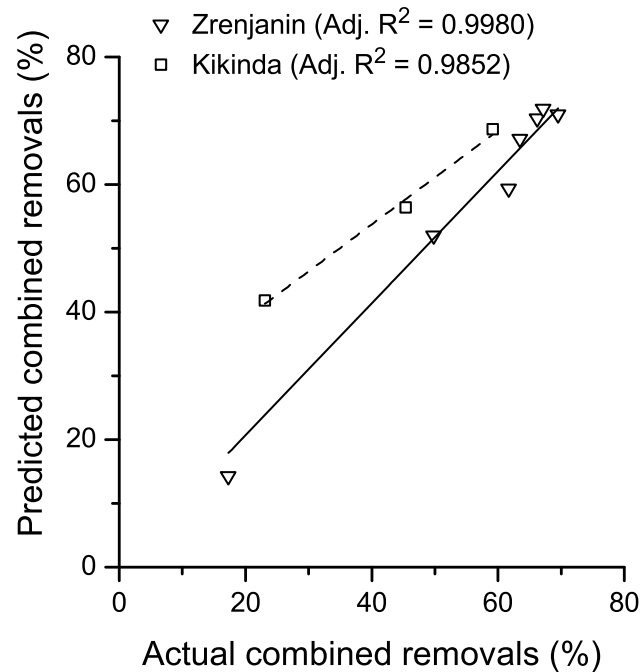


Figure 47. Correlation between the experimentally observed and predicted combined removals of arsenic and DOC from real groundwaters from Zrenjanin and Kikinda.

Slika 47. Korelacija između eksperimentalno dobijenog i teorijski predviđenog kombinovanog uklanjanja arsena i DOC iz podzemne vode sa teritorije Zrenjanina i Kikinde.

The complexity of the As removal response showed the value of utilizing RSM for such investigations, with contrasting influences from the presence of HA observed depending on whether the initial concentrations of As and HA were high or low. At high initial As concentrations, the absorption of As onto the floc surface was observed to be strongly limited by the presence of the sterically hindering HA. The HA removal response was simpler, with the degree of HA removal found to be largely independent from the initial As concentration. As the initial concentration of HA increased, the optimal FeCl_3 required to achieve the best HA removal also increased, ranging from 175 mg/l FeCl_3 at 2 mg HA/l up to 220 mg/l FeCl_3 at 12 mg HA/l.

From the perspective of optimising the coagulation process in actual water treatment plants in Serbia, where significant amounts of both As and NOM have to be removed before the water is ready for disinfection, the combined response surface is the most interesting. This model was compared to data taken from the treatment of groundwater from the cities of

Zrenjanin and Kikinda, and was found to show excellent agreement under similar experimental conditions. A more detailed evaluation of the impact of the structure of NOM on its interactions with arsenic may be the subject of future work, in order to extend the applicability of the models developed to more locations throughout Serbia. Further research could also investigate the effect of other water constituents such as calcium, phosphates or silicates on arsenic and NOM removal by ferric chloride coagulation.

Note that the equal priority given to the arsenic and HA removal responses during the definition of the desirability function (equation 16) was a choice informed by the need to remove both from the Zrenjanin groundwater. At other locations, preliminary investigations might reveal for instance that the need to remove NOM is more severe – perhaps the initial concentration of arsenic is already near the MAC, or the NOM present gives rise to a particularly toxic combination of disinfection by-products. In such cases, one of the great advantages of the RSM approach presented above is its flexibility: the weighting of the responses which make up the combined response may be simply adjusted to favour one over the other, allowing process optimisation to give priority to the water contaminants deemed most worthy of attention by the investigator.

The multiple interaction effects observed during this investigation highlighted the importance of utilizing response surface methodology to carry out the optimisation of drinking water treatment technologies, as such interactions would not be picked up utilising conventional one-factor-at-a-time experimental designs.

6 Conclusion

In many cases, groundwaters used as drinking water resources which are naturally contaminated with arsenic also contain significant amounts of NOM, which may also pose its own health risks or interfere with arsenic removal processes. In order to identify, develop, optimise and implement new drinking water treatment technologies capable of efficiently removing As and NOM from waters, it is therefore necessary to investigate how As and NOM interact in source waters and during their removal. This dissertation presents the results of such an investigation, focusing on the application of two significant treatment technologies: adsorption and coagulation. Methods to improve the adsorption and coagulation processes were also investigated, as were methods for finding the optimal process conditions for particular source–water/treatment combinations.

In the preliminary phase of experiments, the first research objective was to investigate several local groundwaters, to establish the extent of the arsenic problem, confirm the additional presence of NOM, and define the conditions required to create representative synthetic matrices. Well arsenic concentrations were found ranging from 4 to 340 $\mu\text{g/l}$, and speciation analysis confirmed the presence of both As(III) and As(V) in local groundwaters. This allowed the makeup of the synthetic matrices used in the rest of this work to be defined, with NOM contents ranging from 2–12 mg DOC/l and initial arsenic concentrations from 10 to 200 $\mu\text{g/l}$, ranges which encompass the vast majority of the measured made in the waters investigated.

Interactions between As and NOM in synthetic matrices were confirmed in the second phase of experiments, in which solutions of synthetic humic acid were spiked with varying amounts of As(III) and As(V), and then sampled at regular times intervals for speciation analysis. This allowed reductions in the concentration of free inorganic arsenic in solution to be observed over time, implying a corresponding increase in the amount of arsenic now complexed with the humic acid.

The results of this investigation suggest the existence of three different types of interaction, occurring on at least two different types of sites on the surface of the HA molecules:

- a) ***A rapid complexation interaction, which reaches equilibrium within two hours.*** Initial reductions in free arsenic concentrations were, taking less than 8 hours to approach equilibrium.
- b) ***A rapid redox interaction, which may occur at the same sites as the first complexation interaction, and which oxidises As(III) to As(V).*** As(V) concentrations were observed to increase steadily from zero in all the experiments in which only As(III) was initially present in solution.

- c) **A slower complexation interaction between As and HA.** Free As concentrations, in particular for As(V), continued to slowly fall for the duration of the experiments, taking closer to two days to reach equilibrium.

It is possible that the first two interactions are in fact one and the same, with the oxidation step creating a chemical bond between the HA and As(V).

The results suggest that both As(III) and As(V) readily form complexes with HA. However, it should be noted that the simultaneous nature of the interactions observed make it very difficult to decouple the effect of the redox interaction from the complexing interactions: ultimately, it is unclear whether As(III) is more likely to be oxidised first then complexed with HA, or whether it also complexes directly with the HA.

Nonetheless, the strong evidence obtained for the existence of these interactions between As and HA, and thus by extension between As and NOM, affords useful insight into the behaviour of groundwaters such as those found in Vojvodina, which contain significant quantities of both As and HA.

Iron oxide based adsorbents were the first techniques for arsenic removal to be investigated. The arsenic adsorption capabilities of two IOCS prepared in the laboratory, based on FeCl_3 (IOCS1) and $\text{Fe}(\text{NO}_3)_3$ (IOCS2), were compared with the capabilities of IOCSW, a waste IOCS generated in a local treatment plant during the process of removing iron and manganese from water. Characterisation of the IOCS revealed that IOCSW has the largest specific surface area ($33.8 \text{ m}^2/\text{g}$) of the three IOCS investigated. IOCS2 has a slightly higher point of zero charge (pH 8) than the other two, which means attractive electrostatic interactions between the surface of IOCS2 and As(V) anions are likely at pH 7. IOCS2 also had the greatest coverage of iron on its surface (28%). However, as well as 17% Fe coverage, the surface of IOCSW is also 28% Mn, which also has a very good affinity for arsenic, meaning 45% of the total surface of IOCSW is available for arsenic adsorption.

Adsorption isotherm experiments in synthetic matrices containing initial As(V) or As(III) concentrations of $200 \mu\text{g}/\text{l}$ were carried out. In general, arsenic adsorption was best described by the Langmuir isotherm, suggesting monolayer adsorption. Of the three IOCS investigated, IOCS1, based on FeCl_3 , had the lowest arsenic adsorption capacity. According to the Langmuir isotherm, for As(V), the highest adsorption capacity (q_{max}) was observed with IOCS2 ($111 \mu\text{g}/\text{g}$), followed by IOCSW ($78.3 \mu\text{g}/\text{g}$). The opposite trend was observed for As(III), whereby IOCS2 had a lower q_{max} than IOCSW (60.9 and $99.1 \mu\text{g}/\text{g}$ respectively). The significantly better performance of IOCSW in removing As(III) is due to the presence of Mn in addition to Fe on the surface of the adsorbent, which is capable of oxidising the As(III) to As(V), facilitating arsenic removal.

The influence of competitive anions on arsenic adsorption by IOCS was also investigated, with concentrations of phosphates ranging between 1 and $9 \text{ mg PO}_4^{3-}/\text{l}$, silicates between 4 and $12 \text{ mg SiO}_3^{2-}/\text{l}$, and humic acid from 4 to $12 \text{ mg HA}/\text{l}$:

- The impact of **phosphates** was strongly dependent upon the adsorbent and the oxidation state of arsenic. For IOCS1 and IOCS2, the presence of phosphates actually promoted the removal of both As(III) and As(V) at certain phosphate concentrations. Significantly, although the adsorption of As(V) onto IOCSW was worse with increasing phosphate, the adsorption of As(III) was almost completely unaffected, suggesting phosphates may compete directly with Fe adsorption sites on the surface of IOCSW, but not with Mn adsorption sites.
- The presence of **silicates** negatively effected the adsorption of both As(III) and As(V) onto IOCS1. High silicate concentrations also reduced the efficacy of IOCS2 and IOCSW adsorbents.
- **Humic acid** slightly hindered As(V) adsorption onto all three IOCS, with the worst effect observed with IOCS2, which was up to 30% less effective at removing As(V) in the presence of just 4 mg HA/l. As(III) adsorption onto IOCS1 and IOCS2 was also hindered by HA, but was improved on IOCSW, where the best As(III) removals were recorded in the presence of the lowest HA concentration.

In future, more work will be necessary to fully explain the effects of the competing anions, but the results presented are proof that considering the status of IOCSW as a waste material already produced in local water treatment plants, its application has excellent potential as an economically and technically feasible solution for the removal of arsenic from groundwater.

Enhancing coagulation with combined coagulants (FeCl₃, PACl and Al₂S(O₄)₃) and pH correction/preoxidation was the next topic of research. Coagulation was chosen due to its ability to remove both arsenic and NOM. In general, coagulation with ferric chloride was better at removing As, but less effective in removing NOM (expressed as DOC), whereas coagulation with polyaluminium chloride better removed NOM, but was less effective in removing As.

pH correction of the raw water pH from 7.8 down to 7.0 and 6.5 resulted in significant improvements for the FeCl₃ coagulation process, with up to 44% better DOC removals, and excellent As removals of up to 95.6%

Preoxidation with hydrogen peroxide or ozone before combined coagulation increased the efficiency of the coagulation processes sufficiently that lower coagulant doses could be applied to reduce residual As concentrations below the analytical limits of detection. Preoxidation with hydrogen peroxide was capable of reducing the coagulant demand of the already very effective FeCl₃ process, and also improved the efficacy of Al₂S(O₄)₃ coagulation. However, it was not able to overcome the poor affinity of PACl for As to achieve As concentrations below 10µg/l. In contrast, ozone proved to be a much more effective arsenic-oxidising agent. The most significant gains made by both preoxidation steps were observed in the techniques which combined aluminum and ferric chloride based coagulation. As such, the most efficient coagulation treatment investigated for removing As below the MAC involved application of preozonation at a dose of 7.5 mg O₃/l with

subsequent combined coagulation with PACl–FeCl₃ at doses of 30 mg Al/l and 10 mg FeCl₃/l. This FeCl₃ dose is an order of magnitude lower than the doses required by coagulation alone, resulting in not just a more economic treatment process, but also in the generation of much smaller amounts of more concentrated arsenic-bearing sludge.

Arsenic speciation analyses during the pH correction and coagulation processes revealed that As removal by FeCl₃ coagulation is heavily biased in favour of As(V) removal, with the share of As(III) in the residual arsenic steadily increasing at higher coagulant doses. This effect is amplified by pH correction, whereby at lower pH, a shift in the As(III):As(V) equilibrium was observed. This is a consequence of the large amount of NOM present in the water: at low pH, the NOM functional groups are increasingly deprotonated, increasing the number of reactive sites available to participate in the interactions identified above, therefore favouring the oxidation of As(III) to As(V) by NOM. In contrast to the FeCl₃ coagulation results, although PACl coagulation also increased the As(III) share, the effect was minimal, suggesting that both As(III) and As(V) are removed by PACl almost equally.

In general, preoxidation increased the ability of coagulation to remove As, especially with ozone, which proved to be stronger As oxidising agent than hydrogen peroxide. Preoxidation had a broadly negative effect on the DOC removals, but the extent to which these effects were observed varied greatly depending upon the different coagulants and groundwaters investigated. These variations confirmed that when developing and optimising coagulation technologies for a particular water source, the roles of As, NOM and their interactions during the coagulation process must all be considered together. A method for doing so was developed in the final phase of this work.

Interactions between As and NOM were investigated using Response Surface Methodology during ferric chloride coagulation. The effects of the FeCl₃ dose and the initial concentrations of arsenic and humic acid on their simultaneous removal from water by coagulation were investigated. In order to gain greater insight into the interactions between As and HA, three different response functions were modelled as second-order polynomials: As removal, HA removal, and their combined removal. Interaction effects between the initial As and HA concentrations were observed for the modelled As removal response, and an interaction between initial HA and FeCl₃ dose was found for all three responses.

The complexity of the As removal response showed the value of utilizing RSM for such investigations, with contrasting influences from the presence of HA observed depending on whether the initial concentrations of As and HA were high or low. At high initial As concentrations, the absorption of As onto the floc surface was observed to be strongly limited by the presence of the sterically hindering HA. The HA removal response was simpler, with the degree of HA removal found to be largely independent from the initial As concentration. As the initial concentration of HA increased, the optimal FeCl₃ required to

achieve the best HA removal also increased, ranging from 175 mg/l FeCl₃ at 2 mg HA/l up to 220 mg/l FeCl₃ at 12 mg HA/l.

From the perspective of optimising the coagulation process in actual water treatment plants, where significant amounts of both As and NOM have to be removed before the water is ready for disinfection, the combined response surface was the most interesting. Comparison of the modelled response with coagulation results using real groundwaters showed excellent agreement between the predicted and actual values.. The multiple interaction effects observed during this investigation highlighted the importance of utilizing response surface methodology to carry out the optimisation of drinking water treatment technologies, as such interactions would not have been picked up utilising conventional one-factor-at-a-time experimental designs.

In future, a more detailed evaluation of the impact of the structure of NOM on its interactions with arsenic should be attempted, in order to extend the applicability of the models developed to more locations throughout Serbia, and other areas affected by arsenic contamination. It would also be interesting to determine the impact of other competitive anions in the groundwater on the interactions between arsenic and NOM.

As the global population rises, and water scarcity becomes more severe due to climate change, securing adequate supplies of microbiologically safe and chemically clean drinking water will become increasingly challenging. The efficiency of current water treatment technologies will have to improved, and it may become necessary to open up water sources previously thought to be too contaminated to be of exploitation. In this context, the adsorption and coagulation technologies investigated in this dissertation, and the insights gained into the different interactions which occur between arsenic and NOM during removal processes, could prove extremely valuable in finding solutions to this problem, not just locally, but anywhere with elevated concentrations of arsenic in the groundwater resources.

7 Literature

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Biografija/Biography

Malcolm Alexander Watson je rođen 28.02.1979. godine u Newcastle Upon Tyne, UK. Živi u Novom Sadu. Završio je hemiju na Univerzitetu u Edinburgh-u i dobio zvanje MChem, 2002. godine (Diploma nostrifikovana u zvanje Magistar hemijskih nauka, Univerzitet u Novom Sadu, Prirodno-matematički fakultet, 15.12.2005.). Radio je kao analitičar kontrole kvaliteta u GlaxoSmithKline (Speke, UK) 2002 i kao naučnik u GLP (good laboratory practice) laboratoriji na Departmanu za razvoj i tehnologiju za Aventis Pharma (Holmes Chapel, UK). 2005. godine preselio se u Srbiju, gde se zaposlio na Prirodno–matematičkom fakultetu u Novom Sadu na Katedri za hemijsku tehnologiju i zaštitu životne sredine. Od 2006. godine upisan je na doktorske studije na istom fakultetu. Od 2013. godine je angažovan kao stručni saradnik na Katedri za hemijsku tehnologiju i zaštitu životne sredine, PMF-a u Novom Sadu. Tokom studija, kao i na radnim mestima na kojima je bio raspoređen, Malcolm je stekao bogato iskustvo za rad na savremenim instrumentalnim analitičkim tehnikama. Učestvovao je na 36 domaćih i tri međunarodna projekta iz programa FP, EUREKA, IPA. Autor je i koautor 16 radova u međunarodnim časopisima, 29 radova publikovanih na međunarodnim konferencijama, 4 poglavlja u tematskim zbornicima, 10 radova u domaćim naučnim časopisima, 27 radova publikovanih na domaćim konferencijama. Pored maternjeg engleskog jezika, govori i srpski i nemački jezik.



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Izvod: Jedan od najznačajnijih problema koji se javljaju u izvorištima vode za piće jeste prisustvo arsena u podzemnoj vodi. Toksičnost arsena se može izraziti na više načina, pri čemu je hronična izloženost arsenu povezana sa povećanom mogućnošću nastanka kardiovaskularnih i respiratornih oboljenja, promena na koži, kao i kancera kože, jetre, bubrega, pluća i bešike. Smatra se da su neorganski oblici arsena toksičniji od organskih. Veoma negativan efekat koji prisustvo arsena u vodi i hronična izloženost mogu imati na zdravlje ljudi, dovela je do toga da je Svetska zdravstvena organizacija utvrdila maksimalno dozvoljenu koncentraciju arsena u vodi za piće od 10 µg As/l, što je prihvaćeno odgovarajućim regulativama Evropske Unije i Republike Srbije.

U velikom broju slučajeva, podzemna voda koja sadrži arsen i koristi se kao resurs vode za piće, sadrži i prirodne organske materije (POM), koje indirektno mogu predstavljati rizik po zdravlje ljudi, a utiču na ponašanje arsena tokom tretmana. Zbog toga je, pri razvoju, optimizaciji i implementaciji tehnologija uklanjanja arsena i POM iz vode, neophodno sagledati i uzeti u obzir i njihove interakcije u ispitivanoj vodi i tokom odabranih tretmana.

Cilj ovog rada bio je da se ispituju efektivne, ekonomski isplative i održive tehnike/tehnologije uklanjanja arsena tokom pripreme vode za piće, kao i da se ispituju interakcije između arsena i prirodnih organskih materija u sirovoj i vodi nakon odabranih tretmana (adsorpcije i koagulacije). Ovo je postignuto kroz ispitivanje interakcije između arsena i prirodnih organskih materija, kao dva najčešća i najznačajnija kontaminanta prisutna u resursima vode za piće u regionu; razvoj i karakterizaciju novih adsorbenata na bazi oksida gvožđa za uklanjanje arsena iz vode i utvrđivanje uticaja odabranih kompetitivnih jona na njihovu efikasnost; ispitivanje efekata primene procesa koagulacije i kombinovanog procesa oksidacije i koagulacije za uklanjanje arsena iz podzemne vode i identifikovanja kritičnih procesnih parametara; razvoj matematičkog modela (primenom metodologije odzivne površine, eng. response surface methodology) za opisivanje

interakcija između arsena i prirodnih organskih materija tokom procesa koagulacije sa gvožđe(III) hloridom, čijom bi se kasnije primenom olakšala optimizacija procesa koagulacije voda sa različitim sadržajem ovih materija.

Eksperimentalni rad je bio organizovan u 5 faza, od preliminarnih ispitivanja kvaliteta podzemnih voda, preko ispitivanja interakcija između arsena i POM i primene adsorpcije i koagulacije za uklanjanje arsena, do razvoja modela za opisivanje interakcija arsena i POM tokom tretmana koagulacije sa FeCl_3 .

U preliminarnoj fazi eksperimenta, cilj je bio da se ispituju karakteristike više lokalnih podzemnih voda, kako bi se utvrdila količina arsena i prirodnih organskih materija, na osnovu čega su odabrani parametri kvaliteta sintetičkog matriksa vode koji je primenjen u ispitivanjima. Koncentracije arsena u ispitivanim podzemnim vodama kretale su se u opsegu od 4-340 $\mu\text{g As/l}$, a specijacijom je utvrđeno prisustvo As(III) i As(V). Na osnovu dobijenih rezultata odabrane su koncentracije arsena i prirodnih organskih materija na osnovu kojih su pripremljeni sintetički matriksi za dalja ispitivanja (10-200 $\mu\text{g As/l}$; 2–12 mg C/l).

U drugoj fazi eksperimentalnog rada ispitivane su interakcije između As(III)/As(V) i prirodnih organskih materija, u sintetičkim matriksima. Rezultati ispitivanja ukazuju na postojanje tri tipa interakcija, koje se dešavaju na najmanje dve vrste adsorpcionih mesta na površini molekula huminske materije (brze i spore redoks interakcije i kompleksiranje). Takođe, utvrđeno je da se As(III) i As(V) kompleksiraju sa huminskom materijom. Potrebno je uzeti u obzir da su u pitanju simultane interakcije, zbog čega je veoma teško napraviti razliku između efekata redoks i kompleksirajućih interakcija i kojima As(III) prvo podleže u reakciji sa prirodnim organskim materijama. Tokom eksperimenata su utvrđeni jasni dokazi o postojanju i intenzitetu interakcija između arsena i prirodnih organskih materija, što može imati značajan uticaj na ponašanje arsena tokom tretmana vode za piće.

U drugoj fazi eksperimenta izvršeno je ispitivanje adsorpcionog kapaciteta dva peska obložena oksidima gvožđa (eng. *iron coated sand* - *IOCS*), koja su sintetisana u laboratorijskim uslovima primenom FeCl_3 (*IOCS1*) i $\text{Fe}(\text{NO}_3)_3$ (*IOCS2*). Njihova efikasnost u uklanjanju arsena iz vode je upoređena sa efikasnošću otpadog peska obložena oksidima gvožđa (*IOCSW*), koji je dobijen sa postrojenja za tretman vode za piće i potiče iz procesa uklanjanja gvožđa i mangana. Karakterizacijom navedenih *IOCS* utvrđeno je da *IOCSW* ima najveću specifičnu površinu (33,8 m^2/g). *IOCS2* ima nešto veću tačku nultog naelektrisanja (pH=8) u odnosu na druga dva *IOCS*, što znači da su privlačne elektrostatičke interakcije na površini ovog materijala najizraženije pri pH=7. *IOCS2* karakteriše i najveća pokrivenost površine gvožđem (28%). Međutim, *IOCSW* pored gvožđa (17%) na svojoj površini ima i 28% mangana, koji takođe ima visok afinitet prema arsenu, što čini pokrivenost ovog peska adsorpcionim mestima slobodnim za vezivanje arsena od ukupno 45%. Za ispitivanje adsorpcionih procesa korišteni su sintetički matriksi u kojima je početna koncentracija As(III) ili As(V) bila 200 $\mu\text{g As/l}$. Generalno, adsorpcija arsena na ispitivanim adsorbentima može se opisati Lengmirovom izotermom, što ukazuje na to da se adsorpcija odvija na površini adsorbenta. Utvrđeno je da je *IOCS1* pokazao najmanji kapacitet adsorpcije arsena. Na osnovu dobijenih Lengmirovih izoterma, utvrđeno je da *IOCS2* ima najveći adsorpcioni kapacitet ($q_{\text{max}} = 111 \mu\text{g/g}$) za As(V), dok je ova vrednost za *IOCSW* nešto niža i iznosi (78,3 $\mu\text{g/g}$). Adsorpcione izoterme za As(III), pokazuju, međutim, da je vrednost q_{max} za *IOCS2* znatno niža u odnosu na vrednost dobijenu za *IOCSW* (60,9 i 99,1 $\mu\text{g/g}$, redom). Značajno bolja efikasnost *IOCSW* adsorbenta za uklanjanje As(III) može se objasniti činjenicom da se na površini adsorbenta, pored gvožđa, nalazi i mangan, koji ima sposobnost da oksiduje As(III) u As(V), čime se dodatno pospešuje uklanjanje arsena.

Dodatno je vršeno ispitivanje uticaja kompetirajućih jona (fosfata, silikata i huminskih kiselina) na adsorpciju arsena na *IOCS*. Početne koncentracije fosfata u eksperimentima kretale su se u opsegu od 1-9 mg $\text{PO}_4^{3-}/\text{l}$, silikata 4-12 mg $\text{SiO}_3^{2-}/\text{l}$ i huminskih kiselina 4-12 mg C/l. Uticaj fosfata na stepen adsorpcije arsena, u velikoj meri zavisi od vrste adsorbenta i oksidacionog stanja arsena. Prisustvo fosfatnih jona, pri određenim koncentracijama, pozitivno utiče na sposobnost sintetičkih adsorbenasa (*IOCS1* i *IOCS2*) za uklanjanje As(III) i As(V). Povećanje koncentracije fosfatnih jona u vodi, negativno utiče na adsorpciju As(V) na otpadnom pesku (*IOCSW*), dok njihova koncentracija ne utiče na stepen uklanjanja As(III). Ovo ukazuje na to da fosfatni joni učestvuju u kompeticiji za adsorpciona mesta pokrivena gvožđem, ali ne i za mesta pokrivena manganom. Prisustvo silikata u vodi negativno utiče na sposobnost *IOCS1* da uklanja As(III) i As(V). Takođe, visoke koncentracije silikata smanjuju adsorpcioni kapacitet *IOCS2* i *IOCSW*, dok prisustvo ovih jona u malim koncentracijama pospešuje adsorpciju As(III), pri čemu se postiže za 15% bolje uklanjanje na *IOCSW*, u odnosu na vodu bez silikata. Prisustvo huminske kiseline (HA) u vodi negativno utiče na adsorpciju As(V) na sve tri ispitivane vrste *IOCS*. Najveći negativan efekat huminskih kiselina na *IOCS2*, pri čemu se efikasnost adsorpcije As(V) na ovom pesku smanjuje i do 30% u prisustvu 4 mg C/l. Takođe, huminske kiseline negativno utiču na adsorpciju As(III) na *IOCS1* i *IOCS2*, dok je njihov pozitivan uticaj utvrđen u uklanjanju As(III) primenom *IOCSW*. Dobijeni rezultati adsorpcionih eksperimenata ukazuju na to da se ne može vršiti generalizacija zaključaka, već je neophodno sprovesti ispitivanja specifična za određeni tip vode, kako bi se u obzir uzeli uticaji svih njenih relevantnih konstituenata. Ipak, važan zaključak ovih eksperimenata je da primena *IOCSW* kao otpadnog adsorbenta, koji predstavlja balast za postrojenja na kojima nastaje, ima značajan potencijal, kao tehno-ekonomski isplativo rešenje za uklanjanje arsena iz vode.

Druga tehnološka opcija koja je ispitivana, za uklanjanje arsena i prirodnih organskih materija iz vode, jeste koagulacija primenom koagulanata na bazi gvožđa i aluminijuma (FeCl_3 , PACl i $\text{Al}(\text{SO}_4)_3$). U cilju povećanja efikasnosti procesa i smanjenja količine koagulanata koji se primenjuju, za unapređenje koagulacije primenjena je korekcija pH, kombinovanje koagulanata na bazi gvožđa i aluminijuma, kao i oksidacioni predtretmani sa vodonik-peroksidom ili ozonom.

Generalno je utvrđeno da se FeCl_3 pokazao kao efikasniji u uklanjanju arsena, dok je manje efikasan za uklanjanje POM, dok je obrnuto utvrđeno za PACl. Korekcija pH vrednosti sa 7,8 na 7,0 i 6,5, rezultovala je značajnim poboljšanjem efikasnosti procesa koagulacije sa FeCl_3 u pogledu smanjenja sadržaja rastvorenog organskog ugljenika (eng. dissolved organic matter, DOC), pri čemu je zabeleženo do 44% bolje uklanjanje DOC, u odnosu na procese bez koagulacije. Specijacijom arsena prisutnog u vodi nakon koagulacije utvrđeno je da korekcija pH značajno pomera As(V):As(III) odnos u korist As(V).

Primena predoksidacije vodonim-peroksidom ili ozonom omogućila je povećanje efikasnosti procesa koagulacije u uklanjanju arsena do zahtevanih granica za vodu za piće, uz smanjenje potrebne količine primenjenih koagulanata. Optimalna efikasnost koagulacije u uklanjanju arsena i POM iz podzemne vode postiže se primenom kombinacije koagulanata (30 mg Al/l (PACl) i 10 mg FeCl_3/l) uz predoksidaciju ozonom. Navedene doze koagulanata su znatno niže u odnosu na doze koje su potrebne kada se PACl i FeCl_3 primenjuju odvojeno, a osim što je povećana efikasnost procesa koagulacije, količina otpadnog mulja koji sadrži arsen je značajno smanjena. Specijacijom arsena u vodi nakon koagulacije je utvrđeno da FeCl_3 veoma dobro uklanja As(V), dok je ima nešto manju efikasnost u uklanjanju As(III), zbog čega je odnos navedenih vrsta arsena u koagulisanjoj vodi pomeren u korist As(III). Takođe, ovaj efekat je još više izražen u koagulisanjoj vodi

nakon korekcije pH vrednosti. Utvrđeno je da se primenom PACl u procesu koagulacije, As(III) i As(V) uklanjaju u gotovo jednakoj meri, uz malo bolje uklanjanje As(V).

Eksperimentima na različitim vrstama voda utvrđeno je da zavisi od tipa POM i oblika arsena, efikasnost njihovog uklanjanja iz vode koagulacijom varira u velikoj meri. Ovo potvrđuje da se rezultati ne mogu generalizovati i da se pri razvoju optimalne tehnologije za određenu vodu, moraju u obzir uzeti ne samo sadržaj arsena i POM u vodi, već i njihove međusobne interakcije, u čemu u velikoj meri može pomoći statističko modelovanje.

Za ispitivanje interakcija između arsena i POM u ovom radu primenjen je matematički model pod nazivom metodologija odzivne površine (eng. Response Surface Methodology, RSM). Primenom navedene metodologije posmatran je uticaj doze koagulant (FeCl₃), koncentracije arsena i huminske kiseline na efikasnost uklanjanja ovih materija u procesu koagulacije. Utvrđeno je da pri uklanjanju arsena ključnu ulogu imaju interakcije između arsena i huminske kiseline. Takođe, interakcije između huminske kiseline i koagulant predstavljaju važan faktor koji određuje efikasnost uklanjanja arsena, huminske kiseline, kao i njihovo zajedničko uklanjanje. Primenom RSM utvrđeno je da pri visokim početnim koncentracijama arsena, njegova adsorpcija na površini flokula je ograničena interakcijama sa huminskom kiselinom. Sa druge strane, stepen uklanjanja huminske kiseline skoro je potpuno nezavisan od početne koncentracije arsena u vodi. Sa povećanjem početne koncentracije huminske kiseline, optimalna doza FeCl₃ potrebna za njeno uklanjanje se povećava od 175 mg/l FeCl₃ pri koncentraciji od 2 mg C/l do 220 mg/l FeCl₃ pri koncentraciji od 12 mg C/l. Dobijeni model je validovan primenom nezavisnog seta podataka o parametrima koagulacije za dva tipa vode koje sadrže arsen i POM, pri čemu je utvrđeno odlično slaganje eksperimentalnih rezultata i modelom dobijenih podataka. Sagledavanje većeg broja interakcija primenom metodologije odzivne površine potvrđuje važnost njegove primene pri optimizaciji tretmana vode za piće, s obzirom da na drugi način ove interakcije i njihov uticaj na datu tehnologiju ne bi mogle biti sagledane na odgovarajući način.

Sprovedena istraživanja daju odgovore na mnoga pitanja, ali ujedno i otvaraju nova. Stoga bi buduća istraživanja trebalo usmeriti ka detaljnijim ispitivanjima uticaja strukture POM na interakcije sa arsenom, kao i efekte pojedinih kompetirajućih jona na efikasnost uklanjanja arsena različitim tehnikama, a za koje još uvek postoje oprečni stavovi u literaturi.

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Abstract: One of the most wide-spread problems with current drinking water resources is the natural presence of arsenic in groundwaters. The toxicity of arsenic in humans can be expressed in a variety of ways, with chronic exposure being linked to increased likelihoods of cardiovascular disease, respiratory illness, skin lesions, and cancers of the skin, liver, kidney, lung and bladder. The inorganic arsenic species are generally more toxic than the organic ones. The extremely negative impact of chronic arsenic exposure on human health led the World Health Organisation to recommend a maximum allowable concentration of 10 µg As/l for drinking water, which was adopted into EU and Serbian law.

In many cases, groundwaters used as drinking water resources which are naturally contaminated with arsenic also contain significant amounts of NOM, which may also pose its own health risks or interfere with arsenic removal processes. In order to identify, develop, optimise and implement new drinking water treatment technologies capable of efficiently removing As and NOM from waters, it is therefore necessary to investigate how As and NOM interact in source waters and during their removal.

The aim of this dissertation is to investigate effective, affordable and sustainable arsenic removal technologies and to investigate the interactions between arsenic and natural organic matter in raw groundwaters, as well as during the treatments. This was achieved through development and investigation of new adsorbents based on iron oxides for the removal of arsenic from drinking water, and investigation into how certain competitive ions affect their behaviour. Furthermore, the removal of arsenic by a variety of coagulation and combined oxidation/coagulation processes was investigated, in order to identify and optimise the most critical process parameters. Finally, Design of Experiments and Response Surface Methodology (RSM) was utilized to develop mathematical models describing the interactions between arsenic and natural organic matter during the process of iron chloride coagulation, to facilitate the optimisation of coagulation processes for waters with different amounts of these contaminants. These investigations will contribute a

better understanding of how As and NOM interact, not just in raw source waters, but also during the treatment process, knowledge which will be extremely significant for efforts to improve the quality of local drinking water supplies via the development, implementation and optimisation of innovative and sustainable drinking water treatment technologies.

The experimental work was organised into 5 research phases, with a series of preliminary investigations into the quality of the local ground waters, followed by investigations into the interactions between As and NOM, the application of adsorption and coagulation technologies for the removal of As, and the development of models to describe arsenic/NOM interactions during coagulation with FeCl_3 .

In the preliminary phase of experiments, the first research objective was to investigate several local groundwaters, to establish the extent of the arsenic problem, confirm the additional presence of NOM, and define the conditions required to create representative synthetic matrices. Well arsenic concentrations were found ranging from 4 to 340 $\mu\text{g As/l}$, and speciation analysis confirmed the presence of both As(III) and As(V) in local groundwaters. This allowed the makeup of the synthetic matrices used in the rest of this work to be defined, with NOM contents ranging from 2–12 mg C/l and initial arsenic concentrations of 10–200 $\mu\text{g As/l}$.

In the second phase of experiments, solutions of synthetic humic acid were spiked with varying amounts of As(V) and As(III), in order to investigate interactions between As and NOM in synthetic matrices. The results of this investigation suggest the existence of three different types of interaction, occurring on at least two different types of site on the surface of the HA molecules (a rapid complexation interaction, a rapid redox interaction, and a slower complexation interaction). The results suggest that both As(III) and As(V) readily form complexes with HA. However, it should be noted that the simultaneous nature of the interactions observed make it very difficult to decouple the effect of the redox interaction from the complexing interactions: ultimately, it is unclear whether As(III) is more likely to be oxidised first then complexed with HA, or whether it also complexes directly with the HA. The strong evidence obtained for the existence of these interactions between As and HA, and thus by extension between As and NOM, affords useful insight into the behaviour of groundwaters which contain significant quantities of both As and NOM.

Iron oxide based adsorbents were the first techniques for arsenic removal to be investigated. The arsenic adsorption capabilities of two IOCS prepared in the laboratory, based on FeCl_3 (IOCS1) and $\text{Fe}(\text{NO}_3)_3$ (IOCS2), were compared with the capabilities of IOCSW, a waste IOCS generated in a local treatment plant during the process of removing iron and manganese from water. Characterisation of the IOCS revealed that IOCSW has the largest specific surface area (33.8 m^2/g) of the three IOCS investigated. IOCS2 has a slightly higher point of zero charge (pH 8) than the other two, which means attractive electrostatic interactions between the surface of IOCS2 and As(V) anions are likely at pH 7. IOCS2 also had the greatest coverage of iron on its surface (28%). However, as well as 17% Fe coverage, the surface of IOCSW is also 28% Mn, which also has a very good affinity for arsenic, meaning 45% of the total surface of IOCSW is available for arsenic adsorption. Adsorption isotherm experiments were carried out in synthetic matrices containing initial As(III) or As(V) concentrations of 200 $\mu\text{g As/l}$. In general, arsenic adsorption was best described by the Langmuir isotherm, suggesting monolayer adsorption. Of the three IOCS investigated, IOCS1, based on FeCl_3 , had the lowest arsenic adsorption capacity. According to the Langmuir isotherm, for As(V), the highest adsorption capacity (q_{max}) was observed with IOCS2 (111 $\mu\text{g/g}$), followed by IOCSW (78.3 $\mu\text{g/g}$). The opposite trend was observed for As(III), whereby IOCS2 had a lower q_{max} than IOCSW (60.9 and 99.1 $\mu\text{g/g}$ respectively). The significantly better performance of

IOCSW in removing As(III) is due to the presence of Mn in addition to Fe on the surface of the adsorbent, which is capable of oxidising the As(III) to As(V), facilitating arsenic removal. The influence of competitive anions on arsenic adsorption by IOCS was also investigated, with concentrations of phosphates ranging between 1 and 9 mg $\text{PO}_4^{3-}/\text{l}$, silicates between 4 and 12 mg $\text{SiO}_3^{2-}/\text{l}$, and humic acid from 4 to 12 mg C/l. The impact of phosphates was strongly dependent upon the adsorbent and the oxidation state of arsenic. For IOCS1 and IOCS2, the presence of phosphates actually promoted the removal of both As(III) and As(V) at certain phosphate concentrations. Significantly, although the adsorption of As(V) onto IOCSW was worse with increasing phosphate, the adsorption of As(III) was almost completely unaffected, suggesting phosphates may compete directly with Fe adsorption sites on the surface of IOCSW, but not with Mn adsorption sites. The presence of silicates negatively effected the adsorption of both As(III) and As(V) onto IOCS1. High silicate concentrations also reduced the efficacy of IOCS2 and IOCSW adsorbents. However, for both these adsorbents, low silicate concentrations promoted As(III) adsorption, with removals by IOCSW being around 15% better than those observed in the absence of silicates. Humic acid slightly hindered As(V) adsorption onto all three IOCS, with the worst effect observed with IOCS2, which was up to 30% less effective at removing As(V) in the presence of just 4 mg C/l. As(III) adsorption onto IOCS1 and IOCS2 was also hindered by HA, but was improved on IOCSW, where the best As(III) removals were recorded in the presence of the lowest HA concentration. The results presented are proof that given the status of IOCSW as a waste material already produced in local water treatment plants, its application has excellent potential as an economically and technically feasible solution for the removal of arsenic from groundwater.

Coagulation with FeCl_3 , PACl and $\text{Al}(\text{SO}_4)_3$ and their combination with pH correction/preoxidation was the other technology investigated. Coagulation was chosen due to its ability to remove both arsenic and NOM. In general, coagulation with ferric chloride was better at removing As, but less effective in removing NOM (expressed as DOC), whereas coagulation with polyaluminium chloride better removed NOM, but was less effective in removing As. In order to minimise the coagulant doses required, these coagulants were combined together, along with the application of pH correction prior to coagulation. pH correction of the raw water pH from 7.8 down to 7.0 and 6.5 resulted in significant improvements for the FeCl_3 coagulation process, with up to 44% better DOC removals, while the As removal was already excellent (more than 95%). Preoxidation with hydrogen peroxide or ozone before coagulation increased the efficiency of the coagulation processes sufficiently that lower coagulant doses could be applied to reduce residual As concentrations below the analytical limits of detection. The most efficient coagulation treatment investigated for arsenic removal applied preozonation with subsequent combined coagulation with PACl– FeCl_3 at doses of 30 mg Al/l and 10 mg FeCl_3/l . These doses are significantly lower than the doses required by coagulation alone, resulting in not just a more economic treatment process, but also in the generation of much smaller amounts of more concentrated arsenic-bearing sludge. Arsenic speciation analysis during the pH correction and coagulation processes was also carried out. This experiment revealed that As removal by FeCl_3 coagulation is heavily biased in favour of As(V) removal, with the share of As(III) in the residual arsenic steadily increasing at higher coagulant doses. This effect is amplified by pH correction, which even before coagulation, dramatically shifted the As(V):As(III) equilibrium towards As(V). In contrast, although PACl coagulation also increased the As(III) share, the effect was minimal, suggesting that both As(V) and As(III) are removed by PACl almost equally. Experiments on the preoxidation and coagulation of a number of different groundwaters revealed large variations in the As and NOM removal behaviours. This confirmed that when developing and optimising coagulation technologies

for a particular water source, the roles of As, NOM and their interactions during the coagulation process must all be considered together. A method for doing so was developed in the final phase of this work.

Response Surface Methodology was used to investigate the interactions between As and NOM during ferric chloride coagulation. The effect of the FeCl_3 dose and the initial concentrations of arsenic and humic acid on their simultaneous removal from water by coagulation were investigated. In order to gain greater insight into the interactions between As and HA, three different response functions were modelled as second-order polynomials: As removal, HA removal, and their combined removal. Interaction effects between the initial As and HA concentrations were observed for the modelled As removal response, and an interaction between initial HA and FeCl_3 dose was found for all three responses. The complexity of the As removal response showed the value of utilizing RSM for such investigations, with contrasting influences from the presence of HA observed depending on whether the initial concentrations of As and HA were high or low. At high initial As concentrations, the absorption of As onto the floc surface was observed to be strongly limited by the presence of the sterically hindering HA. The HA removal response was simpler, with the degree of HA removal found to be largely independent from the initial As concentration. As the initial concentration of HA increased, the optimal FeCl_3 required to achieve the best HA removal also increased, ranging from 175 mg/l FeCl_3 at 2 mg C/l up to 220 mg/l FeCl_3 at 12 mg C/l. From the perspective of optimising the coagulation process in actual water treatment plants, where significant amounts of both As and NOM have to be removed before the water is ready for disinfection, the combined response surface was the most interesting. This model was compared to data taken from the treatment of groundwater from Zrenjanin and Kikinda, and was found to show excellent agreement under similar experimental conditions. The multiple interaction effects observed during this investigation highlighted the importance of utilizing response surface methodology to carry out the optimisation of drinking water treatment technologies, as such interactions would not have been picked up utilising conventional one-factor-at-a-time experimental designs.

The research conducted provides answers to many questions, but also opens up new ones. Therefore, future research should be directed towards more detailed studies on the impact of the structure of NOM on its interactions with arsenic, as well as the competing effects of certain ions on the removal efficiency of arsenic in various treatment techniques, for which there are still many opposing views in the literature.

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