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Utilization of exhausted coffee waste and date stones for removal of pesticides from aquatic media

-Doctoral dissertation-

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UNIVERZITET U NOVOM SADU
FAKULTET TEHNIČKIH NAUKA U NOVOM SADU

Novi Sad, 2020

MSc. Ali Mohamed Ali Hgeig

Primena otpada od kafe i koštica urme za uklanjanje pesticida iz akvatičnog medijuma

-doktorska disertacija-

Mentor:

dr Ivana Mihajlović, vanr. prof.

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УНИВЕРЗИТЕТ У НОВОМ САДУ ● **ФАКУЛТЕТ ТЕХНИЧКИХ НАУКА**
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Ali Mohammed Ali Hgeig

Abbreviations

SBET	Brunauer–Emmett–Teller surface area
AC	Activated carbon
ACF	Activated carbon fibre
BET	Brunauer–Emmett–Teller
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
LC	Liquid Chromatography
PU	Polyurethane
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
Cbs	Carbamates
OCs	Organochloride
OPs	Organophosphorous
CPs	Chlorophenols
PAs	Phenoxy acids
PhUrs	Phenylurea
ThCbs	Thiocarbamate
WHO	World Health Organization
POP	Persistent organic pollutant
IPU	Isoproturon
PAC	Powered activated carbon
GAC	Granular activated carbon

PVC	Polymers
IUPAC	International Union of Pure and Applied Chemistry
ACF	Activated carbon fibers
CAC	Commercial Activated carbon
PCP	Pentachlorophenol
SCG	Spent coffee grounds
MB	Methylene blue
ICO	International Coffee Organization
MET	Metamizol
ASA	Acetylsalicylic acid
ACE	Acetaminophen
CAF	Caffeine
Ct	Carbonization time
CT	Carbonization temperature
KOH	Potassium hydroxide
DSAC	Date seeds activated carbon

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Apstrakt

Doktorska disertacija je usmerena na ispitivanje procesa uklanjanja fungicida karbendazima i dva herbicida, linurona i izoproturona, iz vode korišćenjem sintetisanih materijala na bazi otpada od kafe i koštica urme, kao i na poređenje sa komercijalnim materijalima kao što su aktivni ugljevi, NORIT SA2, NORIT HYDRODARCO C i zeolit ZSM-5. Osnovni cilj istraživanja je sinteza adsorbenata zasnovanih na otpadnim sirovinama, otpadu od kafe (SCG) i košticama urme (DSAC), po prvi put primenjenih za uklanjanje smeše pesticida (karbendazima, linurona i izoproturona) iz vode.

SCG i DSAC su korišćeni za sintetisanje aktivnog uglja (AC) impregnacijom fosfornom kiselinom pri 600 °C, X_P (H_3PO_4/otpad od kafe): $3{:}1^{30\%}$, $4{:}1^{30\%}$, $3{:}1^{50\%}$, $4{:}1^{50\%}$ i X_P (H_3PO_4/ koštice urme): $3{:}1^{30\%}$. Sintetisani materijali su detaljno okarakterisani morfološkim i fizičko-hemijskim metodama (SEM, BET, FTIR). BET površine za adsorpciju pesticida su 803.422 i 307.450 $m^2\ g^{-1}$ za SCG i DSAC, respektivno. Rezultati dobijeni iz FTIR karakterizacije ukazuju na prisustvo mnogih funkcionalnih grupa na površini aktivnih ugljeva sintetisanih od otpada od kafe i koštica urme.

Tokom razvoja metode prečišćavanja svi parametri važni za efikasnost metode su optimizovani (pH vrednost, kontaktno vreme, temperatura, masa adsorbenta, početna koncentracija selektovanih pesticida). Proučavanje interakcije između odabranih pesticida i adsorbenata, modelovano je pomoću tri izoterme: Langmirove, Frojndlihove i Temkinove izoterme koje su pokazale zadovoljavajuće koeficijente korelacije. Maksimalni adsorpcioni kapaciteti za SCG izračunati iz Langmirovih izotermi bili su 11.990 mg g^{-1} za karbendazim, 5.834 mg g^{-1} za linuron i 4.154 mg g^{-1} za izoproturon na sobnoj temperaturi. S druge strane, maksimalni adsorpcioni kapaciteti za DSAC su bili 10.780 mg g^{-1} za karbendazim, 29.585 mg g^{-1} za linuron i 25.906 mg g^{-1} za izoproturon.

Adsorpcija karbendazima, linurona i izoproturona na aktivnom uglju NORIT SA2 pokazala je dobro slaganje sa Frojndlihovim modelom. Aktivni ugalj NORIT HIDRODARCO C ukazivao je na različita ponašanja za odabrane pesticide: adsorpcija karbendazima i izoproturona dobro su opisane Frojndlihovom izotermom, dok je adsorpcija linurona najbolje predstavljena Langmirovom jednačinom. Adsorpcija karbendazima na zeolitu, tipa: ZSM-5 je najbolje definisana Langmirovim zakonom, linuron je odgovarao Temkinovoj izotermi, a izoproturon je dobro opisan Frojndlihovim i Temkinovim modelima.

Kinetika procesa uklanjanja pesticida iz vode predstavljena je pomoću kinetičkih modela pseudo prvog i pseudo-drugog reda i modela intračestične difuzije. Rezultati kinetike adsorpcije najbolje su odgovarali modelu pseudo-drugog reda.

Ispitivanje termodinamičkih parametara adsorpcije pružilo je dodatne informacije o energetskim promenama tokom adsorpcije. Desorpcionim eksperimentima ispitana je mogućnost za regenaraciju i ponovnu upotrebu sintetisanih materijala. Evaluacija novosintetisanih materijala urađena je u smislu ekonomske prihvatljivosti materijala za uklanjanje odabranih pesticida.

SCG i DSAC adsorbensi, kao ekološki i ekonomski prihvatljivi materijali, pokazali su visok potencijal uklanjanja odabranih pesticida, karbendazima, linurona i izoproturona, sa kraćim vremenom kontakta od adsorbenata koji se koriste u drugim studijama, što je od velikog interesa i važnosti u postavljanju sistema za tretman otpadnih voda.

Ključne reči: otpad od kafe, koštice urme, aktivni ugalj, adsorpcija, pesticidi, kinetički modeli.

1. 0. Uvod

Poljoprivredna proizvodnja zavisi od upotrebe pesticida, kao sredstava za zaštitu od bolesti biljaka [1]. Pesticidi imaju suštinsku ulogu u nastojanju da se povećaju i poboljšaju intenzivne poljoprivredne aktivnosti i proizvodnja hrane u današnjem svetu. Rastuća primena pesticida uzrokuje ekološke probleme povezane sa distribucijom i koncentracijom ovih jedinjenja u životnoj sredini, posebno u izvorištima pitke vode [2, 3]. Samo mali deo pesticida zapravo dostiže svoje ciljeve u zaštiti bilja, dok se ostatak distribuira u medijumima životne sredine što može dovesti do njegovog prenosa u vodene ekosisteme [2, 4 - 6].

Karbendazim ili metil-benzimidazol-2-il karbamat je poznato jedinjenje fungicida iz klase benzimidazola i često je produkt razgradnje drugih fungicida poput benomila ili tiofanatmetila [7]. Ovaj fungicid širokog spektra iz klase benzimidazola se ekstenzivno koristi za kontrolu gljivičnih bolesti u povrću i usevima [8]. U Evropi se karbendazim koristi u količinama većim od 50 tona godišnje [8]. Karbendazim uzrokuje opasnosti po zdravlje ljudi i agroekosisteme zbog njegove stabilnosti i lipofilnosti u zemljištu sa poluživotom do jedne godine [9, 10]. Karbendazim ima slabu rastvorljivost u vodi (8 mg L^{-1}, 25 °C) [11]. Upotreba karbendazima za zaštitu bilja odobrena je u Evropi do 2021. godine [12].

Linuron (3- (3,4-dihlorofenil) -1-metoksi-l-metilurea) se primenjuje za regulisanje širenja trave i korova kako bi se podržao rast biljnih kultura. Linuron ima nizak nivo toksičnosti; njegova primena uključuje eliminaciju korova u pšenici, kukuruzu, šećernoj trski, krompiru i pamuku. U literaturi se navodi da se linuron brzo razgrađuje nakon ulaska u telo životinje, a unos do 125 mg kg^{-1} linurona u toku dve godine ne izaziva kancerogene i/ili mutagene efekte, mada se mogu detektovati rezidue ovog pesticida u krvi, lipidima, jetri, bubrezima i slezini [13 - 15]. Linuron se smatra jednom od važnih komercijalnih urea koja ima veliku sposobnost ubijanja rastućih biljaka [16].

Herbicid izoproturon iz klase feniluree, 3- (4-izopropilfenil) - 1,1-dimetilurea ima široku primenu u evropskim zemljama kao herbicid u tradicionalnoj poljoprivredi [17]. Primenjuje se protiv korova povezanog sa uzgojem pšenice i ječma. Izoproturon (IPU) je relativno otporan u okolini, sa prisustvom od 60 % prvobitno dodate količine u zemljištu tri meseca nakon primene [18]. IPU se obično detektuje u površinskoj i podzemnoj vodi u koncentracijama većim od 0,1 μg L^{-1} (dozvoljena vrednost u vodi za piće Evropske unije) [19]. Ekotoksikološki podaci pokazuju da IPU i njegovi metaboliti mogu izazvati rak kod životinja i ljudi, naškoditi vodenim beskičmenjacima, algama i mikrobnim zajednicama u slatkoj vodi [20 - 24]. Zbog toga postoji značajna pažnja u istraživanju sudbine izoproturona u životnoj sredini, posebno u podzemnim vodama, kao i rekama, potocima i jezerima.

Spiranje pesticida sa poljoprivrednog zemljišta jedan je od vodećih uzroka zagađenja u vodotocima. Iz tog razloga, istraživači su usmerili pažnju na razvoj efikasnih tretmana za uklanjanje pesticida iz vodnog medijuma [25]. Poslednjih godina je urađeno mnogo studija za razvoj komercijalnih i jeftinih adsorbenata za prečišćavanje vode [26, 27]. Kako se povećava potražnja za zelenim, ekološkim pristupom, povećava se korišćenje aktivnog uglja (AC) u industriji za procese tretmana i regeneracije [28]. AC, za koji je karakteristična velika specifična površina, obično se koristi kao adsorbens za uklanjanje zagađujućih supstanci [29]. Hemijska aktivacija se često koristi za proizvodnju AC i zahteva impregnaciju hemikalijama kao što su H_3PO_4, KOH ili NaOH [31]. AC se uglavnom proizvodi od materijala bogatih ugljenikom termalnom i/ili hemijskom aktivacijom. Ovaj proces takođe omogućava razvoj mikroporoznog i/ ili mezoporoznog ugljenika sa visoko razvijenom strukturom pora [32]. Iako se komercijalni AC obično koristi, njegova upotreba je ponekad ograničena zbog većih troškova. Iz ekonomskog razloga, značajna pažnja posvećena je karakterizaciji i razumevanju sorpcionih svojstava AC proizvedenih iz alternativnih materijala, kao što su poljoprivredni otpad ili industrijski nusproizvodi [33 - 35]. Priprema jeftinih adsorbenata iz različitih otpadnih materijala ima ekonomske i ekološke prednosti [27, 31].

Kafa se proizvodi i koristi u svakodnevnom životu širom sveta. Tokom 2016./2017., prema podacima Međunarodne organizacije za kafu, proizvodnja kafe dostigla je oko 9 milijardi kg. Kafa se smatra jednim od najvažnijih poljoprivrednih proizvoda u svetu. Potrošeni talog kafe predstavlja osnovni otpadni proizvod kafe. Sagorevanje 1.000 g kafene mase stvara procenjenih 538 g ugljen-dioksida [37].

Bilo je malo informacija i rezultata u literaturi o proizvodnji AC iz koštica urme (DSAC) [38]. Irak je jedna od najvećih zemalja koje se bave proizvodnjom urmi u svetu, sa više od 21 milion palmi i godišnjom proizvodnjom koja se procenjuje na 566.828 tona. Studije pokazuju da prosečna masa koštice čini oko 10–15 % ploda urme [39, 40]. S obzirom na to, poljoprivredni otpad na bazi lignoceluloze je odličan materijal za dobijanje aktivnog uglja zbog jedinstvene prirodne strukture i niskog sadržaja pepela [41, 42]. Međutim, ova vrsta recikliranog materijala mora da se karbonizuje pre dalje upotrebe [37].

Doktorska disertacija se bavi problemima sprečavanja proizvodnje otpada, koristeći otpad od kafe i koštice urme za proizvodnju adsorbenata za prečišćavanje vode. Supstance su izabrane sa NORMAN liste supstanci koje predstavljaju potencijalni rizik za vodni ekosistem. Termohemijska aktivacija otpada od kafe i koštica urme izvedena je na 600 °C sa fosfornom kiselinom. Uticaj ključnih parametara, kao što su pH, početna koncentracija odabranih pesticida, masa SCG i DSAC, vreme kontakta i temperatura, proučavani su u šaržnim eksperimentima. Takođe su proučavane kinetika adsorpcije, adsorpciona ravnoteža, termodinamika i desorpcija karbendazima, linurona i izoproturona. Ekološki i ekonomski adsorbensi SCG i DSAC pokazali su efikasno uklanjanje odabranih pesticida karbendazima, linurona i izoproturona. Komercijalni ugalj NORIIT SA2, aktivni ugalj NORIT HIDRODARCO C i zeolit, tipa: ZSM-5 korišćeni su bez ikakvih modifikacija kao referentni materijali za uklanjanje odabranih pesticida.

1. 1. Predmet istraživanja

Pesticidi (opšti termin za insekticide, herbicide i fungicide) suzbijaju korov, štetne insekte i gljivične i druge bolesti. Prednost pesticida leži u njihovoj sposobnosti da upravljaju problemom protiv štetočina (korova, insekata ili bolesti) koje potencijalno mogu biti van kontrole i koje mogu ugroziti ljudsko zdravlje, kao i kućne ljubimce i biljke. Iz tih razloga, vrlo je važno istražiti moguće izvore, ponašanje i prostornu raspodelu kontaminanata iz grupe pesticida u vodi.

Proizvodnja i upotreba pesticida u poslednjim decenijama su dramatično porasli i uzrokovali su novi potencijalni rizik po zdravlje ljudi i celokupnu životnu sredinu. Zbog toga postoji potreba za ispitivanjem prisustva pesticida karbendazima, linurona i izoproturona u vodi i postupaka za njihovo uklanjanje iz vodnog medijuma.

Predmet istraživanja u okviru doktorske disertacije je ispitivanje procesa uklanjanja fungicida karbendazima i dva herbicida, linurona i izoproturona, iz vode korišćenjem sintetisanih materijala na bazi otpada od kafe i koštica urme, kao i poređenje sa komercijalnim materijalima kao što su aktivni ugljevi, NORIT SA2, NORIT HYDRODARCO C i zeolit ZSM-5.

Hipoteza disertacije se zasniva na mogućnosti primene sintetisanih adsorbenata od otpadniih sirovina (otpad od kafe i koštice urme), u cilju efikasnog uklanjanja smeše pesticida (karbendazima, linurona i izoproturona) iz vode.

U cilju dokazivanja hipoteze planirani program istraživanja struktuiran je iz sledećih istraživačkih faza:

- Sinteza novih materijala na bazi otpada od kafe i koštica urme i njihova karakterizacija (SEM, BET, FTIR).
- Razvoj analitičkih metoda sa kojima će se sprovesti identifikacija izabranih jedinjenja pesticida (HPLC-DAD).
- Postavljanje eksperimentalne procedure razgradnje pesticida u laboratorijskim uslovima.
- Optimizacija osnovnih parametara procesa uklanjanja pesticida - pH vrednost, temperatura, masa sorbenta, inicijalna koncentracija pesticida, kontaktno vreme.
- Ispitivanje međusobnog uticaja pesticida u procesu uklanjanja iz vode.
- Ispitivanje mogućnosti za regenaraciju i ponovnu upotrebu sintetisanih materijala.
- Evaluacija novosintetisanih materijala u smislu ekonomske prihvatljivosti materijala za uklanjanje odabranih pesticida
- Analiza dobijenih rezultata.
- Modelovanje podataka adsorpcionim izotermama i kinetičkim modelima.
- Definisanje zaključaka o mogućnosti primene novih materijala i poređenje sa komercijalnim materijalima kao što su aktivni ugljevi, NORIT SA2, NORIT HYDRODARCO C i zeolit ZSM-5.

2. 0. Materijal i metode

2. 1. Adsorbensi

Ostatak taloga kafe je prikupljen iz mašine za kafu koju su koristili zaposleni na Departmanu za inženjerstvo zaštite životne sredine, Fakulteta tehničkih nauka, Univerziteta u Novom Sadu. Koštice urme dobijene su iz Ujedinjenih Arapskih Emirata.

Aktivni ugljevi (AC) pripremljeni od otpada od kafe i koštica urme (SCG i DSAC) korišćeni su kao sirovina za uklanjanje odabranih pesticida. Impregnirani su fosfornom kiselinom, H_3PO_4.

Komercijalni aktivni ugalj, NORIIT SA2, aktivni ugalj NORIT HIDRODARCO C i zeolit, tipa: ZSM-5 korišćeni su bez ikakvih modifikacija, kao referentni materijali za uklanjanje odabranih pesticida.

2. 2. Postupak pripreme SCG adsorbensa

SCG je ispran destilovanom vodom da bi se eliminisale nečistoće, prašina i rastvorljive supstance u vodi. SCG je zatim sušen u peći (Memmert, Nemačka) na 60 ° C tokom 24 sata pre aktivacije. Dobijeni proizvod je impregniran tokom 24 h rastvorom H_3PO_4, u različitim koncentracijama od 30 i 50 %, respektivno. Odnos impregnacije (Xp, %) je definisan kao odnos mase H_3PO_4 (g) prema masi prekursora (g osušene kafe i koštica urme). Fizičko-hemijska svojstva AC pripremljenih sa Xp = 30 i 50 % su ispitana.

Impregnirani uzorci su isprani vrućom destilovanom vodom nekoliko puta dok pH vrednosti nisu bile 4,5 do 5 i sušeni su potom na 110 ° C tokom 24 sata. Materijal je zatim karbonizovan u peći na 600 °C. Nakon hlađenja na sobnoj temperaturi i ispranja destilovanom vodom, materijal je sušen u peći 6 sati na 110 °C. Aktivirani proizvod na bazi otpada od kafe je bio spreman za upotrebu kao adsorbentni materijal nakon drobljenja i prosejavanja radi dobijanja čestica veličine između 100 i 200 µm.

2. 3. Postupak pripreme DSAC adsorbensa

Koštice od urme su isprane destilovanom vodom da bi se uklonile nečistoće. Oprane koštice su sušene u peći (Memmert, Nemačka) na 60 °C tokom 24 sata pre karbonizacije na 300 °C u trajanju od 30 minuta. Nakon toga, sušene koštice su mlevene da bi se dobile koštice u prahu i isprane su prokuvanom vodom nekoliko puta pre nego što su osušene preko noći na 110 °C. Dobijeni proizvod je bio spreman za aktiviranje rastvorom H_3PO_4 u koncentracijama od 30 % kao što je opisano u postupku pripreme SCG adsorbensa.

2. 4. Određivanje pesticida pomoću HPLC-DAD uređaja

Selektovani pesticidi su analizirani pomoću tečnog hromatografa visokih performansi (HPLC-DAD). Odvajanje je izvršeno kolonom Eclipse XDB-C18 (3 x 150 mm, veličina čestica 3,5 μm). Radni uslovi su: protok 0,4 ml min^{-1}, temperatura kolone je 30 °C i zapremina ubrizgavanja uzorka 10 μL. Mobilna faza se sastojala od vode (A) i acetonitrila (B). Elucija binarnog gradijenta je započela sa 25 % B u prvom minutu, zatim se linearno povećala na 50 % B u 5. minutu, a na kraju je primenjeno početno stanje, 25 % B u sedmom minutu. Korišćena je maksimalna talasna dužina od 215 nm.

2. 5. Statistička analiza

Podaci su predstavljeni kao srednje vrednosti ± standardno odstupanje od tri ponavljanja. Podaci su analizirani pomoću softvera Microsoft Office Excel 2007. Korišćeni su analiza varijanse (ANOVA). i Tukejev test.

2. 6. Karakterizacija SCG i DSAC

Mikrostrukture SCG i DSAC su određene pomoću SEM JSM 6460LV instrumenta (JEOL, SAD), opremljenog EDX uređajem. Specifična površina SCG i DSAC je određena merenjem N_2 adsorpcije, primenom BET metode i Autosorb iQ instrumenta (Quantachrome, USA). Kumulativni volumen pora za mezoporozne uzorke izračunat je metodom Barrete-Joinere-Halenda (BJH). Da bi se dobila zapremina mikropora primenjen je test Dubinine-Radushkevich (DB). Hemijske karakteristike su proučavane FTIR spektroskopijom kako bi se prepoznale funkcionalne grupe na površini SCG i DSAC. FTIR spektri su snimljeni FTIR / NIR spektrofotometrom Nexus 670 (Thermo Nicolet, USA), na talasnim dužinama od 400 do 4000 cm^{-1}.

2. 7. Izoterme adsorpcije

Istraživanje adsorpcione ravnoteže interakcije između odabranih pesticida i adsorbensa može se dobro opisati pomoću tri najčešće korišćena izotermna modela. Langmirov, Frojndlihov i Temkinov [44] model su od ključne važnosti za optimizaciju mehanizma adsorpcije, izražavanje površinskih svojstava i kapaciteta adsorbensa i dizajn adsorpcionih sistema, jer oni objašnjavaju kako zagađujuće supstance interaguju sa adsorpcionim materijalima [45]

2. 8. Kinetika adsorpcije

Nekoliko kinetičkih modela može se koristiti za ispitivanje kontrolnog mehanizma adsorpcionog procesa [46]. Da bi se proučila adsorpcija pesticida na SCG i DSAC i interpretirali dobijeni eksperimentalni podaci, korišćena su tri kinetička modela: pseudo-prvog reda, pseudo-drugog reda i kinetički model intračestične difuzije.

2. 9. Studije desorpcije i regeneracije

Regeneracija aktivnog uglja je od velikog značaja za sprečavanje potencijalne kontaminacije životne sredine [47]. Mogućnost ponovne upotrebe aktivnog uglja može se proceniti na osnovu stepena desorpcije ciljnih pesticida nakon sanacije i efikasnosti regenerisanog aktivnog uglja. SCG i DSAC uzorci (3,0 g L^{-1}) tretirani su rastvorom karbendazima, linurona i izoproturona (ukupna koncentracija 5 mg L^{-1}) prvo odvojeno, a drugi eksperiment je bio sa smešom ova tri pesticida, 30 minuta na sobnoj temperaturi 25 ± 2 °C. Nakon tretmana izveden je adsorpcioni eksperiment sa razblaženom H_3PO_4. Razblažena H_3PO_4 nastala je kao otpadni tok tokom pranja aktivnog uglja i posle pirolize na 550 °C. Eksperimenti su sprovedeni u šaržnom sistemu. Nakon ispiranja i sušenja aktivirani ugalj je ponovo korišćen kao regenerisani adsorbens, u tri ponovljena ciklusa adsorpcije-desorpcije.

2. 10 Adsorpciona termodinamika

Studije termodinamičkih parametara uključuju ispitivanje i izračunavanje promena entalpije (ΔH), slobodne energije (ΔG) i entropije (ΔS) u cilju ispitivanja spontanosti procesa adsorpcije.

3. 0. Rezultati i diskusija

3. 1. Karakterizacija AC

3. 1. 1. SEM analiza SCG i DSAC

Skenirajuća elektronska mikroskopija (SEM) opremljena EDX uređajem korišćena je za ispitivanje morfologije i komponenata AC površine pre i posle adsorpcije. Rezultati su pokazali da je površina SCG nepravilna i porozna sa raznim rupama i kanalima. Makro i mezopore su primećene na površini SCG. Struktura pora ukazivala je na adsorpciju karbendazima, linurona i izoproturona na površini adsorbensa. Nakon adsorpcije primećene su značajne promene površinske morfologije AC, pošto su pore bile ispunjenje ispitivanim pesticidima.

Za DSAC, površina je bila prilično glatka s porama, kao što se vidi na SEM slikama. Nakon procesa aktivacije, SEM slike ukazuju na dobro razvijenu i ujednačenu površinu, formirajući urednu poroznu strukturu i pretežno mikroporozan karakter koji je odgovoran za visoko razvijenu površinu ovog materijala.

3. 1. 2. FTIR spektri SCG i DSAC

FTIR spektar korišćen je za razumevanje hemijske strukture i funkcionalnih grupa. FTIR spektar SCG 30% i SCG 50% predstavlja karakteristične vrhove koji odgovaraju funkcionalnim grupama tipičnim za AC. Široki pik na 3418,6 cm^{-1} pripisan je vibracijama rastezanja hidroksilnih funkcionalnih grupa, uključujući vezivanje vodonikom. Spektar čistog AC ukazivao je na prisustvo O-H. Prisustvo pika na 2922.97 cm^{-1} odgovara vibracijama C – H u metilnim i metilenskim grupama. Pik na 1562,56 cm^{-1} pripisuje se karbonilnoj C-O grupi na koju utiče manje preklapanje sa vibracijom C-C aromatičnog prstena. Oštar pik unutar opsega 1158,71–1068,18 cm^{-1} pripisan je C – O grupama, koje potvrđuju ligninsku strukturu SCG. Pored toga, rame na 1068 cm^{-1} se pripisuje vezama P-O-C u kiselim fosfatnim esterima, kao i simetričnim vibracijama u P-O-P lancu. Ovi pojasevi su dobro definisani jer se odnos impregnacije sa H_3PO_4 povećava i nije uočljiv u pripremljenom AC.

FTIR analiza ukazuje na adsorpciju karbendazima, linurona i izoproturona i njihove smeše na DSAC i pokazuje sličan oblik i iste funkcionalne grupe. Široki pik u spektru (3000 –3500 cm^{-1}) pripisuje se načinu rastezanja hidroksilne grupe O – H sa adsorbovanom vodom savijanjem vodonika. Pikovi (2900 - 2950 cm^{-1}) dodeljuju se asimetričnim i simetričnim vibracijama rastezanja aciklične veze –CH, $–CH_2$ i $–CH_3$, dok pikovi oko 1580 cm^{-1} mogu nastati usled prisustva aromatične vibracije rastezanja C = C prstena. Pikovi na 2854 cm^{-1} odgovaraju vibraciji asimetričnih i simetričnih rastezanja C – H grupe [51]. Pik na 1160,78 cm^{-1} može se pripisati estrima (R-CO-O-R '), etrima (R-O-R') ili fenolnim grupama [52]. Malo rame na 1117,89 cm^{-1} i relativno intenzivan opseg oko 1040,25 cm^{-1} mogu se dodeliti alkoholima (R – OH). Ova funkcionalna grupa nastaje kao posledica dehidracijskog uticaja H_3PO_4, potencijalno usled uklanjanja H atoma i OH grupa iz aromatičnih prstenova tokom faza impregnacije i termičke obrade. Pik na 1064 cm^{-1} odgovara vibraciji S-O izduženja [53]. Pojas oko 871,62 cm^{-1} pripisan je C-H deformaciji [54]. Pik na 874,04 cm^{-1} može se pripisati alifatičnom ili aromatičnom istezanju P – O– C, P – O istezanju u P = OOH ili P – OH savijanju ili P – O– P asimetričnom istezanju u polifosfatima. Pik na 1064,79 cm^{-1}

može biti posledica P – O veze u kiselinama fosfatnih estara i simetrične vibracije polifosfatnog lanca P – O – P, dok se u oblasti oko 1160,78 cm $^{-1}$ može dodeliti vibracija rastezanja O – C u aromatskim grupama P – O – C ili u P-O fosfatne ili polifosfatne grupe vezane za vodonik [55, 56].

3. 1. 5. BET površine za SCG i DSAC

SCG i DSAC imaju visoko razvijenu BET površinu (803.422 i 307.450 m2 g^{-1}) što je osnovna karakteristika AC. Kumulativni volumen pora adsorpcije BJH za SCG i DSAC bio je 0,083 i 0,018 cm3 g^{-1}. Ukupna zapremina pora SCG i DSAC bila je 0,423 i 0,1452 cm^3 g^{-1}, respektivno.

3. 2. Uticaj koncentracije H_3PO_4 na hemijsku aktivaciju

Dobijeni rezultati pokazali su da je SCG veoma dobar adsorbens za uklanjanje odabranih pesticida (karbendazima, linurona i izoproturona). Dokazano je da se visoka specifična površina AC može dobiti hemijskim aktiviranjem otpada od kafe sa H_3PO_4. Oslobađanje vlage tokom karbonizacije uzorka tretiranog H_3PO_4, ukazuje na to da je H_3PO_4 važno sredstvo koje inhibira odvajanje katrana tokom karbonizacije.

3. 4. Uticaj pH rastvora na adsorpciju

3. 4. 1. Uticaj pH rastvora na adsorpciju SCG

Najvažniji parametar adsorpcionog procesa je pH rastvora koji utiče na efikasnost i prirodu procesa. pH rastvora utiče na hemiju odabranih pesticida, kao i na prirodu i aktivnost funkcionalnih grupa adsorpcionog medijuma. Uticaj pH na uklanjanje SCG za karbendazim, linuron i izoproturon proučavan je u opsegu pH od 3,0 do 10,0. Rastvori izabranih pesticida koncentracija 5 mg L^{-1} bili su u kontaktu sa adsorbensom koncentracija 1,0 g L^{-1} za karbendazim, 2,0 g L^{-1} za linuron u trajanju od 30 minuta i 1,5 g L^{-1} za izoproturon tokom 20 minuta na sobnoj temperaturi.

Moglo bi se zaključiti da pH vrednost nije uticala na efikasnost uklanjanja karbendazima. Postignuta je maksimalna efikasnost uklanjanja od 95,83 % pri pH = 5,00. Za razliku od karbendazima, značajan uticaj pH vrednosti primećen je kod uklanjanja linurona. Najveća efikasnost uklanjanja linurona bila je 92,45 % pri pH = 5,00. Visoka efikasnost uklanjanja karbendazima i linurona pri nižim vrednostima pH može biti posledica veće koncentracije i pokretljivosti H$^+$ jona u rastvoru. Površina naizmeničnog naprezanja je bila pozitivnije naelektrisana, pa je bila okružena hidronijum-jonima, H_3O^+ i elektrostatičkom odbojnom silom između odabranih pesticida i površine. Najveća efikasnost uklanjanja od 91,83 % za izoproturon, bila je na pH = 7,00. Na osnovu rezultata ispitivanja uticaja pH na efikasnost adsorpcije pesticida, kao optimalna vrednost za dalje eksperimente izabrana je pH = 5,00 za karbendazim i linuron i pH = 7,00 za izoproturon.

3. 4. 2. Uticaj pH rastvora na adsorpciju DSAC

Uticaj pH na uklanjanje karbendazima, linurona i izoproturona pomoću DSAC, ispitan je u opsegu pH od 3,0 do 10,0. Rastvori odabranih pesticida (5 mg L^{-1}) su bili u kontaktu sa adsorbensom (3 g L^{-1}) tokom 60 minuta na sobnoj temperaturi. Rezultati efikasnosti uklanjanja karbendazima i linurona pokazali su da nema značajne razlike ($P \leq 0,05$) između pH = 5,00 do 8,00 i pH = 3,00 do 8,00 za kontaktno vreme od 60 min. Efikasnost uklanjanja karbendazima, linurona i izoproturona pri pH = 7,00 iznosila je 94,26 %, 95,37 % i 90,03 %, respektivno. Vrednost pH = 7,00 je odabrana kao optimalna vrednost.

3. 5. Uticaj doze adsorbenta

3. 5. 1. Uticaj doze adsorbenta SCG

Efikasnost uklanjanja karbendazima, linurona i izoproturona kretala se u rasponu od 77,73 % do 97,65 %, od 21,50 % do 91,80 %, i od 45,66 % do 94,00 %, respektivno, sa povećanjem doze adsorbensa SCG sa 0,2 na 2,4 g L^{-1} za karbendazim i linuron i od 0,2 do 4 g L^{-1} za izoproturon. Sa daljim povećanjem doze adsorbensa, efikasnost uklanjanja je dostigla konstantne vrednosti koje verovatno ukazuju na veći broj vezivnih mesta na raspolaganju za sorpciju. Statistička analiza za karbendazim, linuron i izoproturon pokazala je da postoji značajna razlika ($P \leq 0,05$) između odabrane doze SCG pri pH = 5,00 za karbendazim i linuron i pH = 7,00 za izoproturon za kontaktno vreme od 30 min. Optimalne izabrane doze bile su 1,00, 2,00 i 3,00 g L^{-1} za karbendazim, linuron i izoproturon, respektivno.

3. 5. 2. Uticaj doze adsorbenta DSAC

Doza adsorbensa DSAC od 1,00 do 4,00 g L^{-1} korišćena je za ispitivanje uticaja ovog parametra na uklanjanje odabranih pesticida. Efikasnost uklanjanja kretala se u rasponu od 67,80 % do 93,99 %, od 87,15 % do 95,98 %, odnosno od 54,00 % do 88,25 %, respektivno.

Statistička analiza primenjena je za određivanje optimalne mase koja daje najveći adsorpcioni kapacitet ili najveći procenat uklanjanja. Statistička analiza pokazala je da postoji značajna razlika ($P \leq 0,05$) između odabrane doze DSAC za karbendazim, linuron i izoproturon pri pH = 7,00 i za kontaktno vreme od 60 min. Optimalne izabrane doze bile su 3,00, 2,00 i 3,00 g L^{-1} za karbendazim, linuron i izoproturon, respektivno. Kapacitet adsorpcije za sva tri pesticida pokazuje isti trend; smanjenje adsorpcionog kapaciteta sa povećanjem DSAC doze. Smanjenje adsorpcionog kapaciteta pri većoj dozi DSAC pripisuje se povećanju BET površine adsorbensa, tj. povećanju broja dostupnih adsorpcionih mesta za vezivanje jona čija koncentracija unutar rastvora je stabilna. Zanemarljiva promena u efikasnosti uklanjanja DSAC iznad 3,00 g L^{-1} za (karbendazim i izoproturon) i iznad 2,00 g L^{-1} za linuron može se pripisati prisustvu viška aktivnih mesta na površini DSAC, u odnosu na konstantnu koncentraciju karbendazima, linurona i izoproturona u rastvoru. Efikasnost uklanjanja i adsorpcioni kapacitet karbendazima, linurona i izoproturona ne rastu pri većim dozama DSAC zbog preklapanja i agregacije, kao i elektrostatičkog odbijanja adsorbentnih čestica, što rezultuje smanjenjem efektivne površine DSAC i broja dostupnih aktivnih lokacija [58]. Štaviše, veće doze DSAC takođe smanjuju efikasnost mešanja suspenzije, izazivajući spor prenos mase.

3. 6. Uticaj vremena kontakta

3. 6. 1. Uticaj vremena kontakta SCG i pesticida

Ispitivana je adsorpcija karbendazima, linurona i izoproturona na SCG pri različitim vremenima kontakta u rastvoru sa početnom koncentracijom karbendazima, linurona i izoproturona od 5 mg L^{-1}. Može se videti da je efikasnost uklanjanja karbendazima i linurona za kontaktno vreme od 20 minuta bila 95,13 % i 92,13 %, respektivno, u dozama 1,00 i 2,00 g L^{-1} SCG i pH vrednosti 5,00. Takođe, efikasnost uklanjanja izoproturona za 5,00 min je bila 93,02 % u dozi od 3,00 g L^{-1} SCG i pH vrednosti od 7,00. Produženje vremena kontakta ne bi moglo značajno da poboljša kapacitet adsorpcije karbendazima, linurona i izoproturona.

Na osnovu statističke analize, postoji mala značajna razlika u efikasnosti uklanjanja ($P \leq 0,05$) između odabranih vremena kontakta SCG i karbendazima i linurona. Slika 5. 15 (a, b) pokazala je da je najveća efikasnost uklanjanja karbendazima i linurona zabeležena za 120 min, i iznosila je 96,64 % i 93,22 %, dok je za 20 min bila 95,13 %, odnosno 92,13 %. Kontaktno vreme od 20 min moglo bi se koristiti za buduće eksperimente uklanjanja karbendazima i linurona. Za izoproturon, već nakon 5 min utvrđena je zadovoljavajuća efikasnost uklanjanja od 93,02 %. Kontaktno vreme od 5 min korišćeno je za buduće eksperimente. Rezultati ukazuju na to da je proces sorpcije brz na početku kontaktnog perioda, dok postaje sporiji u blizini ravnoteže, zbog teškoća sorpcije na preostalim površinskim mestima. Zapravo, na početku procesa površinske reakcije predstavljaju vodeći proces, dok blizu ravnoteže difuzija unutar čestica igra važnu ulogu.

3. 6. 2. Uticaj vremena kontakta DSAC i pesticida

Ravnotežni adsorpcioni kapacitet karbendazima, linurona i izoproturona na DSAC ispitivan je da bi se odredilo vreme potrebno za postizanje ravnoteže između adsorbensa i odabranog rastvora pesticida (5 mg L^{-1}) pri pH = 7,00. Rezultati su pokazali da procenat uklanjanja karbendazima, linurona i izoproturona raste sa 22,20 % na 94,14 %, 82,51 % na 95,11 % i 33,63 % na 91,81 % sa povećanjem vremena kontakta sa 5 na 120 min. Na osnovu rezultata može se primetiti da se adsorpcija odabranih pesticida odvija u dve faze. Inicijalna faza je brza zbog visoke koncentracije slobodnih aktivnih mesta na površini DSAC i zbog visoke početne koncentracije pesticida. U drugoj fazi dolazi do smanjenja broja raspoloživih aktivnih mesta DSAC i smanjenja koncentracije pesticida u rastvoru. Ova dva fenomena značajno smanjuju stepen adsorpcije. Pored toga, postoji mogućnost pojave elektrostatičkog odbijanja na površini zbog velike količine katjona [59]. Tokom prvih 10 min, procenti uklanjanja karbendazima, linurona i izoproturona bili su 84,47 %, 82,55 % i 57,94 %, respektivno. Nakon 10 minuta, može se primetiti da se efikasnost uklanjanja povećava sa kontaktnim vremenom dok se ne postigne ravnotežno stanje na 30, 40 i 90 min za karbendazim, linuron i izoproturon, respektivno. Zatim se primećuje lagani porast efikasnosti uklanjanja do 120 min. Ispitivanjem uticaja vremena kontakta na efikasnost adsorpcije pokazano je da posle 30, 40 i 90 min nije došlo do značajne promene brzine adsorpcije za karbendazim, linuron i izoproturon, respektivno, te su ove vrednosti usvojene kao optimalno vreme kontakta adsorbenta i pesticida.

3. 7. Uticaj početne koncentracije pesticida

3. 7. 1. Uticaj početne koncentracije pesticida na adsorpciju na SCG

Uticaj početne koncentracije karbendazima, linurona i izoproturona proučavan je u sledećim koncentracijama: 2, 4, 5, 6, 8, 10, 12 i 15 mg L^{-1}, dok su svi ostali parametri, sobna temperatura, pH rastvora, masa adsorbensa i vreme kontakta, podešeni na optimalne vrednosti.

Efikasnost uklanjanja karbendazima, linurona i izoproturona povećana je sa 52,69 % na 99,32%, sa 78,32 na 92,38% i sa 58,97 na 95,70%, respektivno. Efikasnost uklanjanja je smanjena kada su povećane koncentracije pesticida.

Primećena je značajna razlika ($P \leq 0,05$) između koncentracija karbendazima od 2 do 15 mg L^{-1}. Najveća efikasnost uklanjanja od 99,32 % registrovana je kod 2 mg L^{-1} kada je doza SCG bila 1,00 g L^{-1}, pri pH = 5,00 i vremenu kontakta od 20 min. Na osnovu koncentracije linurona od 2, 4 i 5 mg L^{-1} primećena je veća efikasnost uklanjanja. Za linuron je takođe najveća efikasnost uklanjanja postignuta pri najmanjoj koncentraciji od 2 mg L^{-1}, i istim vrednostima pH i vremena kontakta, dok je doza SCG bila 2,00 g L^{-1}.

Adsorpcioni kapacitet se povećavao s povećanjem početne koncentracije izoproturona, ali se za efikasnost uklanjanja pesticida iz rastvora pokazao obrnut trend. Najveća efikasnost uklanjanja za izoproturon postignuta je pri koncentraciji od 2 mg L^{-1}, kada je pH vrednost bila 7,00, a vreme kontakta 5,00 min, dok je doza SCG bila 3,00 g L^{-1}.

Pri višim početnim koncentracijama pesticida postoji manje dostupnih mesta za adsorpciju na SCG i efikasnost uklanjanja odabranih pesticida se smanjuje. Ovi rezultati su u dobroj saglasnosti sa rezultatima postignutim za adsorpciju izabranih pesticida na drugim adsorbentima, kao što su prethodno naveli Leite i sar. i Tsai i sar. [60, 61]. Povišena početna koncentracija pesticida dovodi do konkurentne adsorpcije pri stalnom broju dostupnih aktivnih mesta [62, 63]. Slika 5. 20 (a, b i c) pokazuje da se količina pesticida adsorbovanih na SCG povećavala sa povećanjem početne koncentracije odabranih pesticida. Pri početnoj koncentraciji od 15 mg L^{-1}, maksimum adsorpcije je dostignut na 9,66, 4,83 i 3,63 mg g^{-1}, za karbendazim, linuron i izoproturon, respektivno.

3. 7. 2. Uticaj početne koncentracije adsorpcije pesticida na DSAC

Početna koncentracija pesticida karbendazima, linurona i izoproturona na DSAC ispitivana je u različitim početnim koncentracijama, od 2 do 15 mg L^{-1} (pri pH 7, za doze DSAC 3,00, 2,00 i 3,00 g L^{-1}, pri sobnoj temperaturi 25 ± 1 ˚C i vremenu kontakta od 30, 40 i 90 min), respektivno.

Rezultati su pokazali da su adsorpcioni kapaciteti bili visoki kada je početna koncentracija pesticida bila 15 mg L^{-1}. Kapaciteti adsorpcije za karbendazim, linuron i izoproturon na DSAC bili su 4,46, 7,07 i 4,50 mg g^{-1}, respektivno. Kapacitet adsorpcije raste s povećanjem početne koncentracije zbog povećane verovatnoće sudara šupljine sa aktivnim centrima ili funkcionalnim grupama. U rastvoru sa visokim početnim koncentracijama dolazi do brzog zasićenja funkcionalnih grupa na površini aktivnog uglja [64].

Efikasnost uklanjanja pesticida karbendazima, linurona i izoproturona smanjena je sa 96,05% na 80,61%, sa 96,78% na 85,32% i sa 94,67% na 83,95%, respektivno kada su koncentracije pesticida povećane sa 2 na 15 mg L^{-1}. Efikasnost uklanjanja bila je visoka na najnižoj početnoj koncentraciji odabranih pesticida. Efikasnost adsorpcije pesticida opada sa povećanjem njihovih početnih koncentracija. Povišena početna koncentracija pesticida dovodi do konkurentne adsorpcije pri konstantnom broju dostupnih aktivnih mesta [62, 63].

3. 8. Modelovanje adsorpcionih izotermi

3. 8. 1. Modelovanje adsorpcionih izotermi za SCG

Proučavanje interakcije između odabranih pesticida i SCG, modelovano je pomoću tri izoterme: Langmirove, Frojndlihove i Temkinove izoterme koje su pokazale zadovoljavajuće koeficijente linearne korelacije ($r > 0.900$). Za karbendazim, najmanje vrednosti srednje kvadratne greške, RMSE, i χ^2 i najveće vrednosti r dobijene su pomoću Frojndlihovog modela. Za linuron rezultati pokazuju najbolje slaganje sa Langmirovom izotermom. Prema modelu Langmira, postignut je adsorpcioni kapacitet za karbendazim i linuron: 11.918 mg g^{-1} i 5.834 mg g^{-1}, respektivno. Ovaj rezultat je u skladu sa hipotezom Langmuirove izoterme koja pretpostavlja da se adsorpcija odvija samo na određenim lokalizovanim mestima na površini i da je površina energetski homogena. Teorijski i eksperimentalni maksimalni adsorpcioni kapaciteti su u dobroj saglasnosti.

Konstanta K_f predstavlja adsorpcioni kapacitet, a parametar n stepen odstupanja od linearnosti kod adsorpcije. Ako je vrednost n = 1, adsorpcija sledi linearnu funkciju; za vrednosti n <1, adsorpcija je nepovoljna, a ako je n> 1, adsorpcija je favorizovana. Frojndlihov koeficijent n postigao je uslov n> 1, što ukazuje na to da je adsorpcija favorizovana. Fojndlihov model je zasnovan na površinskoj heterogenosti adsorbensa, što dovodi do zaključka da je površina SCG napravljena od malih heterogenih konfiguracija koje su povoljne za fenomen adsorpcije. Afinitet adsorpcije za vezivanje pesticida na SCG je visok.

3. 8. 2. Modelovanje adsorpcionih izotermi za DSAC

Proučavanje interakcije između odabranih pesticida i DSAC, ukazuje na to da su najniže vrednosti RMSE i χ^2 i najviše r vrednosti (r> 0,900) dobijene sa Temkinovim modelom za karbendazim i sa Frojndlihovim modelom za linuron i izoproturon. Za sva tri odabrana pesticida proces je zasnovan na fizičkoj adsorpciji na energetski heterogenoj površini gde adsorbovani molekuli međusobno interaguju. Koeficijenti korelacije za adsorpciju linurona i izoproturona su veći u Frojndlihovom modelu, u poređenju sa Temkinovim modelom. Iz ovog razloga, prihvaćena je interpretacija Frojndlihovih konstanti: adsorpcioni kapacitet koji je opisan konstantom Kf i stepen odstupanja od linearnosti adsorpcije koji je prikazan sa n. U disertaciji, vrednosti dobijene za n su veće od jedan i prema tome, favorizuje se adsorpcija, a adsorpcioni afinitet za vezivanje linurona i izoproturona na DSAC je visok. Sa druge strane, veće vrednosti koeficijenata korelacije (r = 0,975) i najniže RMSE = 4,766 i χ^2 = 0,576 dobijene su pomoću Temkinovog modela za karbendazim.

3. 9. Kinetika adsorpcije

Da bi se konstruisao efikasni model tretmana adsorpcije, sprovode se studije brzine adsorpcije. Primenjena su tri kinetička modela za interpretaciju rezultata brzine procesa adsorpcije, pseudo-prvog reda, pseudo-drugog reda i model intračestične difuzije.

3. 9. 1. Kinetika adsorpcije na SCG

Fenomeni kinetike adsorpcije su neophodni za razumevanje mehanizama adsorpcione reakcije [66]. Grafik log (q_e-q_t) u funkciji vremena *t* opisuje model pseudo-prvog reda i t/q_t u funkciji t primenjuje se za model pseudo-drugog reda. Izračunate qe vrednosti, dobijene modelom pseudo-prvog reda, nisu imale smisla i bile su vrlo niske u poređenju s eksperimentalnim rezultatima. Utvrđeno je da model pseudo drugog reda ima jaku korelaciju r = 0,999 između t i t/qt za kinetiku adsorpcije odabranih pesticida na SCG. Teorijske vrednosti za adsorpcioni kapacitet dobijene modelom pseudo-drugog reda su bliske vrednostima eksperimentalnih rezultata. Ova zapažanja sugerišu da se adsorpcija karbendazima, linurona i izoproturona na SCG odvija u skladu sa mehanizmom reakcije drugog reda, da je proces vezivanja kinetički kontrolisan i da pripada procesima hemisorpcije. Iz rezultata se može zaključiti da se ponašanja adsorpcije karbendazima, linurona i izoproturona na SCG mogu bolje objasniti modelom pseudo-drugog reda, prema kome snažne hemijske sile na površini nastaju razmenom elektrona.

3. 9. 2. Kinetika adsorpcije na DSAC

Proverena je primenljivost tri kinetička modela za adsorpciju pesticida na DSAC. Rezultati sumiraju koeficijente korelacije r, izračunavaju se konstante brzina procesa pseudo-prvog i pseudo-drugog reda k_1 i k_2 dobijene iz nagiba odgovarajućih linearnih pravih sa grafika. Iz rezultata se uočava da se adsorpcija karbendazima, linurona i izoproturona ne može dobro opisati jednačinom pseudo-prvog reda. Koeficijenti korelacije su bili visoki za model pseudo-drugog reda što implicira da adsorpcioni proces pesticida najbolje može predstaviti modelom pseudo-drugog reda. Takođe, vrednosti za adsorpcione kapacitete, eksperimentalni i teorijski, $q_{e,exp}$ i $q_{e,}$ određene iz modela pseudo-drugog reda su bile bliske.

Ispitivanja pokazuju da se adsorpcija karbendazima, linurona i izoproturona na DSAC dešava kao reakcija drugog reda i da je postupak vezivanja pesticida u velikoj meri kinetički kontrolisan i to metodom hemisorpcije [67].

3. 10. Termodinamički pristup

Termodinamički parametri kao što su promena entalpije (ΔH°), promena Gibsove slobodne energije (ΔG°) i promena entropije (ΔS°) izračunati su sa Van't Hoffovih krivih koje predstavljaju funkciju ln K_L prema 1/T za karbendazim, linuron i izoproturon na SCG, DSAC, aktivnim ugljevima (NORIT SA2, NORIT HIDRODARCO C) i zeolitu, tipa: ZSM-5 na različitim temperaturama (298, 308 i 318 K).

Temperatura utiče na adsorpcioni mehanizam i difuziju molekula u porama adsorpcionih materijala [69]. Negativne vrednosti ΔH° ukazuju na egzotermnu prirodu adsorpcije, što objašnjava smanjenje efikasnosti adsorpcije pesticida kako temperatura raste. Vrednosti za ΔH° <20 kJ mol^{-1} potvrđuju da je fizisorpcija dominantan proces na površini adsorbensa. Fizičku adsorpciju obično karakterišu slabe Van der Valsove veze. Pozitivne vrednosti za ΔS°, ukazuju na povećanje neuređenosti na čvrsto/tečnoj površini tokom adsorpcije pesticida na adsorbense. Negativne vrednosti za ΔG° pokazuju spontanost adsorpcionog procesa koji je termodinamički povoljan.

3. 11. Ispitivanja procesa desorpcije i regeneracije

3. 11. 1. Ispitivanja desorpcije i regeneracije SCG

Izvedeni su eksperimenti desorpcije kako bi se istražile mogućnosti za ponovnu upotrebu i regeneraciju adsorbensa SCG. Rezultati pokazuju da je nakon tri ciklusa adsorpcije-desorpcije (C1, C2 i C3), efikasnost desorpcije 100 % za sve ispitivane uzorke. Piroliza na 500 °C je bila dovoljna za razgradnju karbendazima, linurona i izoproturona.

Adsorpcija karbendazima se promenila sa 96,00 % na 81,23 % tokom tri ciklusa. Za razliku od karbendazima, efikasnost adsorpcije za linuron na regenerisanom adsorbensu neznatno se izmenila između tri ciklusa. Ciklusi adsorpcije i desorpcije (C1, C2 i C3) pesticida izoproturona, doveli su do blagog pada efikasnosti procesa sa 93,70 % na 89,66 % u trećem ciklusu. Ukupno smanjenje efikasnosti adsorpcije karbendazima, linurona i izoproturona na SCG bilo je 14,77 %, 0,95 % i 4,04 % nakon tri ciklusa adsorpcije-desorpcije, respektivno. Tokom tri ciklusa procenat uklanjanja karbendazima i linurona u smeši smanjio se sa 96,1 % na 88,55 % i 94,65 % na 84,72 %, respektivno. Poređenjem sa rezultatima dobijenim pojedinačnom adsorpcijom pesticida, dobijeno je nešto bolje procentualno uklanjanje za linuron.

3. 11. 2. Studije desorpcije i regeneracije DSAC

Iz ekonomske perspektive, potencijal adsorbenta DSAC za regeneraciju je vrlo značajan. Studije desorpcije pomažu u odvajanju pesticida od zasićenog adsorbensa i njegovu ponovnu upotrebu. Opisani su rezultati ciklusa adsorpcije i desorpcije (C1, C2 i C3) karbendazima, linurona i izoproturona. Adsorpcija i desorpcija su bile 92,7 3% i 100 % za karbendazim, 95,70 % i 100 % za linuron i 87,85 % i 100 % za izoproturon, posle prvog ciklusa regeneracije. Nakon trećeg ciklusa regeneracije adsorpcija i desorpcija su smanjene na 66,39 % i 100 % za karbendazim, 79,42 % i 100 % za linuron i 69,59 % i 100 % za izoproturon. Takvi rezultati pokazali su obećavajući potencijal regeneracije DSAC koji bi se mogao uspešno koristiti tri puta nakon regeneracije za ekstrakciju i uklanjanje pesticida iz vode. Pesticidi se mogu efikasno ukloniti iz aktivnog uglja, kao što je DSAC, koristeći razblažene kiseline. Za razliku od jakih kiselina (HCl, H_2SO_4), H_3PO_4 ima blago negativan uticaj na adsorpcioni potencijal i strukturu regenerisanog DSAC, kao i veoma visok kapacitet desorbcije pesticida. Pesticidi koji se vežu za aktivna mesta adsorbensa, oslobađaju se na površini DSAC tokom procesa regeneracije. Na osnovu ovih karakteristika DSAC se može oceniti kao isplativ i ekološki prihvatljiv medijum za adsorpciju polutanata i uspešno se može koristiti za prečišćavanje vode.

3. 12. Mehanizam adsorpcije pesticida na SCG i DSAC

Mehanizam adsorpcije pesticida u tretmanu vode nije mogao da se opiše kao jedinstveni mehanizam zbog složenih interakcija između različitih polutanata. Izbor primarnog mehanizma zasnovan je na fizičko-hemijskim svojstvima adsorbensa (SCG i DSAC), kao hemijskim i strukturnim karakteristikama odabranih pesticida [327]. Prema rezultatima FTIR analize i utvrđenim funkcionalnim grupama na površini adsorbensa, predložen je adsorpcioni mehanizam izabranih pesticida na SCG i DSAC.

Površine SCG i DSAC pogodne su za specifične interakcije elektro-donor-akceptor (EDA), zasnovane na prenosu elektronskog naboja između molekulskih entiteta i udruživanju molekula, što dovodi do p - p interakcije između aromatičnih struktura adsorbensa i pesticida. Takođe, aromatična struktura odabranih pesticida učestvuje u n - p interakcijama usled vezanja -OH, -COOH ili polifosfatnih grupa adsorbensa. Aromatični prsten pesticida bio je akceptor elektrona, dok karbonilni kiseonik iz funkcionalnih grupa SCG i DSAC igra ulogu donora elektrona.

Specifične interakcije vodonik-donor-akceptor (HDA), poput interakcije dipola-dipola H-veze (između -OH grupe na površini adsorbensa i atoma azota iz pesticida) i Jošida veze (između -OH ili -COOH grupe adsorbensa i aromatičnog prstena pesticida) predloženo je na osnovu prisustva polarnih kiseonika i hidroksilnih grupa u odabranim pesticidima, ali i funkcionalnih grupa koje sadrže fosfor (pikovi detektirani na 3000-3500 cm^{-1}, 1160,78 cm^{-1} i 874,04 cm^{-1} za DSAC, i pikovi detektirani na 3433,06 cm^{-1} i 1046,60 cm^{-1} za SCG).

3. 13. Ekonomski benefit

Jedno od najvažnijih pitanja pri izboru odgovarajućeg adsorbensa je cena adsorbensa. Stoga je potrebno uzeti u obzir ekonomski benefit ispitanih adsorbenasa prilikom evaluacije njihove efikasnosti i moguće primene u komercijalne svrhe prečšćavanja voda. Adsorbensi SCG i DSAC, koji se hemijski aktiviraju fosfornom kiselinom i žarenjem, zahtevaju dodatne troškove obrade. Takođe, troškovi mlevenja koštica urmi moraju biti uključeni u ukupne troškove pripreme adsorbensa. Troškove prikupljanja i transporta adsorbensa nije moguće proceniti i izračunavaju se kao režijski troškovi, odnosno dodatih 10 % neto troškova [334]. Uzimajući u obzir troškove prikupljanja i transporta predloženih materijala (otpada od kafe i koštica urme), sredstava za aktiviranje (fosforna kiselina i destilovana voda) i električne energije za sušenje materijala, finansijski trošak SCG i DSAC bio bi oko 0,5 i 0,55 USD po kg, respektivno (Tabela 5.19). Troškovi komercijalnog aktivnog uglja variraju od 2,2 do 5 USD po kilogramu u zavisnosti od kvaliteta aktivnog uglja. Pripremljeni aktivni ugljevi iz otpada od kafe i koštica urme su isplativa alternativa postojećim komercijalnim aktivnim ugljevima, i mogu da se koriste kao ekološki kompatibilni adsorbensi. SCG i DSAC mogu se klasifikovati kao ekonomski i ekološki efikasni adsorbensi za prečišćavanje vode.

3. 14. SWOT analiza

Ispitivanje i upotreba jeftinih adsorbenasa dobijenih termohemijskom konverzijom lignoceluloznog otpada podrazumevaju bolje mogućnosti u upravljanju sistemima za prečišćavanje vode. Efikasnost, konkurencija, rizik i trenutni i budući potencijal procesa tretiranja zasnovan na adsorbentima proizvedenim od otpada kafe i koštica urme može se utvrditi SWOT analizom (snage, slabosti, mogućnosti i pretnje).

Slabost se zasniva na potrošnji fosforne kiseline za modifikaciju i regeneraciju adsorbensa. Procesi regeneracije odabranih adsorbensa su efikasni tri do pet puta, nakon čega se postiže zasićenost sorbentom i smanjuje efikasnost uklanjanja polutanata. Stoga, pretnja je stvaranje mulja koji može biti toksičan i zahteva pravilno upravljanje otpadom. Pored toga, nedostaje iskustva i znanja o ispitivanju materijala sa realnim uzorcima industrijskih otpadnih voda.

Tehnička primenljivost u stvarnim sistemima, jednostavnost rada i ekonomičnost, kao i zaštita životne sredine su ključni faktori koji određuju pogodan proces tretmana.

Na osnovu SWOT analize, moglo bi se zaključiti da adsorbensi sa niskim troškovima koji se baziraju na lignoceluloznom otpadu imaju obećavajuće mogućnosti u procesima tretmana vode. Adsorbensi sa niskim troškovima, kao što su SCG i DSAC, mogu zameniti sistem tretmana zasnovan na konvencionalnim metodama i komercijalnim adsorbensima kao što su aktivni ugljevi NORIT SA2 ili HIDRODARCO C.

Buduća analiza mora uzeti u obzir PEST (političku, ekonomsku, socijalnu, tehnološku) analizu zajedno sa SWOT analizom kako bi se dobile bolje informacije o mogućnostima primene predloženih materijala u procesu adsorpcije za uspešan i efikasan tretman u realnim industrijskim sistemima.

4. 0. Zaključak

U doktorskoj disertaciji ispitan je kapacitet aktivnih ugljeva proizvedenih od taloga kafe (SCG) i koštica urme (DSAC) kao otpadnih sirovina, po prvi put primenjenih za uklanjanje pesticida: karbendazima, linurona i izoproturona iz vode. Proizvedeni adsorbenti SCG i DSAC su upoređeni sa komercijalnim aktivnim ugljevima (NORIIT SA2, NORIT HIDRODARCO C) i zeolitom, tipa: ZSM-5. Iz rezultata se može zaključiti da su SCG i DSAC pokazali veoma dobre mogućnosti u uklanjanju odabranih pesticida iz vode. Takođe, komercijalni adsorbensi su bili veoma efikasni. Uticaj glavnih parametara kao što su vreme kontakta, početna koncentracija pesticida, doza adsorbensa, pH i temperatura na efikasnost procesa odvajanja su ispitivani u šaržnom sistemu. Urađene su adsorpcione izoterme, kinetička i termodinamička studija procesa koji mogu adekvatno opisati adsorpcioni proces. Na osnovu sveobuhvatnih eksperimenata i analize svih dobijenih rezultata može se zaključiti sledeće:

- Visoka površina aktivnog uglja može se pripremiti iz hemijske aktivacije otpada od kafe i koštica urme sa H_3PO_4 kao aktivirajućim agensom. Temperatura aktivacije i povećanje hemijske koncentracije (sa 30 % na 50 %) takođe su uticali na prinos ugljenika, zbog fosfatnih veza formiranih tokom procesa aktivacije. Uzorak impregniran sa 30 % -tnim rastvorom fosforne kiseline i odnosom fosforne kiseline i adsorbensa od 3: 1 pokazao je najbolje rezultate koji vode do većih adsorpcionih kapaciteta.
- SEM analiza SCG i DSAC pre i posle adsorpcije pesticida pokazuje izmenjenu morfologiju površine adsorbensa. SEM mikrografije jasno pokazuju razvijenu poroznu strukturu adsorbensa.
- FTIR analiza SCG i DSAC pokazala je prisustvo funkcionalnih grupa koje su tipične za aktivni ugalj i neophodne za adsorpciju analiziranih polutanata, kao što su pesticidi. Utvrđeno je da se pored kovalentnih veza, interakcija pesticida sa aktivnom površinom adsorbensa odvija i van der Valsovim vezama. Specifične interakcije elektro-donor-akceptor (EDA), vodonik-donor-akceptor (HDA), poput interakcije dipola-dipola H-veze (između -OH grupe na površini adsorbensa i atoma azota iz pesticida) i Jošida veze (između -OH ili -COOH grupe adsorbensa i aromatičnog prstena pesticida) karakteristični su mehanizmi vezivanja pesticida za površinu adsorbenasa SCG i DSAC.

- SCG i DSAC imaju visoko razvijenu BET površinu (803.422 i 307.450 m2 g^{-1}), respektivno.
- Kinetika adsorpcije najbolje se može objasniti teorijskim modelom pseudo-drugog reda, sugerišući da je hemijska adsorpcija ograničavajući faktor brzine.
- Adsorpcija karbendazima, linurona i izoproturona na aktivnom uglju NORIT SA2 pokazala je dobro slaganje sa Frojndlihovim modelom. Aktivni ugalj NORIT HIDRODARCO C ukazivao je na različita ponašanja za odabrane pesticide: adsorpcija karbendazima i izoproturona dobro su opisane Frojndlihovom izotermom, dok je adsorpcija linurona najbolje predstavljena Langmirovom jednačinom. Adsorpcija karbendazima na zeolitu, tipa: ZSM-5 je najbolje definisana Langmirovim zakonom, linuron je odgovarao Temkinovoj izotermi, a izoproturon je dobro opisan Frojndlihovim i Temkinovim modelima.
- Negativne vrednosti za $\Delta H°$ ukazuju na egzotermnu prirodu adsorpcije, što objašnjava smanjenje efikasnosti adsorpcije pesticida kako temperatura raste.
- Proračun ekonomskog benefita proizvedenih adsorbenasa je pokazao da je cena SCG i DSAC 0,5 i 0,55 USD po kg, respektivno što je 5 - 10 puta niža cena od cene komercijalnog aktivnog uglja za uklanjanje kontaminanata iz vode
- Uzimajući u obzir efikasnost i zadovoljene kriterijume u oblasti zelenih tehnologija, može se zaključiti da primenjeni adsorbensi, dobijeni termohemijskom konverzijom lignoceluloznog otpada, mogu uspešno zameniti komercijalni aktivni ugalj koji se koristi u adsorpciji polutanata, kao što su pesticidi iz deponijskih i industrijskih otpadnih voda u tercijarnom tretmanu.
- SCG i DSAC mogu se klasifikovati kao ekonomski i ekološki efikasni adsorbensi za prečišćavanje vode.
- Značajnost ovih alternativnih adsorbenasa je u činjenici da se proizvode od pristupačnih sirovina, tj. otpada i da imaju visoku efikasnost u uklanjanju ispitivanih polutanata. Svakodnevna konzumacija kafe i urme dovodi do stvaranja taloga od kafe i koštica urme kao otpada. Ako se tim vrstama otpada ne upravlja dobro, mogu prouzrokovati zagađenje životne sredine.
- Efikasnost procesa regeneracije ispitivanih adsorbenasa, uz visoku efikasnost ponovne primene u uklanjanju polutanata, podržava značajnost upotrebe jeftinih bioadorbenasa.

- Mogućnosti za upotrebu SCG i DSAC adsorbensa su ekonomičnost, shodno smanjenim troškovima tretmana i ekološki značaj, jer se otpadni materijali koriste kao adsorbensi.
- Modifikacija predloženih adsorbenasa rezultuje poboljšanjem njihovih fizičko-hemijskih svojstava za efikasno uklanjanje odabranih polutanata, kao i njihovom mogućnošću primene u tržišne proizvode.

Abstract

The PhD thesis deals with problems of preventing the generation of waste, by using the spent coffee grounds (SCG) and date stones (DSAC) for production of activated carbon adsorbent for water treatment. The substances for water removal were selected from those presenting potential risk to aquatic environment according to the NORMAN list of emerging substances and belong to the group of pesticides: carbendazim, linuron and isoproturon. The results from three analyses of commercial adsorbents (Activated carbon (NORIIT SA2), Activated carbon (NORIT HYDRODARCO C) and Zeolite, type: ZSM-5) and low-cost adsorbents made from SCG and DSAC were analysed and compared with competitive advantages.

SCG and DSAC have been used for the production of activated carbon (AC) by impregnation with phosphoric acid at 600 ˚C, X_P (H_3PO_4/coffee): 3:$1^{30\%}$, 4:$1^{30\%}$, 3:$1^{50\%}$, and 4:$1^{50\%}$ and X_P (H_3PO_4/ date stones): 3:$1^{30\%}$. The obtained AC was characterized by BET, FTIR, and SEM. BET surface area corresponds to 803.422 and 307.450 m^2 g^{-1} for SCG and DSAC, respectively. The influences of the main parameters such as contact time, the pesticides initial concentration, adsorbent dose, pH and temperature on the efficiency of separation process were investigated during the batch operational mode. Results were modelled by adsorption isotherms: Langmuir, Freundlich and Temkin isotherms, which gave satisfactory correlation coefficients. The maximum adsorption capacities on SCG calculated from the Langmuir isotherms were 11.990 mg g^{-1} for carbendazim, 5.834 mg g^{-1} for linuron and 4.154 mg g^{-1} for isoproturon at room temperature. On the other hand, the maximum adsorption capacities on DSAC were 10.780 mg g^{-1} for carbendazim, 29.585 mg g^{-1} for linuron and 25.906 mg g^{-1} for isoproturon which, calculated from the Langmuir isotherms. For SCG and DSAC the adsorption kinetics of carbendazim, linuron and isoproturon have been studied by the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion model. The results of adsorption kinetics have been fitted the best by pseudo-second-order model.

On the other hand, adsorption of carbendazim, linuron and isoproturon pesticides on Activated carbon NORIT SA2 fitted very well to the Freundlich model. Activated carbon NORIT HYDRODARCO C indicated different behavior for selected pesticides: carbendazim and isoproturon pesticides sorptions are well described by Freundlich isotherm, while linuron was fitted the best by the Langmuir equation. Adsorption of carbendazim on Zeolite, type: ZSM-5 was defined the best by the Langmuir law, linuron fitted the Temkin isotherm, and isoproturon was well described by the Freundlich and Temkin models. The experimental data were followed the best by the second-order kinetic model for all commercial adsorbents.

The resulted data from FTIR characterization pointed out the presence of many functional groups on the AC surface which prepared from spent coffee grounds and date stones. SCG and DSAC adsorbent, as an eco-friendly and low-cost material, showed high potential for the removal of selected emerging pesticides, carbendazim, linuron and isoproturon, with shorter contact time then adsorbents used in other studies, which is of great interest and importance in setting up real treatment systems.

Keywords: coffee grounds, date stones, activated carbon, adsorption, pesticide, kinetic models.

1. 0. Introduction

The production of agriculture depends extremely on the use of pesticides, as protection agents for plant diseases [1]. Pesticides have an essential role in the endeavor to increase and improve intensive agricultural activities and food production in today's world. The rising application of pesticides causes actual and hazard environmental problems connected with the distribution and concentration of these compounds in the environment, particularly of wells of drinking water quality [2,3]. According to Pimentel (1995) and Carriger *et al.* (2006), an insignificant portion of the used pesticide actually reaches its goals, while the rest is distributed in the environmental medium which can lead to its transportation to water ecosystems [2,4–6].

Carbendazim, or methyl-benzimidazole-2yl-carbamate, is a somewhat known member of benzimidazole fungicides and is frequently a degradation product of other fungicides like benomyl or thiophanatemethyl [7]. This broad-spectrum benzimidazole fungicide is extensively employed to manage fungal illness in vegetable and crops [8]. In Europe, carbendazime is used in quantities over 50 tons per annum [8]. Carbendazim causes hazards to human health and agro-ecosystem because of its stability and lipofilicity in the soil with a half-life of up to 1 year [9,10]. Carbendazim has poor water solubility (8 mg L^{-1}, 25°C) [11]. The use of carbendazim for plant protection products is approved in Europe until 2021 [12].

Linuron (3-(3, 4-dichlorophenyl)-1-methoxy-1-methylurea) is applied to regulate grass and weeds spreading to support the growth of economic crops. Linuron has a low toxicity level; its applications include the elimination of weeds bean, wheat, corn, sugarcane, potato and cotton. In the literature it is reported that linuron degrades fastly after entering the animal body and the ingestion of 125 mg kg^{-1} of linuron for two years does not produce detectable distortion, carcinogenic and/or mutagenic effects, although minor residues can be found in blood, fat, liver, kidney and spleen [13–15]. Linuron is considered as one of the important commercial ureas, which has great ability to kill emergent herbs [16].

The phenylurea herbicide isoproturon, 3-(4-isopropylphenyl)- 1,1-dimethylurea (IPU), has extensive uses in European countries as a herbicide in traditional agriculture [17]. It is applied against weeds associated with growing wheat and barley. Isoproturon is relatively resistant in the environment with 60% of the initially added amount in the soil three months after its implementation [18], IPU is usually detected in the surface and groundwater at concentrations over 0.1 µg L^{-1} (the European Union drinking water limit) [19]. Ecotoxicological data indicate that IPU and several of its major metabolites could cause cancer for animals and humans, damaging to water invertebrates, the algae in the fresh water and the microbial communities [20–24]. Therefore, there is significant attention in investigating the fate of IPU in the environment, especially in groundwater, as well as rivers, streams and lakes.

Pesticide leaching, from fields and forests, is one of the leading causes of pollution in water streams. Thus, the researchers have concentrated on developing efficient remediation treatments to remove pesticides from the water environment [25]. In recent years, many studies have been made for the development of commercial and inexpensive adsorbents for water treatment [26,27]. As the demand for the greener, ecological approaches increase, activated carbons (ACs) are more frequently used in industry for treatment, and recovery operations [28]. ACs, which are characterized by high specific surface area, are commonly utilized as adsorbents and catalysts for the elimination of pollutants in the treatment process or recovery of different materials [29]. The application of ACs in adsorption tasks mostly relay on the surface chemistry and pore structure of material used [30]. The chemical activation is often used to produce ACs and requires impregnation with chemicals such as H_3PO_4, KOH or NaOH [31]. AC is mainly manufactured from carbon-rich materials by either thermal or chemical activation. This process also enables the development of microporous and/or mesoporous carbon with a highly developed pore structure [32]. Even though, the AC is commonly used its utilization is sometimes limited due to the higher cost. For that economic reason, significant attention is paid to the characterization and understanding of the sorption properties of AC produced from low-cost alternative materials such as agricultural waste or industrial byproducts [33–35]. The preparation of low-cost adsorbents from different waste materials has economic and environmental advantages [27,31].

Coffee is produced and used in everyday life globally. During the year 2016/2017, according to the “International Coffee Organization,” the production of coffee reached to about 9 billion kg. Coffee is considered one of the most important agricultural commodities in the world. It is a widely popular drink brewed from the roasted bean [36]. Spent coffee grounds (SCG) present an essential waste product of the coffee industry. The combustion of 1,000 g of coffee grounds produces an estimated 538 g of carbon dioxide [37]. SCG is used as the material for soil remediation or as an adsorbent for odour.

Further, there were few of information and results in the literature about the production of AC from Dates seed (DSAC) [38]. Iraq is one of the largest countries as dates producer in the world, with more than 21 million date-palm trees and its annual production estimated to 566,828 tons. Studies indicate that the average mass of date stones is about 10–15 % of the date fruit [39,40]. Considering this, lignocellulosic-based agricultural waste is an excellent material to produce the activated carbon according to unique natural structure and low ash content [41,42] However, these types of recycled material have to be carbonized before further usage [37]. The study deals with problems of preventing the production of waste, by using the SCG and DSAC for production of AC adsorbents for water purification. The substances were selected from those presenting a potential risk to the aquatic environment according to the NORMAN list of emerging substances. The thermochemical activation of SCG and DSAC was performed at 600 ˚C with phosphoric acid. The influence of key parameters, such as pH, an initial concentration of selected pesticides, SCG and DSAC dosage, contact time and temperature were studied in batch experiments. The adsorption kinetics, equilibriums, thermodynamics and desorption of carbendazim, linuron and isoproturon were also studied. Eco-friendly and low-cost SCG and DSAC adsorbents showed efficient removal of selected pesticides carbendazim, linuron and isoproturon with shorter contact time than adsorbents used in other studies, which is of great interest in setting up real treatment systems.

Commercial Activated charcoal NORIIT SA2, Activated Carbon NORIT HYDRODARCO C and Zeolite, type: ZSM-5 were used without any modification, as reference materials for removal of selected pesticides, too.

1. 1. Research questions

Pesticides (the generic term for insecticides, herbicides and fungicides) control weeds, insect pests and fungal and other diseases. The benefit of pesticides lies in their ability to manage a pest (weed, insect or disease) problem that potentially could become out of control and could endanger human health, as well as pets and plants. For these reasons, it is very important to investigate possible entry sources, behaviour and spatial distribution of possible contaminants in water.

Production and usage of pesticides, in the last decades has increased dramatically and caused new potential risk to human health and the whole environment. Hence, there is a need to investigate the presence of carbendazim, linuron and isoproturon pesticides in water samples.

The dissertation hypothesis is based on the possibility of using synthesized adsorbents from waste materials (spent coffee grounds and date stones) in order to effectively remove the mixture of pesticides (carbendazim, linuron and isoproturon) from water.

In order to prove the hypothesis, the planned research program is structured from the following research stages:

- Synthesis of new materials based on spent coffee grounds and date stones and their characterization (SEM, BET, FTIR).
- Development of analytical methods to identify selected pesticide compounds (HPLC-DAD).
- Setting up an experimental procedure for pesticide degradation under laboratory conditions.
- Optimization of basic parameters of the pesticide removal process - pH, temperature, sorbent mass, initial pesticide concentration, contact time.
- Investigation of the interaction of pesticides in the process of removal from water.
- Examining the possibilities for the regeneration and reuse of synthesized materials.
- Evaluation of newly synthesized materials in terms of the economic benefits of materials to remove selected pesticides.

- Analysis of the obtained results.
- Data modeling by adsorption isotherms and kinetic models.
- Defining conclusions about the possibility of using new materials and comparing them with commercial materials such as activated carbon, NORIT SA2, NORIT HYDRODARCO C and zeolite ZSM-5.

2. 0. Target compounds – pesticides

Pesticides are considered as significant in the attempt to grow food production in today's agriculture. Moreover protecting the growing crop, pesticides are used to conserve harvested food and to control illnesses. The application of pesticides ensures productivity, high quality and conservation of crops. At the same time, it has environmental damage to human and feed chain [43]. There are predicting problems in the toxicity of pesticides due to the lack of explanation of the action mechanism for pesticides. Although pesticides are allowed, they are mostly low to slightly recalcitrant to degradation by microorganisms and could be transported from the agrosystems to various environments such as (air, soil and water) as pollutants. Exposure to pesticides generally causes adverse effects on humans and animals [44,45] and participate in degrading the quality of the environment and reducing the biodiversity [46,47].

2. 1. Classification of pesticides

FAO, (2005) defined a pesticide as "any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies". On the other side, the pesticides utilised for the protection of products are also described as phytosanitary products or phytopharmaceuticals (directive 91/414/EEC).

There are more than 500 pesticides that can be used to eradicate agricultural pests worldwide. The term pesticide is classified in various groups as insecticides, fungicides, herbicides, acaricides, rodenticides, avicides, algicides mollusicides and nematacides etc. There are several classifications of pesticides depends on different parameters such as the target group of pests, mode of action, time of the action or chemical nature [6]. Table 2.1 showed the classification of different pesticides.

Table 2. 1. Classification of the pesticides based on their targets, mode of action and chemical structure

By target		By mode or time of action		By chemical structure
Type	Target	Type	Action	
Bactericide (sanitizers or disinfectants)	Bacteria	Contact	Kills by contact with pest	Pesticides can be either organic or inorganic chemicals. Most of today‘s pesticides are organic.
Defoliant	Crop foliage	Eradicant	Effective after infection by pathogen	
Desiccant	Crop foliage	Fumigants	Enters pest as a gas	
Fungicide	Fungi	Nonselective	Toxic to both crop and weed	
Herbicide	Weeds	Post-emergence	Effective when applied after crop or weed emergence	Commonly used inorganic pesticides include copper-based fungicides,
Insecticide	Insects	Pre-emergence	Effective when applied after planting and before crop or weed emergence	Lime-sulfur used to control fungi and mites, boric acid used for cockroach control, and ammonium sulfamate herbicides
Miticide (acaricide)	Mites and ticks	Preplan	Effective when applied prior or planting	
Molluscicide	Slugs and snails	Protectants	Effective when applied before pathogen infects plant	
Nematicide	Nematodes	Selective	Toxic only to weed	Organic insecticides can either be natural (usually extracted from plants or bacteria) or synthetic.
Plant growth regulator	Crop growth processes	Soil sterilant	Toxic to all vegetation	
Rodenticide	Rodents	Stomach poison	Kills animal pests after ingestion	
Wood preservative	Wood-destroying organisms	Systemic	Transported through crop or pest following absorption	Most pesticides used today are synthetic organic chemicals. They can be grouped into chemical families based on their structure

Source: *Arias-Estevez et al. (2008) [6]*.

Pesticides can be classified into nine major groups, based on their chemical structures (Ministry of Environment, Ontario, Canada, 2010) [48].

1. Triazine (N-Containing pesticides): contain three nitrogen atoms and an unsaturated ring of three carbon.
2. Carbamates (Cbs): a salt or ester containing the anion NH_2COO^-, derived from compound carbamic acid**.**
3. Organochloride (OCs): pesticides containing chloride.
4. Organophosphorous (OPs): pesticides containing phosphorus.
5. Chlorophenols (CPs): 2-chlorophenol, pentachlorophenol, dichlorophenol, trichlorophenol.
6. Phenoxy acids (PAs): a family of chemicals related to the growth hormone indoleacetic acid (IAA).
7. Quaternary ammonium compounds (Q) are positively charged polyatomic ions of the structure NR^{4+} with R being alkyl or aryl groups. Examples of the pesticides in this group are Diquat and Paraquat.
8. Phenylurea (PhUrs): a chemical compound on which relatively nontoxic herbicides are based.
9. Thiocarbamate (ThCbs): a family of organosulfur compounds.

The World Health Organization (WHO, 2005) suggested classifying of the pesticides based on the toxicity and technical compounds and formulations as a response to social pressure highlighting the risk of pesticides for the environment [49]. Table 2. 2 shows the classification of pesticides. This classification was based only on the measurement of oral and dermal toxicity of the pesticides in liquid and solid phases on rats which acknowledged as standard methods in toxicology. LD_{50} is "Deadly Dose, 50%" or median deadly dose which gives the amount required to kill 50% of the test population. In most of the cases, the classification is performed on the oral LD_{50} value; however, dermal LD_{50} value is also of prime interest since exposure to pesticides occurs essentially through dermal contact.

Table 2. 2. Classification of pesticides based on their toxicity

Class		**LD50 Rat (mg kg^{-1} b.w.)**			
		Oral		**Dermal**	
		Solids	Liquids	Solids	Liquids
Ia	Extremely hazardous	5 or less	20 or less	10 or less	40 or less
Ib	Highly hazardous	5 - 50	20 - 200	10 - 100	40 - 400
II	Moderately hazardous	50 - 500	200 - 2000	100 - 1000	400 - 4000
III	Slightly hazardous	Over 500	Over 2000	Over 1000	Over 4000

Source: WHO (2005)[49].

2. 2. Production and usage of pesticides

Most of the pesticides are consumed to improve fruit production and vegetable crops in the whole world. For the countries of the developed world, the focus is on the use of herbicides to increase maize production [50]. Pesticide production is estimated at more than $ 35 billion per year. About 500 pesticides have comprehensive applications. Some of them are very toxic [50]. About 4.6 million tons of chemical pesticides are sprayed into the environment. In general, pesticide consumption has changed significantly since the 1960s. In addition, pesticide consumption resulted in a reduction of insecticides, fungicides and germs. In contrast, herbicides consumption have increased [50]. At present, global consumption accounts for 47.5% of herbicides, 29.5 % are insecticides, and 17.5% are fungicides, with all others accounting for 5.5% [51]. The consumption of pesticides decreased to 50% in Europe compared to 1980s [50]. In the United States and many other countries DDT and chlorine organic pesticides have been banned since the 1972s. Then, the use of pesticides has dropped to 35% in the United States without affecting agricultural crops [50]. However, in the United States, the world's second-largest pesticide consumer, consumption is around 410 000 tones. The other large consumers of pesticides are Brazil, Argentina and Mexico, which consume 396 000, 208 000 and 99 000 tones, respectively, followed by Ukraine with 78 000 tones, Canada with 73 000 tones and France, Italy, Spain and India with around 60 000 tones each [52]. (Figure 2. 1) displays the average pesticide application per unit of cropland. Generally, the consumption of each pesticide category depending on the country, some factors control the quantities of consumption as pedoclimatic conditions and agricultural practices which profoundly influence the crops being planted and the kind of pests to treat.

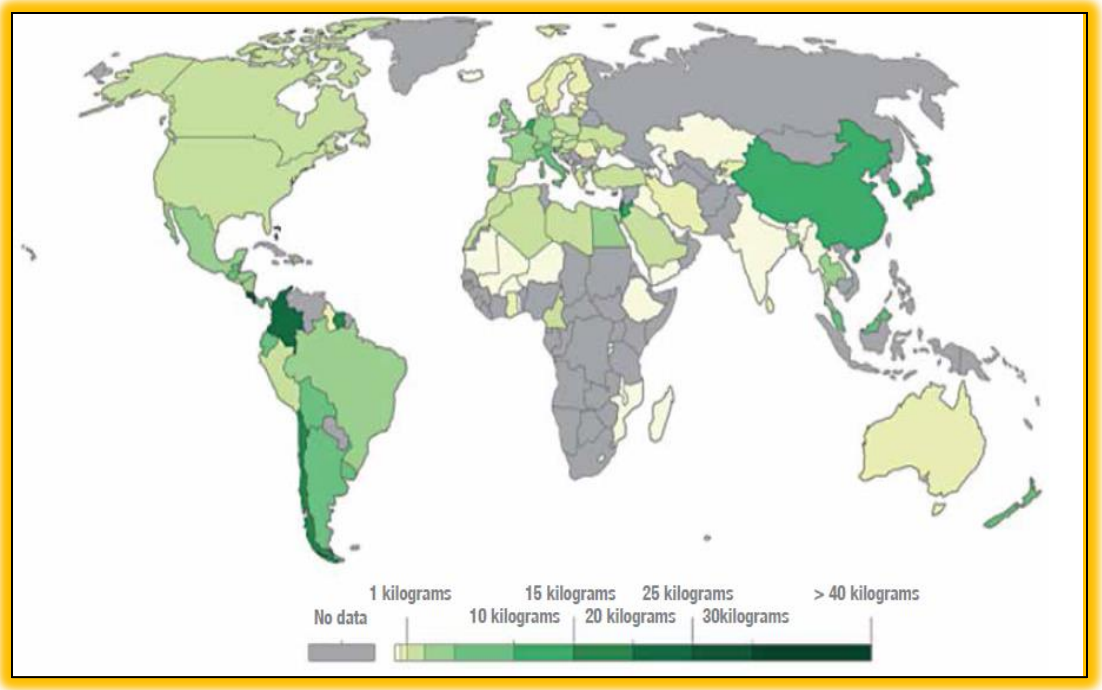


Figure 2. 1. The world pesticide use per hectare of cropland

Source: Javier *et al.*, (2018) [52]

Aspelin & Lyle (1997) [53]reported that around 85 % of the pesticides are applied in agriculture, it had noted that companies and consumers rely entirely on the use of pesticides to control pests and increase production and maintenance . Knutson *et al. (1990)* [54] published the reduction of using pesticide in agriculture will lead to an impact overall economy and consumers. Nevertheless, in spite of this economic challenge, pesticides should be used with care to ensure environmental protection, consumer and enhance production.

There are many factors which impact on the efficacy of the pesticides to eliminate pests such as physico-chemical properties of the pesticides and the soil, characteristics of the crops, environmental conditions and behavior of the target organisms. The method of work of pesticide is the essential mechanism by which the pesticide kills or interacts with the pest organisms. The mechanisms depend on the target pest organisms and select pesticides.

2. 3. Physico-chemical properties of pesticides

The most critical factors determining the fate of pesticides in the environment, as well as their toxicity and their decomposition, are the physico-chemical properties. There is a relationship between degradation and molecular structure. The chemical structure of a molecule changing will affect the degradability potential [55,56]. For example, adding a third atom of chlorine to a molecule of 2,4-D would reduce biodegradability.

Persistence is a significant indicator of predicting the fate of pesticides in the environment, especially in the surface and groundwater which can be contaminated by pesticides several years after their application.The persistence of pesticides leads to their transfer and distribution over a long time. Pesticides can be classified as non-persistent, moderate persistent (a few days to 12 weeks), persistent (1 to 18 months) and permanent (months to many decades).

Solubility is one of the physico-chemical properties that affect the pesticides in the soil solution. The positive relationship was noticed between the increase of pesticide solubility and the availability of pesticide to microbial communities in the soil, thus increasing the rate of degradation [56,57] The application of surfactants which raises the solubility of pesticides was suggested to extend the accessibility and biodegradability of the pollutants including pesticides in some polluted soils [58–60] The fate of pesticides in the soil is influenced by two interactive and parallel processes: adsorption and biodegradation. Adsorption of pesticides in the soil reduces their availability and thus decreases their biodegradation [61]. Sorption of the pesticides in soils is estimated by K_{oc} which is the partition coefficient of the contaminant in the organic fraction of the soil. The K_{oc} is related to the physicochemical characteristics of the contaminant.

The behavior of pesticide degradation in the soil is related to the concentration of the applied pesticides. The same pesticide can degrade during the metabolic or co-metabolic process, depending on its concentration in the soil solution [62].

Biodegradation of pesticides is influenced by the physico-chemical properties of pesticide and soil as well as climatic conditions. Biodegradation is influenced by some of the factors available in soil such as oxygen availability and pH, and biotic factors such as rhizosphere. These conditions, in general, do not the only effect on the biodegradability of the pesticides, but have an impact on the division, diversity, size and activity of microbial groups.

2. 4. Fate of pesticides in the environment

The dispersion and distribution of pesticides in the environment is an important process which specifies the fate of pesticides. In some cases, the movement of pesticides is essential to attack the controlling pests of crops. However, the movement of pesticides may cause them to depart from their targets and thus create other undesirable environmental damage. There are different ways of moving and transport pesticides in the environment such as surface runoff, sorption, leaching [63].

When pesticides are used in soil, part of it becomes a volatile part of the atmosphere [64]. Sometimes the loss of volatile pesticides is more than degraded pesticides, runoff or leaching. The rate of volatilization of these pesticides is estimated at 90% [65]. Volatility is a major cause of air pollution, rain and fog water as well as other lands where pesticides have not been used [66]. The quantities of pesticide volatilization in the air do not depend on soil type and climatic conditions such as soil texture, temperature and air velocity containing moisture in the soil [67–69] but other factors such as the physiochemical properties of the pesticide (vapor pressure) and the method of pesticide use. To determine the extent of pesticide volatilization, a vapor pressure factor must be determined. When vapor pressure increases for the pesticide, the volatilization rate will increase. One of the disadvantages of volatile pesticides is their lack of impact due to reduced contact with pests. To prevent pesticides volatilization, pesticides can be incorporated into the soil or not used in adverse environmental conditions such as high temperatures and high moisture content. Few studies have suggested that volatilization can occur through plants, where the plants absorb the pesticide, and from there it releases into the air [70,71].

As is known, a large part of pesticides dissolved remain in the soil and this amount represents the mobile part. Pesticides are transmitted either by surface runoff during rainfall or by vertical movement by leaching. The choice of pesticide transfer depends on the type of techniques used such as ploughing [72], irrigation technique [73] and the properties of the soils like porosity, compaction, texture and structure etc [74] and the amount of rainfall. The delay in groundwater contamination is due to the slow leaching of pesticides during the soil as the leaching process takes a long time [75]. This phenomenon has posed several problems in the European Union and some other countries [76].

2. 4. 1. The behavior of pesticides in the soil

When pesticides are used for agricultural purposes in the soil, many interactive processes occur, including evaporation, runoff, volatilization, absorption etc. Soil not only acts as a filtering agent for pollutants such as pesticides, but is an indispensable source of pollution of water, air, animals and crops through several factors such as flow, runoff, drainage and [77,78] In accordance with, after their utilization, the pesticides are moving in the solid, liquid and gaseous phases in the vadose zone [43,79] depending on the constants of adsorption, desorption and volatilization. All these processes are highly influenced by the environmental factors and the physicochemical properties of the pesticides and soils.

Sorption of the pesticide in the soil environment can occur in soil components such as clay particles and organic matter. It is recognized that the use of pesticides will be sorbed into the soil and kept in the solid phase of the soil. This will affect other processes such as leaching, volatilization and uptake etc. The physiochemical properties of pesticides and soil can cause a difference in the sorbed portion in varying percentages There are several complex reactions to sorb the pesticides in the soil such as hydrogen bonding, Van Der Waals forces, ion exchange or hydrophilic interactions [80,81]. The adsorption characteristics of the pesticides are reflected by the division or diffusion coefficient (K_d) determining the partitioning equilibrium of the pesticide among the solid phase (adsorbed) and the liquid phase (available) [64]. Pesticide sorption is usually high in the presence of organic content [82–87] The rapidity, intensity and the reversibility of pesticides adsorption on soil depend not only upon the physicochemical properties of the soil and pesticides, but also the environment [88,89]. Hydrophilic and hydrophobic properties, positions of the exchanges, solubility and charges on the pesticides also influence on the adsorption of the pesticides in the soil. Several soil factors such as nature and amount of organic matter effects on sorption of the pesticides [90,91] clay content [92], nature of the clay [93,94] existence of oxides hydroxide [82], organo-mineral associations [95], soil pH [96,97] and the existence of dominant cations in the soil solution [93,94]. The most important of these factors is organic and clay content. Most of the previous studies have shown there are positively correlated with organic matter content. Aromatics are also a key element in determining the sorption of some non-ionic pesticides [91,98] The sorption of the pesticides is mainly linked to the reactive component of the soil, i.e. clay if the soils having low organic matter [99].

The temperature and moisture content are environmental factors effect on adsorption of pesticides. Nevertheless, these effects are variable. For example, the effect of increasing the temperature on the adsorption of the *s*-triazines pesticide is contradictory either by increasing or decreasing depending on the chemical or physical bonds [89,100]. Low moisture content plays a crucial role in the adsorption of pesticides to dissolved organic carbon, for example [101].

The solid phase of the soil retains a small fraction of the pesticides due to the irreversible phenomenon of these pesticides from the soil and cannot be extracted or absorbed immediately [102]. These remaining parts of the pesticides accumulate over time and persist in the soil for several years. The quantity of constrained residues in soil ranges from a few per cent to up 80 % of the adsorbed fraction [85] on the physicochemical characteristics of the pesticides as well the soil components and the ageing of the pesticides in the soil [85,102]. Different hypotheses explain the type of physico-chemical bonds including:

- The covalent bonds between the soil constituents and pesticides,
- The preventing the pesticides in the micro-pores of the soil etc. [81,103].

Nevertheless, the mechanisms responsible for delayed release of pesticides are still poorly understood although it has been suggested that residues might be leached following profound physicochemical changes of the soil or through the degradation of the soil organic matter [103]. Some studies indicate that pesticides remain in the soil for hundreds of years because their degradation is very low in the soil [104].

2. 4. 2. Soil pollution by pesticides

Agricultural crop pests are usually treated with pesticides to eliminate pests such as fungal worms, insects, fungi and weeds etc. The percentage of pesticides that exceed their target and reach the soil surface is estimated at 50%. Some of these pesticides settle in soil components such as clay and organic matter and are bonded together, and keep in the soil for several years. As a result of the use of pesticides in agricultural land as well as the characteristics of these pesticides will cause significant contamination of the soil. For example, despite the ban on the use of DDT in some countries such as Turkey, China, Europe and America have been twenty years but were reported the existence of these compounds.

2. 4. 3. Surface and groundwater pollution by pesticides

Pesticides are mainly used on agricultural soil. At the same time, these pesticides can be exported to groundwater sources, for example through leakage, filtration or runoff. Direct contamination of drinking water sources is a source of concern as it threatens the quality of water, which is the primary source of human beings. There are other sources of pollution, which are the largest source of contamination of surface and groundwater when compared to sources of direct pollution such as leaching and from these sources: seepage of sprinkle equipment, spray leftovers, spills of rinsing water from cleaning of spray equipment and spills through the filling processes etc. Some examples illustrate the presence of pesticides in water after twenty years of banned use such as organochlorine insecticides [105]. This type of pesticides is classified as a persistent organic pollutant (POP) according to the Stockholm Convention, and this type is considered the most dangerous and more toxic to water sources [106,107]

2. 4. 4. Atmospheric pollution by pesticides

It is possible and easy to contaminate the air when spraying pesticides. Small particles are formed after evaporation and are transported to long distances by the air current, causing air pollution with pesticides. The transfer of pesticides through the air has caused problems for spray workers and farmers as well as animals that reach pollution by air. The result was a lack of efficiency of these pesticides on agricultural pests because of their transfer from the place to be treated elsewhere [108]. As a result, many studies have explored the occurrence of such a phenomenon in the air ; some studies have shown concentrations of pesticides in rain and fog water [109,110].

2. 5. Selected pesticides

2. 5. 1. Carbendazim

Carbendazim has been frequently detected in surface waters[111]. This substance is classified by the World Health Organization (WHO) as "unlikely to present a hazard in normal use" [112]. This chemical is toxic for humans, animals and plants [113]. Due to the slow rate of degradation and low solubility in water, carbendazim interacts with soil colloids and may stay for a long time in an immobilized status in the soil [114]. The exposure to carbendazim is considered to be within acceptable levels [115].

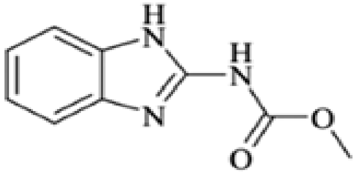
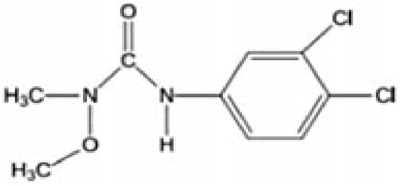
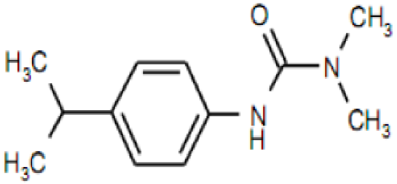
2. 5. 2. Linuron

Linuron is a systemic herbicide used in the pre- and post-emergence control of annual grass and weeds, such as cotton, corn, potato, bean, winter wheat, carrot and fruit crops. It is also used on crops stored in warehouses and storerooms [116]. Linuron has been classified as toxic to reproduction and carcinogenic, with the capability to induce malformations, infertility or cell tumours to target organs such as liver and red blood cells [117].

2. 5. 3. Isoproturon

Isoproturon (IPU, 3-(4-isopropylphenyl)-1,1-dimethylurea) is a worldwide used phenylurea herbicide for control of annual grass and broadleaved weeds in cereal crops [118]. The active substance is considerably discovered in surface- and groundwater overriding the threshold concentration of pesticides in drinking water ($0.1 \mu g\ L^{-1}$) in EU [119]. A new report from EFSA showed that IPU is also endocrine-disrupting, in addition to being potentially carcinogenic, which led to the ban of IPU in the EU since July 2016 [120]. Isoproturon is comparatively insurgent in the environment with 60% of the initially added amount residual in the soil 3 months after its application [18]. There is conclusive attention in research the fate of IPU in the soil environment which acts as a recharge zone for underlying groundwater aquifers as well as nearby rivers, streams and lakes. Carbendazim, linuron and isoproturon pesticides could cause environmental and health problems initiated by their physicochemical properties (Table 2. 3) toxicity and occasionally their high stability [114].

Table 2. 3. Physicochemical properties of selected pesticides

Pesticide	Structure	Molecular mass (g mol^{-1})	Log K_{ow}	Water solubility (mg L^{-1})	Henry'slaw constant (Pa m^3 mol^{-1})	Vapor pressure (Pa at 20 ˚C)
Carbendazim		191.21	1.5	29.0	3.6×10^{-3}	9×10^{-5}
Linuron		249.1	3.0	81.0	2.0×10^{-4}	5.1×10^{-3}
Isoproturon		206.289	2.87	65	1.46 X 10^{-05}	5.5×10^{-3}

Source: Berglöf *et al.* (2002) [114]

3. Water treatment processes for removal of pesticides

The elimination of pesticides from aqueous medium is one of the great environmental concerns today. In the past few years pesticide remains in the groundwater resources has grown considerably and has become an important question and discussion of debate. Different techniques are available for pesticide elimination: photocatalytic degradation [121,122], combined biological oxidation and photo- Fenton [123], advanced oxidation processes [124], aerobic degradation [125], nanofiltration membranes [126], ozonation [127], coagulation [128], fluid extraction [129], solid phase extraction [130], and adsorption [131,132]. Adsorption of pesticides on activated carbon and polymeric materials from water medium has been published by Kyriakopoulos & Doulia (2006) [133]. Recently, many researchers are interested in the removal of pesticides by activated carbon. Adsorption is equilibrium separation process which presents efficient technique for water treatment. Adsorption has advantages by comparing to other treatment processes such as flexibility, and simplicity of design, initial cost, ease of operation, and insensitivity to toxic pollutants.

3. 1. Adsorption on activated carbon

Adsorption is the separation process based on collection of large number of chemical species at the surface of liquid or solid phase. Generally, carbonaceous substances present the main adsorbents, eligible of adsorbing different organic pollutants. Activated carbon is considered as efficient in removing different varieties of pesticides from water and wastewater, due to the high surface area and porosity. It is a multilateral material that can be applied in many technological processes.

Adsorption of molecules of chemicals and materials happens at the surface since it decreases the imponderables of attractive forces, and, thus, the surface free energy of the various systems. The forces included in the adsorption of either gas, liquids, or vapors may be non-specific (van der Waals) forces termed physical adsorption or stronger specific forces caused by the creation of chemical bonds, named chemisorptions.

The physical adsorption forces occur based on the electric charge density of Single atoms. The attracted Non-polar molecules to each other by weak induced dipole-dipole interactions, London forces (hydrophobic bonding). Usually, the hydrophobicity of organic pollutants measured by the logarithm of the octanol-water partition coefficient, K_{ow}•

The utilization of carbon extends so far back in time that its origin is impossible to know precisely. The first registered case dates back to 3750 BC, when both the Egyptians and Sumerians used wood char for the decrease of copper, zinc and tin ores in the production of bronze, and also as a smokeless fuel [134]. In 2650 BC, the Egyptians utilized bone char to wall paint Perneb's grave. The first proof of the medicinal use of carbon was found in Thebes (Greece), in a papyrus document from 1550 B.

Today, term activated carbon is used to define carbon-based materials that have developed high surface area, porous interior structure and wide spectrum of oxygenated functional groups. A wide variety of materials were selected as carbon precursors; since their physicochemical characteristics, besides the preparation method, are responsible for carbon adsorption properties, microstructure, textural features, and the possible applications.

AC is the common name for carbonaceous adsorbents, which are usually non-hazardous materials. AC has a large surface area ranging from 600 to 2000 $m^2 g^{-1}$, essentially after the activation operation and high porosity [135–137]. AC is usually considered to be one of the most popular and widely used adsorbents for the elimination of a broad variety of pollutants from water and wastewater [135,138]. AC before preparation contain a high percentage of organic (carbon) and a low percentage inorganic. In addition to that, the activation should be easy.AC is commercially ready in a formed (cylindrical pellets), powered (PAC) or granular (GAC) form. AC is produced from non-renewable charcoal, which increases the price as well as the environmental impact [139]. To lower remediation costs, efforts have been made to develop activated carbon from alternative raw materials that are abundant and cheap [135,138]. For example, charcoal and lignocellulosic materials are generally used as the precursors for AC. The literature in this area also includes reports of materials such as coffee residue being used as the precursor for activated carbon production.

The use of lignocellulosic resources has had an important impulse in last year's[140,141], as previously mentioned. Selection of the precursor for the development of low-cost activated carbons depends on various factors, such as availability and price of precursors, structural and textural characteristics, low amount of ash and high contents of fixed carbon [141] [135]. Producing activated carbon from lignocellulosic has several advantages: the precursors are various, abundant, and renewable and it contributes to reducing costs of waste disposal and the negative impact on the environment [142].

3. 2. Types of Carbon Materials

All the carbon materials composed of the carbon element has unique bonding with other components and with itself. Depending on the main allotropic forms of carbon, carbon materials are classified as diamond, graphite, graphene and fullerenes and type of hybridization of the carbon atoms [143]. For diamond, each carbon atom is bonded to four other carbon atoms with pure covalent bonding [144]. Diamond has the highest atomic density of any solid and is the hardest material with the highest thermal conductivity and melting point [145]. The structure of graphite consists of layers in hexagon shapes with some weak bonding between these layers [146]. The carbon atoms within a Fullerene molecule are sp^2 and sp^3 hybridized, of which the sp^2 carbons are responsible for the considerably angle strain presented within the molecule (Figure 3. 1) C_{60} and C_{70} exhibit the capacity to be reversibly reduced with up to six electrons [147].

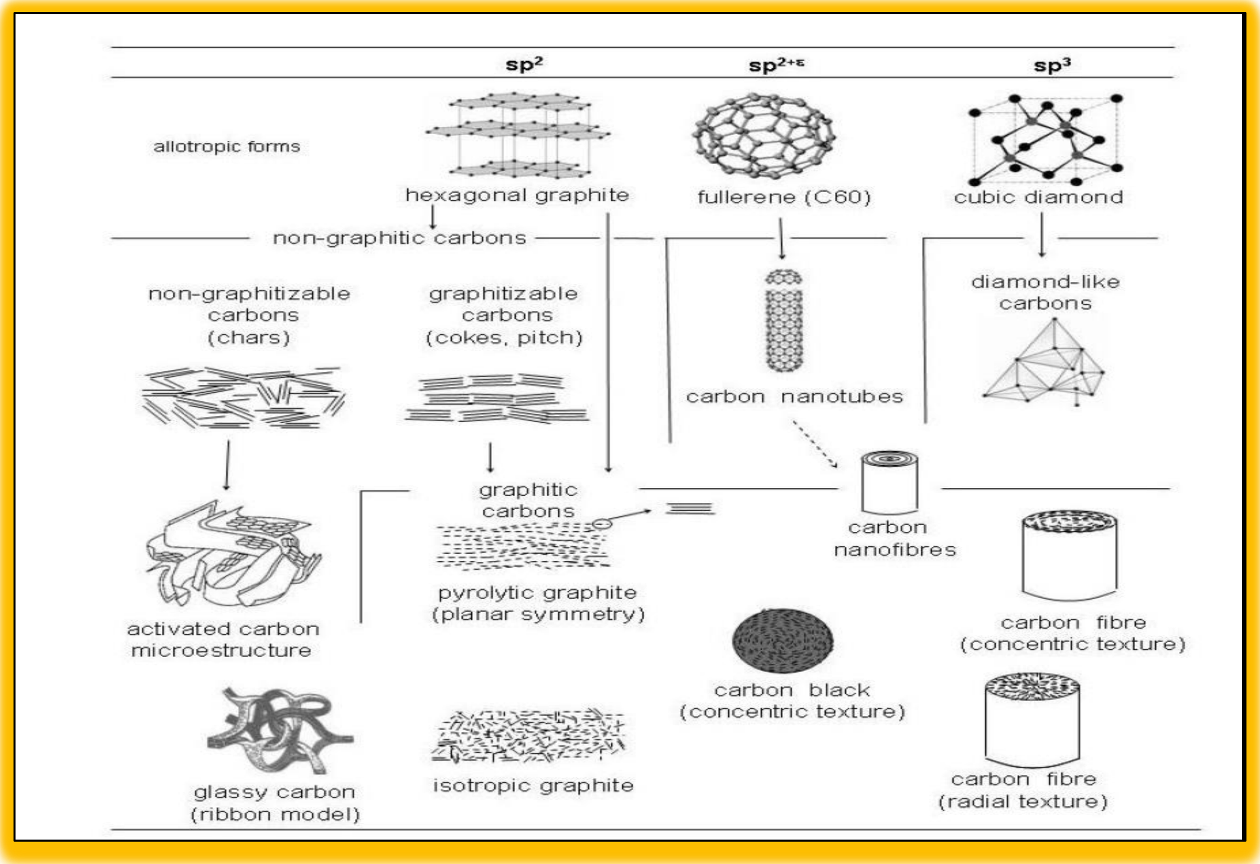


Figure 3. 1. *Major allotropic forms of carbon and some of carbon structures derived from these forms*

Source: Menendez *et al.* (2006) [134]

3. 3. Preparation of Activated Carbon

Any carbonaceous materials with a high concentration of carbon can be simply activated by chemical or gas activation methods into activated carbon. The common materials such as wood, charcoal, fruit pits, lignite, nut shells, and synthetic polymers are used for production of activated carbon. Production of AC was achieved typically through two routes, physical activation and chemical activation [148].

3. 3. 1. Physical activation

Physical activation is a two-step the process that starts with the carbonization of the materials followed by the activation of the resulting char in an inert (Ar or N_2) or oxidizing atmosphere (CO_2 or O_2) at the elevated temperature range of 600°C to 1000˚C [149]. Physical activation of various raw materials was shown in Table 3. 1.

Table 3. 1. Various physical activating agents and precursors used for AC production

Activating agent	Material
Steam	Rice husk, corn cob, olive residues, sunflower shells, pinecone, rapeseed, cotton residues, olive-waste cakes, coal, rubberwood sawdust, fly ash, coffee endocarp
CO_2	Oak, corn hulls, coconut shells, corn stover, rice straw, rice hulls, pecan shells, pistachio nutshells, coffee endocarp, sugarcane bagasse, corn cob, waste tyres, textile fibers, anthracite
Air	Peanut hulls, almond shells, olivetree wood, almond tree pruning, coal

Source: Gottipati (2012)[145]

3. 3. 2. Chemical Activation

Chemical activation occurs at a high temperature in the presence of agents such as KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $ZnCl_2$, and H_3PO_4, which are used to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. The remaining chemicals are removed from the carbon by acid or water wash. The physically activated carbon has a relatively lower specific surface area than the chemical activated carbon. Comparing both methods, chemical activation has advantages such as low energy and operating cost, higher carbon yields and larger surface areas, which can also generate a higher development of microporous structure [150]. The most commonly used chemical activating agents are H_3PO_4, $ZnCl_2$, and KOH. Table 3. 2 shows various chemical agents used for the activation of AC prepared from different raw materials.

Table 3. 2. Various chemical activating agents and precursors used for AC production

Activating agent	Material
$ZnCl_2$	Corn cob, coconut shells, macadamia nutshells, peanut hulls, almond shells, hazelnut shells, apricot stones, rice husk, tamarind wood, cattle-manure, pistachio-nut shells, bagasse, sunflower seed hulls.
KOH	Rice straw, corn cob, macadamia nutshells, peanut hulls, olive seed, rice straw, cassava peel, petroleum coke, coal, cotton stalk, pine apple peel.
H_3PO_4	Coffee, Hemp, Peanut hulls, almond shells, pecan shells, corn cob, bagasse, sunflower seed hulls, lignin, grain sorghum, rice straw, oak, birch, sewage sludge, chestnut wood, eucalyptus bark, rice hull, cotton stalk, jackfruit peel.
K_2CO_3	Pine apple peel, corn cob, cotton stalk, almond shell, coconut shell, oil palm shell, pistachio shell, walnut shell, bamboo.

Source: Gottipati (2012)[145]

3. 4. Structure of Activated Carbon

The adsorption capacity of AC highly depends on the structure of activated carbon.

3. 4. 1. Porous Structure

The adsorption capacities of activated carbons are strongly linked to porous characteristics such as surface area, pore volume, and pore size distribution. All activated carbons have a porous structure, containing up to 15% of the mineral matter in the form of ash content [151]. The porous structure of AC created during the carbonization process was developed further during activation, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The pore size distribution and structure of pores depends on the process of activation and the nature of the raw material. Disorganized carbon was removed by activation process which leads to the addition of the porous structure. Individual pores may vary greatly shape and size. Active carbons are linked with pores starting from less than a nanometer to several thousand nanometers. A conventional classification of pores according to their average width (w), published by *Dubinin et al. (1960)* [152] and officially adopted by the International Union of Pure and Applied Chemistry (IUPAC) is summarized in Table 3. 3.

Table 3.3. Classification of pores according to their width

Type of pores	**Width (w)**
Micropores	< 2 nm
Mesopores	2 – 50 nm
Macropores	> 50 nm

Source: Sing *et al.*1972 [153]

The adsorption of micropores with effective radii less than 2 nm, happens during volume filling and there is no capillary condensation. Generally, micropores have a pore volume of 0.15 to 0.70 $cm^3 g^{-1}$ and form about 95 % of the total surface area of the AC [145]. Dubinin, (1979) [154] moreover classified that the micropores can be parted into two overlapping microporous areas such as ultra-micropores (with effective pore radii less than 0.7 nm), and super-micropores (having radii of 0.7 to 2 nm). Generally, the microporous structure of an adsorbent is characterized by adsorption of gases and vapours and, to a small extent, by small-angle x-ray technique. Mesopores are also defined as transitional pores, with width from 2 to 50 nm. The surface area of mesopores does not constitute more than 5% of the total surface area and their volume varies between 0.1 and 0.2 $cm^3 g^{-1}$. Nevertheless, by using special methods, it is possible to improve mesopores attaining a volume of 0.2 to 0.65 $cm^3 g^{-1}$ and surface area of 200 $m^2 g^{-1}$. Capillary condensation and adsorption-desorption hysteresis are the characteristic features of mesopore. The typical pore size distribution of activated carbon can be observed in (Figure.3. 2).

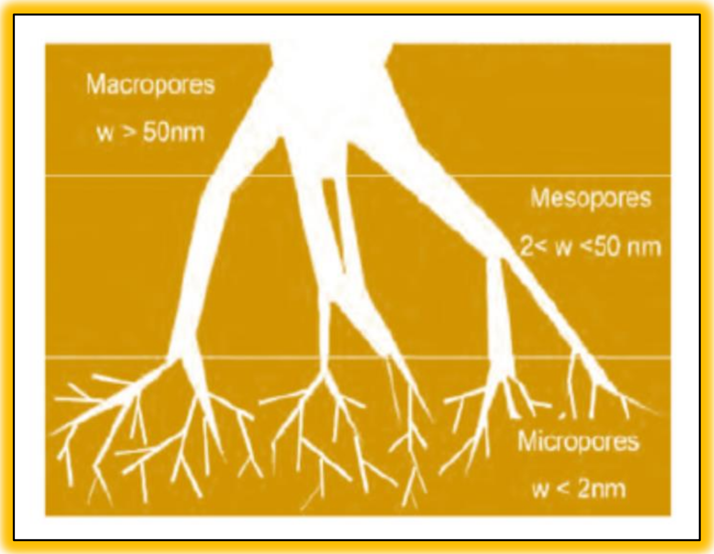


Figure 3. 2. Graphical representation of pore structure in activated carbon, Source: Gottipati (2012)[145]

3. 4. 2. Crystalline Structure

Microcrystalline structure of activated carbons begins to form through the carbonization process. The crystalline structure of activated carbons differed from the graphite concerning the interlayer spacing. The interlayer spacing classifies between 0.34 and 0.35 in active carbons, which is 0.335 in case of graphite. The basic structural unit of activated carbon is similarly approximated by the structure of graphite. The graphite crystal is composed of layers of fused hexagons held by weak van der Waals forces shown in (Figure 3. 3). During the carbonization process, free valences were produced due to the regular bonding disruption of micro-crystallites. Also, process conditions and presence of impurities influence the formation of vacancies (pores) in microcrystalline structure [155].

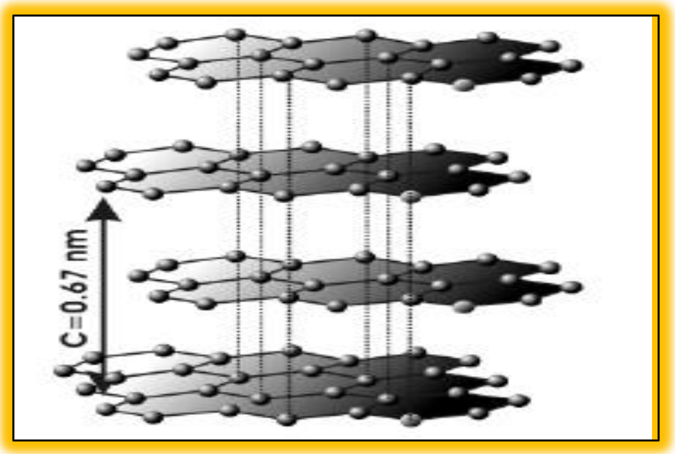


Figure 3. 3. Layered structure of graphite, Source: Gottipati (2012) [145]

3. 4. 3. Physical Structure of Activated Carbon

Franklin, (1951) [156] reported the structure on carbonized materials showed two distinct well-defined classes; non-graphitizing carbons and graphitizing carbon (Figure 3. 4). The graphitizing carbons are formed from substances containing more hydrogen. The non-graphitizing carbons are prepared from substances containing little hydrogen or more oxygen. Heating such substances, at low temperature develops a strong system of cross-linking of crystallites forming the porous mass. The crystallites remain relatively mobile during the early stages of carbonization and cross-linking is much weaker [145,157].

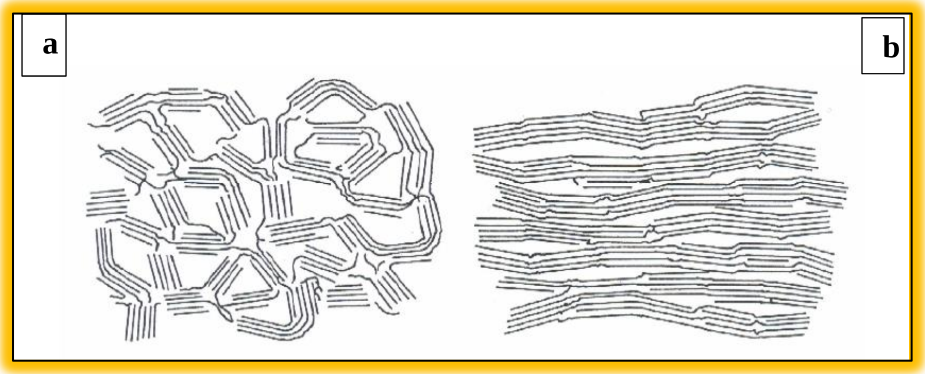


Figure 3. 4. Schematic Representation of (a) Non-graphitizing and (b) Graphitizing Structure of Activated Carbon

Source: Pradhan (2011) [158]

3. 5. Classification of Activated Carbon

Classification of AC is complex. The classification of AC depends on several factors such as surface characteristics, preparation methods and physical characteristics.

3. 5. 1. Powdered activated carbon (PAC)

Traditionally, AC is produced in particulate form as powders or fine granules less than 0.10 mm in size with an average diameter of 0.015-0.025 mm. Typical applications of PAC are industrial and municipal waste water treatments, sugar decolorization, in the pharmaceutical, and food industry, and for mercury and dioxin removal from a flue gas [158–161].

3. 5. 2. Granular activated carbon (GAC)

GAC has a comparatively larger particle size compared to PAC and consequently, presents a smaller external surface. GAC is specified by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapor phase applications. AWWA (1992) B604 uses the 50-mesh sieve (0.297 mm) as the minimum GAC size [158]. GAC has an advantage over PAC, which give a lower pressure drop along with the fact that it can be renewed. In addition to the proper micropore size distribution, its high hardness, high virtual density and a low abrasion index made GAC more suitable than PAC for various applications [162–165].

3. 5. 3. Activated carbon fibers

Activated carbon fibers (ACF) are porous carbons with aspect ratio higher than 10 and contain a well-defined porous structure in fiber shape with high adsorption capacity [166]. ACF are usually prepared from general-purpose carbon fibers by a heat treatment to fulfill requirement of specific applications and achieve high porosity. ACF is characterized by its extremely high surface area around 2000 $m^2\ g^{-1}$. It is thought that ACF could be one of the best absorbents in adsorption applications because of its considerable advantages over other commercial storage materials [167].

3. 6. Adsorption of pesticides on different sorbents

A diversity of activated carbon materials have been used, such as granular activated carbon (GAC) [168,169], powdered activated carbon (PAC) [170,171], carbon cloth [172,173], carbon fibers [26], black carbon [174], activated carbon composites[175], and commercial Activated carbon (CAC) [176]. GAC and PAC are the most used adsorbents since they are considered as very capable and effective materials for the adsorption of a variety of pesticides [133].

Salman & Hameed (2010) [177] used commercial granular activated carbon, Filtersorb 300 (GAC F300) for removal of carbofuran pesticide. The adsorption capacity of GAC F300 was 96.15 mg g^{-1}. Equilibrium data was fitted to Langmuir and Freundlich isotherms. The adsorption kinetics was found to follow closely the pseudo-second-order kinetic model for carbofuran pesticide.

Spaltro *et al.*(2018) [178] explored the influence of two types of commercial activated carbons, hydrogen Sulfide CAT-Ox 4 mm pellet Activated Carbon (UMI2000) and CARBOPALMB 4S (Donau) for efficient removal of bentazon pesticide. With the increase of temperature and pH, the adsorption capacity decreases. The kinetics indicated that pesticide followed pseudo-second-order model on both adsorbents. The adsorption capacities of bentazon pesticide were 391.65 mg g^{-1} and 185.07 mg g^{-1} on CAT and CARBOPAL, respectively.

Activated carbon is common selection as an adsorbent for the elimination of pesticides from water medium, but it is a cost-effective economic problem. Therefore, researchers have turned to search for the best, cheapest and available materials, which can be used more widely and more economically. This opened the doors for researchers to develop alternative adsorbents to replace the highly cost-effective activated carbon recently. The waste materials and byproducts from the agriculture and other industries are the sources of low-cost adsorbents due to their abundance in nature and because they have processing requirements.

Recently, the researchers have focused on preparation of activated carbons for elimination of assorted pollutants using renewable and cheaper precursors, which were fundamentally manufacturing and agricultural by-products. Various types of carbons have been obtained from biomass and other wastes, such as date stone [179,180], wood [181], biochar [182], coconut shell [183,184], coconut fibers [183], bagasse [183], sal wood [183,185], green waste [186], peat moss [187], horseshoe sea crab shell [188], corn stillage [189], and oil palm fronds [190]. These adsorbents were products or residues of agricultural wastes and are used as precursors for the production of inexpensive and efficient activated carbon adsorbents. The adsorption capacities of carbonaceous materials depend on the raw materials selected, preparation and treatment conditions such as pyrolysis temperature and activation time. Other factors such as surface chemistry (heteroatom content), surface charge, and pore structure can effect on adsorption capacity. A proper carbon should possess not only a porous structure, but also high surface area.

Ayranci & Hoda (2005)[191] found the value of adsorption capacity 421.58 mg g^{-1} of high-specific area activated carbon cloth.

Hameed *et al.* (2009) [192] studied the removal of 2, 4-D pesticide on the activated carbon prepared from date stones and reported maximum adsorption capacity of 238.10 mg g^{-1}. The results referred that date stone activated carbon is very effective for the adsorption of 2, 4-D from aqueous medium.

Ignatowicz, (2009) [184] published the removal of phenoxyacetic acid pesticides from aqueous solutions by adsorption on activated carbon prepared from coals and coconut shells. The results showed that coconut shell-based carbon is the most effective for the adsorption of phenoxyacetic acid from aqueous solutions.

3. 6. 1. Polymeric Adsorbents

Polymer resins were produced as an alternative to activated carbon due to high costs, especially when reused. Polymer resins are known to be used in water treatment [193]. Recently, hypercrosslinked polymeric adsorbents have been developed that possess common applicability because of their great surface area and special functional groups tagged to a matrix of polymeric bands. Hypercrosslinked resins are excessively used in industries as well as analytical scales [194]. Sundry detected that hypercrosslinked polymers have high potential for the adsorption of contaminates, storage of hydrogen, etc [195]. The use of polymeric adsorbents to eliminate organic compounds from water medium, to purify process streams, and to recover valuable compounds from aqueous solutions has been inspected [196]. Experiments on the removal of pesticides using polymeric resins are limited [197,198]. Chang *et al.*(2008) [199] studied the behavior of methomyl when use hypercrosslinked polymers Macronet MN-150 and MN-500 as adsorbent materials. The study presents that MN-150 has a good properties to be used as an adsorbent for elimination of methomyl from water. In contrast to this, the adsorption capacity of methomyl on MN-500 was low, possibly attributed to forces between sulphonic acid functional groups and lone-pair electrons of methomyl. Kyriakopoulos *et al.*(2005)[200] studied removal of herbicides, alachlor, amitrole, trifluralin, and prometryn on porous polymeric adsorbents. Two adsorbent resins were studied: XAD-4 and XAD-7. The XAD-4 resin was more efficient for hydrophobic herbicides (prometryn, alachlor, trifluralin), whilst XAD-7 resin was superior for more hydrophilic molecules (amitrole molecule). The lower pH values positive influenced on both types of resins in herbicides adsorption.

3. 6. 2. Industrial wastes adsorbents

Sludge, fly ash, and carbon slurry as industrial wastes are classified as low-cost, easy access locally and efficient in removing pesticides. The lignite coal-fired thermal power factories produce the fly ash; solid waste has been used as a low-cost adsorbent material and has shown significant adsorption capacity for organic pollutants [201]. Very limited studies on the adsorption of pesticides using fly ash were found [202,203]. Singh, (2009) [203] studied the adsorption of metribuzin, metolachlor, and atrazine on coal fly ash, and found significantly high retention capacity for these selected pesticides. The adsorption capacity of atrazine was the highest, followed by metolachlor and metribuzin. The removal efficiency of pesticide on fly ash depended on the initial concentration in the solution; it was observed that lower concentrations of pesticide gave the high removal.

3. 6. 3. Inorganic Adsorbents

Clay minerals are known to humans since ancient times. Clay minerals have advantages as high sorption properties, and potential for ion exchange, and thus could be strong adsorbents. Recently, the using clay minerals such as cloisite, clinoptilolite, eluthrilithe, kerolite, faujasite, montmorillonite, bentonite, and palygorskite as absorbent materials was frequent according to their capacity to adsorb not only inorganic ions but also organic molecules. Suciu & Capri (2009) [204] studied the effectiveness of various clays materials and modified clays to eliminate pesticide residues at levels of different concentrations for wastewater. Three pesticides were studied onto the two micelle-clay complexes and unmodified montmorillonite clay. The adsorption of selected pesticides was evaluated. The relationship between the maximum quantity of pesticides and the doses of adsorbents was determined for practical applications. Urena-Amate *et al.*(2008) [205] published the behavior of chloridazon adsorption on modified kerolite-rich materials. The best removal of the chloridazon pesticide from the aqueous solution was achieved at 600 °C in batch experiments. The column experiments also indicated that 600°C heat-treated kerolite is more suitable for removing chloridazon from water.

Crystal zeolites including faujasite are unparalleled adsorbent materials characterized by void volumes of 18 %–50 %. The surface area of faujasite was ranged between 903 to 1132 m^2/g. Natural zeolites has a strong relationship with water and have the ability of adsorbing or desorbing water molecules without mischievous the crystal structure of zeolites [206]. The polarity, shape and size of the diffusing molecules present one of the essential characteristics to choose the adsorption relative to the geometry of pores of the zeolites, the presence of exchangeable cations and impurities in the zeolite structure, and the chemical and physical treatments of zeolites. Tsai & Lai (2006) [207] studied the adsorption of paraquat onto clay mineral renewed from spent bleaching earth. The adsorption of paraquat by clay was rapid. The experiment showed the ion exchange process explained by competitive adsorption was dominant. Increase of the adsorption was observed with an increase in the temperature, which indicates that the adsorption process is endothermic.

3. 6. 4. Bioadsorbents

Biosorption is used as a reference of number of metabolism-independent processes (electrostatic interaction, physical and chemical adsorption, ion exchange, complexation, chelation, and microprecipitation) taking place basically, in the cell wall instead of oxidation during anaerobic or aerobic metabolism (biodegradation). The characteristics of biosorption are high selectivity and efficacy, cost effectiveness, and good removal performance. Sea weeds, fermentation wastes and activated sludge process wastes which are either abundant can be used as biosorbents, often comparable with ion exchange resins. For removal of pesticides living and dead (heat killed, dried, acid, and/or otherwise chemically treated) biomass could be used. Dead microbial cells as adsorbent are more advantageous for aqueous medium remediation, because dead organisms are not influenced by toxic wastes, stored or used for long time at room temperature without rot. The operations and regeneration are simple. Ghosh *et al.* (2009) [208] studied the adsorption of lindane on Rhizopus oryzae biomass. They found there is no relation between the adsorption process and pH of the solution or incubation temperature. Hydrophobic interaction is principally responsible for this adsorption process. Chatterjee *et al.*(2010) [209] studied the interaction behavior of malathion on Rhizopus oryzae biomass. They published that the amine groups of chitosan are responsible for chemical interaction between malathion and Rhizopus oryzae cell wall. Bell & Tsezos (1987) [210] studied the biosorption of pesticide pentachlorophenol (PCP) onto mixed culture of aerobic activated sludge and a pure culture of Rhizopus arrhizus. It was concluded that biosorption process includes uptake by both the cell walls and other cellular components of the microorganisms. Dead cells of Rhizopus arrhizus have more biosorption capacity for PCP compared to dead activated sludge.

3. 6. 5. Agricultural wastes adsorbents

Recently, a new group of adsorbents and specifically lignocellulosic materials has been investigated for the same purposes: their attraction resulting from their availability, low cost, and biodegradation. Some prior studies published their capability to quantitatively accumulate heavy metals and various organic compounds such as dyes and pesticides [179, 211, 212]. Accumulation of pesticides on agricultural adsorbents as special type of biosorbents is mostly achieved during interactions with the hydroxyl and carboxyl groups in polysaccharides and lignin, [213]. Moreover, the functionalization of this substance by the grafting of organic molecules bearing active groups was executed very successfully. Hybrid materials used as an adsorbent gave significant increases in adsorption capacity compared to raw materials [214, 215]. Recent publications presented the using of economical and locally available adsorbents, e.g., rice bran [216], tea leaves [217], wood sawdust [218], chestnut shells [219], peanut shells [220], watermelon peels [221], bamboo canes [220], oak sawdust [222], pine sawdust [222], straw [220, 223, 224], date stones [225], Ayous sawdust [226], rice husk

[214,216] mango kernel [227] and peach nut shells [227]. Bakouri *et al.* (2009) [228] studied the potential use of natural organic materials to remove pesticide in ground water samples. The higher removal was achieved with date and olives stones and, in minor measurement, Raphanus raphanistrum and Cistus ladaniferus. Results presented that the pH and temperature of pesticide solutions negatively affects the adsorption process.

Ioannidou *et al.* (2010) [229] studied the adsorption of an acaricide and Bromopropylatea pesticides from aqueous solution on activated carbon produced from agricultural remains (olive kernel, corn cobs, rapeseed stalks and soya stalks) and compared them with commercial activated carbons (F400 and Norit GL50). The results showed that corn cobs had a better adsorption capacity than the other biomass activated carbons. The activated carbon from biomass residues proved to have similar or even better Bromopropylate removal capacity than the commercial ones (F400 and NORIT GL50).

3. 7. Exhausted coffee waste as a biosorbent for pollutants removal

As explained in advance, processes of biosorption had become a cost-efficient technique for metal ions removal from water medium. Being a type of agriculture product, exhausted or residue coffee waste, the solid remains from soluble coffee, could be used for pesticides biosorption. Lamine *et al.*(2014) [36] reported that coffee residue, a low-cost agricultural by product, was tested as a precursor for the production of porous carbons in a chemical scheme using phosphoric acid. The adsorption equilibrium was reached after forty minutes. Xiaodong *et al.*(2013) [29] published how activated carbon prepared from spent coffee grounds by phosphoric acid activation had been employed as the adsorbent. It was confirmed that pore structure played an important role during the adsorption testes. Boudrahem *et al.* (2009) [230] reported the results of study suggesting that activated carbon produced from coffee residue is an effective adsorbent for the removal of lead from aqueous solutions. Kyung *et al.* (2016)[231] prepared granular and powder activated carbon (SCG-GAC) from spent coffee grounds for the elimination of acid orange 7 (AO7) and methylene blue (MB) from aqueous solution. The maximum adsorption capacities of SCG-GAC for AO7 (pH

3.0) and MB (pH 11.0) adsorption were found to be 665.9 and 986.8 mg $g^{-}1$ at 30 C, respectively.

3. 7. 1. Coffee and exhausted coffee waste

Coffee was first used by Arabs in Yemen for more than 800 years when they brought coffee from Ethiopia and based the first farm [232]. Kaffa area in Ethiopia is considered as the source of coffee production and seeds. Over the past 150 years, coffee has grown in various countries around the world [233]. Right now, coffee is the most popular drink in the world (over 400 billion cups yearly), and is the second largest trade commodity after petroleum [234]. According to the International Coffee Organization (ICO), production of coffee in 2012-2013 seasons is estimated to145 million bags. Recently, the soluble coffee industry has experienced a constant growth as soluble coffee has become one of the most popular kinds of coffee drunk by millions of people around the world. About 50% of coffee product is treated for soluble coffee elaboration [235]. Coffee preparation goes through several stages: roasting, grinding, extraction and concentration of water soluble. The raw coffee is obtained after five years of coffee tree planting [236].

Coffee seed are consisting of two coffee beans covered by a thin parchment like hull and further surrounded by core. There are two ways to remove pulp and peel: wet or dry, roasting coffee seeds to get the required characteristics as flavors, aromas and color. This operation depends on time-temperature which leads to various alterations in the chemical structure and biological effectiveness coffee as a result of the transmutation of naturally occurring polyphenol constituents in a complex mixture of Maillard reaction products, the organic compounds formation as result of pyrolysis. Then, roasted grains are grinded in several stages to obtain soluble coffee. Water is used to separate soluble solids. To remove soluble contents from coffee, hot water was used under pressure. After extraction, the concentrated extracts are dried by freeze drying or spray drying to produce the soluble coffee. The amount of exhausting coffee as a waste was estimated about 6 million tons annually [237].

3. 7. 2. Re-use of exhausted coffee waste

Recently, there are some concerns about organic materials of exhausted coffee and how to use it as a natural fertilizer and a compost feedstock rather than disposed of [238,239]. As it's known, the exhausting coffee is rich in polyphenolic compounds and lipids. It was discovered that the exhausted coffee is an absorbent substance, it is considered to be economic when used in the removal of dyes [240,241], phenolic compounds [242], phenol and methylene blue [243], Pb(II) [244], adsorption of pharmaceuticals (metamizol (MET), acetylsalicylic acid (ASA), acetaminophen (ACE), and caffeine (CAF)) [245] and 4-chloro-2-methyl phenoxy acetic acid pesticide [246] from aqueous solution.

3. 7. 3. Characterization of exhausted coffee waste

Coffee waste is rich in organic compounds as fatty acids, lignin, cellulose, hemicellulose and other polysaccharides. When re-used, coffee waste can be used to produce biofuels and activated carbon, which in turn can be used as adsorbent material [237,247]. Since the cost of residual coffee is low, it has been used to treat the selected pesticides in this study. Due to the existence of complex chemical compounds in a combination of exhausting coffee as lipids, fatty acids, carbohydrates like lignin, hemicellulose, cellulose and various indigestible sugars, after the extraction process these compounds can be kept in water [234,237]. Generally, the exhausted coffee is one of lignocellulosic [248] which include a difference in structural compounds (lignin, cellulose and hemicellulose) [249]. The (Figure 3. 5) showed the structural compounds of lignocellulosic materials.

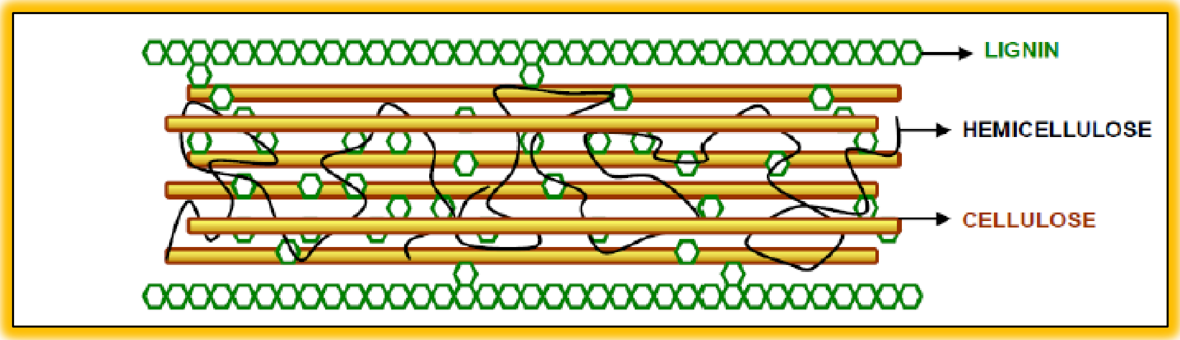


Figure 3. 5. Lignocellulose structure fractions: cellulose, hemicellulose and lignin, Source: Memon et al. (2007) [219]

3. 8. Date stone as biosorbent for pollutants removal

Recently, there was a wide realization of the significance of agricultural waste as an inexpensive, reused and easy to get of raw materials for AC production. Chemical and physical activation (activation using oxidizing agents such as steam or CO_2) are qualified in the literature for preparation of AC. For chemical activation, the precursor is impregnated with an activating agent such as zinc chloride or phosphoric acid followed by carbonization at high temperatures between 400 to 800 ˚C. Then, leaching process was applied to remove the activator [250–252]. Although the characteristics of the produced AC depend on the used precursor, the most effective factors are related to preparation of AC such as carbonization time (Ct), the impregnation ratio (R) and carbonization temperature (CT). The weight ratio of the activator to the dry precursor, seems to influence the porosity of the resulting products. The chemistry of pyrolytic processes affected by activation agent (acting as a dehydrating agent) is limited to a minimum and the pyrolysis temperature is lowered. This seems to promote the development of a porous structure [250,253]. Usually micropores take control at low values of R, while wide micropores and mesopores predominate at higher values [254,255]. The rapidity and extent of the pyrolysis reaction taking place will depend on the temperature and time of carbonization, respectively. These factors are interrelated and play important role in determining the characteristics of the product [250,254,255]. Many studies [252,256] detected that zinc chloride is the best amongst other studied activators.

Table 3. 4 shows the optimum conditions published in recent literature for production of activated carbon from dates' stones. It can be noticed that almost all experiments were performed by using H_3PO_4 as an activator. The optimum conditions reported varied widely depending on the method of evaluation where optimum CT varied between 500 to 800 ˚C and R from 0.4 to 2 depending on the assessment method used and the activator.

Table 3. 4. *Summary of optimum conditions reported in recent literature for production of Activated carbon from dates stones*

Activator	Evaluated Parameter	Maximum Value	Optimum conditions				Comments	Ref.
			Ct (h)	CT (OC)	R	PS (mm)		
H_3PO_4	$(q_m)_{MB}$	240 mg g^{-1}	2	700	1.2		Only Ct = 2 hr was investigated (See Tables 5 and 6 in this reference).	Lal and Rup (1982) [56]
H_3PO_4	K_{MB}	100 mg g^{-1}	2	700	1.2			
H_3PO_4	IN	528 mg g^{-1}	2	500	1.68			
H_3PO_4	PhN	166 mg g^{-1}	2	700	1.2			
H_3PO_4	IN	495 mg g^{-1}	1	800	0.4	0.6	Used fluidized bed	Welp and Brümmer (1999) [57]
None	$(q_m)_{MB}$	80.3 mg g^{-1}	NA	NA	NA		Raw dates pits are better than activated ones	Fu and Alexander (1995) [58]
$ZnCl_2$	PMBR	99%	0.5	600	2			Aronstein *et al.*,1991 [59]

$(q_m)_{MB}$ = Maximum capacity as estimated from Langmuir isotherm, k_{MB} = Unit capacity estimated using Freundlich equation, IN = Iodine number, PhN = Phenol number, and PMBR = percentage of methylene blue removal. PS = particle size.

The previous results display the need for further inquiry about the production of AC from dates' stones to bring about more conception of the influence of preparation conditions on the quality of the produced AC and the effect of the assessment method in the qualification of the optimum conditions.

3. 8. 1. Activated carbon prepared from date stones

The growing demand of dates enhanced their production which reached 7.2 million tons in 2010, and approximately 720,000 tons of date pit wastes could be produced annually [257]. The chemical composition of the date stones is shown in Table 3. 5.

Table 3. 5. Chemical composition of date stones

Characteristic	Value (%)
Moisture	5 – 10
Ash	1 – 2
Protein	5 – 7
Oil	7 – 10
Crude fiber	10 – 20
Carbohydrates	55 – 65

Source: Torrellas *et al.(*2016) [258]

The yield and porous characteristics of activated carbons prepared from date pits by various activation techniques are summarized in Table 3. 6.

Table 3. 6. Comparison of yield and textural characteristics of ACs prepared from date pits by various activation techniques

Activator	**Activation conditions**	**S_{BET} (m^2 g^{-1})**	**V_t (cm^3 g^{-1})**	**V_{mic} (cm^3 g^{-1})**	**d_p (nm)**	**Yield (%)**	**Ref.**
Chemical activation							
Zncl$_2$	600 ˚C, 3h, 0.5	999	0.532	0.35	1.29	46	Alhamed and Bamufleh, 2009[259]
NaOH	600 ˚C, 1h, 3	1282	0.66	0.38	2.073		Islam et al., 2015 [260]
H_3PO_4	450 ˚C, 1.2h, 3	952	1.38	0.36	2.91	41	Reddy et al., 2012b [261]
KOH	800 ˚C, 1h, 0.5	1032	1.21	0.56	4.689		Merzougui and Addoun, 2008 [42]
$FeCl_3$	700 ˚C,1h, 1.5	780	0.573	0.468	2.938	47	Theydan and Ahmed, 2012a [262]
Physical activation							
CO_2	900 ˚C, 4h	490	0.229	0.165	1.869		El-Naas et al., 2010b [263]
Steam	800 ˚C, 1h	702	0.321		0.94	17	Awwad et al., 2013 [264]

Activator	**Activation conditions**	**SBET (m2 g-1)**	**Vt (cm3 g-^{1})**	**Vmic (cm3 g^{-1})**	**dp (nm)**	**Yield (%)**	**Ref.**
Physico-chemical activation							
HNO_3/Steam	600 ˚C, 3h,10%	950	0.75		3.157		Hazourli et al., 2009 [265]
H_3PO_4/Steam	600 ˚C, 3h,1	1100	0.85		3.091		Hazourli et al., 2009 [265]
KOH/CO_2	850 ˚C, 2h, 3,9	763	0.424	0.215	2.618	20	Hazourli et al., 2009 [265]

3. 8. 2 Adsorption application of date stones

The use of activated carbon as an adsorbent material has proven to be highly efficient in removing organic and inorganic substances. This is due to its high surface area, porous structure and adsorption capacity [266]. Parameters of isotherms were used to evaluate the adsorption behavior and maximum capacity [267,268]. Date stones are used as adsorbent material for elimination of aldrin, dieldrin, endrin, bentazon, carbofuran and 2,4-D as summarized in Table 3. 7.

Table 3. 7. Comparison of adsorption capacities onto ACs from date pits by various techniques

Activator	**Adsorbate**	**Adsorption conditions**	**C_0 (mg L^{-1})**	**q_L (mg g^{-1})**	**Isotherm**	**Ref.**
Steam	Aldrin	1g L^{-1}, 3.5h, 25 °C	0.5 - 20	6.975	Freundlich	El Bakouri *et al.*, 2009 [225]
Steam	Dieldrin	1g L^{-1}, 3.5h, 25 °C	0.5 - 20	6.369	Freundlich	El Bakouri *et al.*, 2009 [225]
Steam	Endrin	1g L^{-1}, 3.5h, 25 °C	0.5 - 20	5.982	Freundlich	El Bakouri *et al.*, 2009 [225]
KOH/CO_2	Bentazon	1g L^{-1}, 24h, 30 °C, pH = 5.5	25 - 250	86.26	Freundlich	Salman *et al.*, 2011 [269]
KOH/CO_2	Carbofuran	1g L^{-1}, 30h, 30 °C	25 - 250	135.1	Langmuir	Salman and Hussein, 2014 [270]
KOH/CO_2	2,4-D	1g L^{-1}, 9h, 30 °C, pH = 3.6	50 - 400	238.1	Langmuir	Hameed *et al.*, 2009 [180]

El-Baqouri *et al.* (2009) [225] studied the possibility of using thermally and chemically treated date stones to remove aldrin, dieldrin and endrin from aqueous solutions. The Langmuir, Freundlich and Dubinin-Radushkevich model were used to explain the adsorption isotherms. The results were fitted by the Freundlich isotherm and the maximum adsorption capacities were 373.728, 295.305, and 228.047 mg g^{-1} for aldrin, dieldrin, and endrin, respectively. These results displayed that the equilibrium conditions reached at 210 min, the adsorbed amounts were 16.37, 14.49, and 11.85 mg g^{-1} for aldrin, dieldrin, and endrin, respectively. The uptake was raised with rising of pesticide initial concentration and decreasing of sorbent particle size due to a significant increase in surface area.

Salman *et al.* (2011) [269] explored the adsorption behavior of bentazon and carbofuran onto date stones activated carbon by physiochemical activation by potassium hydroxide (KOH) and carbon dioxide (CO_2) as the activating agents. The results were fitted better with the Freundlich model for both pesticides. The maximum Langmuir capacities of 86.26 and 137.04 mg g^{-1} were for bentazon and carbfuran, respectively. The molecular size of the carbofuran is smaller than the partial size of the bentazon, thus easily penetrating activated carbon pores.

Salman & Hussein (2014) [270] studied the relation of adsorption between the bentazon, carbofuran and 2,4- Dichlorophenoxyacetic acid (2,4-D) and date seeds activated carbon which was prepared by KOH/ CO_2 physico-chemical activation. The equilibrium data were analyzed by non-linear fitting using Langmuir, Freundlich and Temkin isotherm models and evaluated the equilibrium data. The maximum adsorption capacities for Freundlich, Langmuir and Temkin models were 78.13,135.14 and 175.4 mg g^{-1}, for bentazon, carbofuran and 2,4-D, respectively, at initial concentrations ranged between 25 – 250 mg L^{-1}, 1g L^{-1} dose, and 30 ˚C for 30 h to reach equilibrium. The equilibrium was attained at 36, 16, and 14 h with high uptakes of 80, 105, and 179.59 mg g^{-1} for bentazon, carbofuran, and 2,4-D, respectively.

Hameed *et al.* (2009) [180] examined the activated carbon prepared from date stones, activated by KOH/CO_2 as adsorbent material for removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D). Obtained experimental data were analyzed by Freundlich, Langmuir and Temkin isotherms. The Langmuir model fitted with the results and the maximum adsorption capacity was 238.10 mg g^{-1}. The adsorption equilibrium was achieved in 4h at low initial concentration (50 – 100 mg L^{-1}). In contrast, the time at high initial concentration (200–400 mg L^{-1}) the reached equilibrium time was 7 h and 30 min.

4. 0. Material and methods

This chapter specifies the raw materials, activation and modification techniques and methods, chemicals and characterization methods which are used in experiments. The adsorption studies were performed with batch adsorption experiments to explore the influence of pH, sorbent dosage, contact time, the initial concentration of selected pesticides, and temperature. As well, isotherm, kinetic and thermodynamic parameters were evaluated.

4. 1. Materials and modifications

4. 1. 1. Adsorbents

The Spent coffee grounds (Figure 4. 1) were collected from a coffee machine used by employees at the Department of Environmental Engineering, Faculty of Technical Sciences, University of Novi Sad. The date seeds were obtained from United Arab Emirates (Figure 4. 2)

Activated carbons (AC) prepared from the residue of coffee and date stones were employed as a raw material for removal of selected pesticides and named (SCG and DSAC), respectively. AC_c were impregnated by phosphoric acid H_3PO_4.

Commercial Activated charcoal, NORIIT SA2 (Figure 4. 3), Activated Carbon NORIT HYDRODARCO C (Figure 4. 4) and Zeolite, type: ZSM-5 (Figure 4. 5) was used without any modification, as reference materials for removal of selected pesticides, too.

4. 1. 2. Chemicals

The carbendazim, H_3PO_4 (phosphoric acid), acetonitrile and methanol were purchased from Sigma-Aldrich Co. (St. Louis, USA). Linuron, isoproturon were obtained from (LGC, Germany). HCl and NH_4OH were obtained from J.T. Baker (USA) and Centrohem (Serbia), respectively.

4. 1. 3. Instruments

HPLC-DAD (Agilent 1260), shaker (Heidolph Unimax 1010), pH meter (model PHD 21), scales (KERN), oven (Memmert), furnace (ELECTRON), Ultrapure Water (Thermo Scientific), Sieve Analysis (different number), Ventilation.

4. 1. 4. Water

In this study the water used was initially demineralized, filtered through an Ultrapure Water (Thermo Scientific) system. Distilled water was used for equilibrium and kinetic experiments.

4. 2. Experimental and analytical methods

4. 2. 1. Reagents

All chemicals used were of analytical grade. The Stock solution of carbendazim ($C_9H_9N3O_2$), linuron ($C_9H_{10}C_{l2}N_2O_2$) and isoproturon ($C_{12}H_{18}N_2O$) (200 ppm) were prepared by dissolving 5 mg of 191.19, 249.091 and 206.289 g. mol^{-1}, respectively in 25 mL of methanol. The experimental solutions of desired concentration were prepared by diluting the stock solution with distilled water. The residual concentration of selected pesticides was determined by HPLC. pH of solutions was adjusted using 0.1M HCl and 1M NH_4OH.

4. 2. 2. Procedure of SCG adsorbent preparation

The SCG was washed with boiled water to eliminate the impurities, dust and water-soluble substances, followed by washing with distilled water. The washed SCG was dried in the oven (Memmert, Germany) at 60 C° for 24 h before their activation. The dried SCG was then sieved. The resulting product was impregnated over 24 h by H_3PO_4 solution at different concentrations of 30 and 50%, respectively. The impregnation ratio (Xp, in wt. %) is defined as the ratio of the weight of H_3PO_4 (g) to the weight of precursor (g of dried coffee grounds and date stones). The physicochemical properties of the AC prepared with Xp = 30 and 50 wt. % (namely SCG^{30} and SCG^{50}, respectively) were studied.

The impregnated samples were washed with hot distilled water several times till the pH values are 4.5 to 5 and dried at 110 C° for 24 h. The impregnation ratio was determined according to the method described by Ching *et al.* (2011) [271].

(X_p) = (weight of the H_3PO_4 /weight of the SCG)

where (X_P) is the impregnation ratio.

The material was then carbonized in the furnace at 600 C°, where the heating rate was (10 ˚C min^{-1}) for one hour according to the method described by Ching *et al.* (2011) [271]. After that, it is cooled at room temperature and washed with distilled boiling water. Then, material is dried in oven for 6 hours at 110 ° C. Activated product based on SCG was ready for use as adsorbent material after crushed and sieved to obtain particles with sizes between 100 and 200 μm Fig. 4. 6. The yield of SCG which is an indication of production process mass efficiency was calculated according to the (Eq. (1)) [271].

$$\text{Yield} = \left(\frac{W_1}{W_0}\right) \times 100 \tag{1}$$

The weight loss or the weight ratio of the final product to that of raw materials was calculated from (Eq. (2)) [271]:

$$Weightloss\ (\%) = \frac{(\ w_0 - \ w_1)}{w_0} \times 100 \tag{2}$$

where W_0 is the weight of original SCG (dry basis) and W_1 is the weight of the resulted AC.

4. 2. 3. Procedure of DSAC adsorbent preparation

The date stones were washed with boiled water to eliminate the impurities. The washed date stones were dried in the oven (Memmert, Germany) at 60˚ C for 24 h before their carbonization at 300 ˚C for 30 min. Afterward, dried date stones were milled in the grinder in order to obtain a powder date stones, and washed with boiled water several time before dried over night at 110˚C. The resulting product was ready to activation by H_3PO_4 solution at concentrations of 30% as described by the procedure of SCG adsorbent preparation (Figure 4. 7).

4. 3. Determination by HPLC-DAD

The target pesticides were analyzed by HPLC-DAD. Separation was performed with a reversed phase column Eclipse XDB-C18 (3 x 150 mm, particle size 3.5µm). The operating conditions were: the flow of 0.4 mL min^{-1}, the temperature of the column was 30 C° and injection volume of 10 µL. The mobile phase consisted of water (A) and acetonitrile (B). The binary gradient elution started at 25% B in the 1st minute, then linearly increased to 50% B in the 5th minute, and at the end, initial condition was applied, 25% B in the 7th minute. The maximum wavelength of 215 nm was used.

4. 4. Statistical analysis

Data were reported as the mean ± standard deviation of three replications. Data were analyzed by an analysis of variance (one way ANOVA). The level of significance was (α-value) 95 % in all cases ($P \leq 0.05$). Tukey's test was used for the pair of means. All the data were analyzed using Microsoft Office Excel 2007 software.

4. 5. Characterization of SCG and DSAC

The microstructures of the SCG and DSAC were determined using the SEM JSM 6460LV instrument (JEOL, USA), equipped with an EDX attachment. The specific surface area (S_{BET}) of SCG and DSAC was determined by measuring N_2 adsorption, applying the BET method and an Autosorb iQ instrument (Quantachrome, USA). The cumulative pore volume for mesoporous was calculated using Barrete-Joynere-Halenda (BJH) method. The Dubinine-Radushkevich (DB) test was applied to get the micropore volume. Chemical characterizations were studied by FTIR spectroscopy in order to recognize the functional groups at the surface of the SCG and DSAC. FTIR spectra were recorded with an FTIR/NIR spectrophotometer Nexus 670 (Thermo Nicolet, USA), at wavenumbers from 400 to 4000 cm^{-1}.

4. 6. Batch Adsorption Experiments

4. 6. 1. Batch Adsorption Experiments for coffee

Different impregnation ratios of H_3PO_4/coffee (w/w) 3:1, 4:1 for different concentrations of H_3PO_4, 30% and 50%, respectively were studied for each of the parameters such as pH, dosages of adsorbent, the initial concentration of pesticides and contact time. The uptake per mg of adsorbent, q_e and the percentage of carbendazim, linuron and isoproturon adsorbed, %Ad-s, were calculated using (Eq. (3) and (4)) [114], as follows:

$$qe = \frac{(C_{\circ} - C_f\ )}{m} * V \tag{3}$$

$$\%Ads = \frac{(C_{\circ} - C_f\ )}{C_o} * 100 \tag{4}$$

where qe is the adsorption capacity (mg g^{-1}), C_0 and C_f are the initial and final carbendazim or linuron concentrations, respectively (expressed in mg L^{-1}), V is the solution volume (mL) and m is the adsorbent dosage (g) .

Furthermore, the residual root mean square error (RMSE) and Chi-square ($\chi 2$) tests （Eq. （5，6）） [272] were used to analyze the errors in experimental data. Smaller RMSE and χ^2 mean that the equation can predict the experiment results more accurately.

$$RMSE = \sqrt{\frac{1}{n-p} \sum_{i=0}^{n} (q_e - q_{e\,m})^2} \tag{5}$$

$$x^2 = \sum_{i=0}^{n} \frac{(q_e - q_{e\,m})^2}{q_{e\,m}} \tag{6}$$

where q_e is the observation from the batch experiment, q_{em} is calculated adsorbate concentration with kinetic and isotherm models, n is the number of the samples and p is the number of parameters to be determined. Smaller RMSE and χ^2 mean that the equation can predict the experiment results more accurately [273, 274].

4. 6. 2. Batch Adsorption Experiments for date stones

Impregnation ratios of H_3PO_4/date stones was (w/w) 3:1 and concentrations of H_3PO_4 was 30%. The physico-chemical parameters such as pH, dosages of adsorbent, the initial concentration of pesticides and contact time were explored as the steps in batch Adsorption experiments for coffee.

4. 7. Adsorption isotherms

The adsorption equilibrium study of the interaction between selected pesticides and adsorbent can be well described by three commonly used isotherm models. Langmuir, Freundlich and Temkin [275] models are essential for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and productive design of the adsorption systems, since they explain how pollutants cointerrelate with the adsorbent materials [276].The mathematical expression of Langmuir isotherm model (Eq. (7)) [277] is expressed by the following respective equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{7}$$

The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant, separation factor (R_L), which is represented as (Eq.(8)): [278].

$$R_L = \frac{1}{1 + K_L\ C_O} \tag{8}$$

Freundlich model (Eq. (9)) [27] is exhibited as:

$$logq_e = logK_f + \frac{1}{n}logC_e \tag{9}$$

where q_e is the amount of selected pesticides adsorbed per unit mass of adsorbent (mg g^{-1}), q_{max} is maximum monolayer coverage capacity (mg g^{-1}), R_L is separation factor, C_e is the equilibrium concentration of selected pesticides in solution (mg L^{-1}), C_o is the initial concentration and K_L (L mg^{-1}) is the Langmuir adsorption equilibrium constant. The value of K_L was calculated from the slope and intercept of the plot of C_e/q_e versus Ce, respectively. K_F is the Freundlich adsorption constant related to the adsorption capacity of adsorbent, $1/n$ is the adsorption intensity, which indicates the favorability of adsorption. The values of K_F and $1/n$ were calculated from the slope and intercept of the plot of log qe versus log C_e, respectively.

Temkin model (Eq. (10)) [279] is exhibited as:

$$q_{e=}\ \frac{RT}{b}\ln A+\frac{RT}{b}\ln C_e \tag{10}$$

$B=\frac{RT}{b}$ is the constant related to heat of sorption (J mol^{-1}) obtained from the Temkin plot q_e versus ln C_e,

A (slope) is Temkin isotherm equilibrium binding constant (L g^{-1}),

b (intercept) is Temkin isotherm constant,

R is universal gas constant (8.314 J mol^{-1} K^{-1})

T is thermodynamic temperature at 298 K [279].

4. 8. Adsorption kinetics

Several kinetic models may be used to examine the controlling mechanism of adsorption process and the potential rate-limiting steps such as transfer and chemical reaction [280].

In order to study the adsorption of carbendazim and linuron on the SCG and to interpret the experimental data obtained, three kinetic models, the pseudo-first order, pseudo-second order and intraparticle kinetic model have been used.

The pseudo-first kinetic model (Eq. (11)) [281] is expressed by the following equation:

$$\log(q_e-q_t)=\log q_e-\left(\frac{k_1}{2{,}303}\right)\mathrm{t} \tag{11}$$

where K_1 (1 min^{-1}) is the equilibrium rate constant of the pseudofirst order adsorption and it is determined from the plot of log (q_e-q_t) as a function of t.

The pseudo-second-order kinetic model (Eq. (12)) [281] can be represented by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e}t \qquad (12)$$

where K_2 (g mg $^{-1}$ min^{-1}) is the pseudo-second order rate constant and it is determined from the plot of t/q_t as a function of t.

Weber —Morris kinetic model of intraparticle diffusion (Eq. (13)) [281] is given by an equation:

$$q_t = k_{id} \cdot t^{\frac{1}{2}} + C_i \qquad (13)$$

where K_i (mg g $^{-1}$ min$^{-1/2}$) is the intra particle diffusion rate constant and it is determined from the plot of qt as a function of $t^{1/2}$.

C_i (mg g^{-1}) is a constant that indicates the thickness of the boundary layer, i.e. the higher the value of C_i, the greater the boundary layer effect.

4. 9. Adsorbent dosage

Adsorption experiments were carried out by adding various amount of sorbents (0.01 to 3 g) depending on the type of adsorbent to carbendazim, linuron and isoproturon into conical flasks (150 mL), which containing (50 mL in each case), at different impregnation ratios of SCG and DSAC at pH 7. The flasks were placed in an orbital (Unimax 1010) and agitation was provided at 140 rpm for 30 min at room temperature [271] . The same steps were applied with the other three commercial adsorbents (NORIIT SA2, Activated Carbon NORIT HYDRODARCO C and Zeolite, type: ZSM-5).

4. 10. Contact time

Adsorption experiments were carried out by adding a fixed amount of sorbent and concentration of pesticides into a number of 150 mL conical flasks, at optimum impregnation ratios of the weight (H_3PO_4/coffee) and (H_3PO_4/date stones) was 3:1 where the concentration of 30% H_3PO_4 coffee ground and date stones activated carbons at room temperature and pH was 7.00. Already impregnated AC was added to the conical flasks. The flasks were placed in an orbital shaker (Unimax 1010) and agitation was done at 140 rpm. The samples were taken at preset time intervals after (5 - 90 min) for selected pesticides. The same procedures were applied with the other three commercial adsorbents (NORIIT SA2, Activated Carbon NORIT HYDRODARCO C and Zeolite, type: ZSM-5).

4. 11. Initial carbendazim, linuron and isoproturon concentrations

The initial carbendazim, linuron and isoproturon concentrations were 2, 4, 5, 6, 8, 10, 12 and 15 mg L^{-1}. The adsorbent dosage, contact time and pH were used the optimum results which optioned. The conical flasks were shaken on the orbital shaker at 140 rpm at room temperature. The reaction of samples was conducted followed by filtration through (Ø125 mm) membrane filters followed by filtration using a syringe to make sure to get rid of colour before the measurement of carbendazim, linuron and isoproturon.

4. 12. Point of zero charge (pHpzc)

The pH “drift” method was conducted to determine the pH_{pzc} (point of zero charge) of activated carbons (SCG, DSAC, NORIIT SA2, Activated Carbon NORIT HYDRODARCO C and Zeolite, type: ZSM-5). That is pH when the charge in the activated carbon surface is zero. The procedure of this method can be described as follows: 0.1 g of activated carbon was taken to nine 50 mL plastic bottles containing 30 mL of 0.1 mol L^{-1} KNO_3 with adjusted pH values from 2 to 10 ($pH_{initial}$). The plastic vials were sealed and placed in a mechanical stirrer Heidolph Unimax 1010 (Heidolph, Germany) for 24 h. After 24 h, the content of the flasks was filtered, the pH of solutions was measured using pH meter (model PHD 21) and noted as pH_{final}. The pH_{pzc} of biochar is the point when $pH_{initial} = pH_{final}$ [282].

4. 13. Desorption and regeneration studies

The regeneration of activated carbon is of great importance to the prevention of potential contamination of the environment [283]. The possibility reused of activated carbon can be evaluated on the basis of desorption degree of target pesticides after the remediation and the efficiency of regenerated activated carbon. The SCG and DSAC samples (3.0 g L^{-1}) were treated with a solution of carbendazim, linuron and isoproturon (total concentration of 5 mg L^{-1}) first separately, the second experiment was mixed these three pesticides, for 30 min at room temperature 25 ± 2 ˚C. After the treatment, adsorption experiment was performed with diluted H_3PO_4. After washing and drying it, the activated carbon was reused as a regenerated adsorbent, in three repeated adsorption-desorption cycles. A diluted H_3PO_4 was produced as a waste stream during the washing of the activated carbon and after pyrolysis at 550˚C. The experiments were conducted in a batch system. Desorption efficiency was determined using the following equation:

$$dE = \frac{qd}{qa} \times 100 \tag{14}$$

where d_E is desorption efficiency (%), q_d is amount of pesticides desorbed (mg g^{-1}) and q_a is adsorption capacity of pesticides adsorbed on the activated carbon, (mg g^{-1}).

4. 14. Adsorption thermodynamics

The thermodynamics parameters studies include enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS). They can be calculated from the following equations [284,285].

$$\Delta G^\circ = -\,\mathrm{RT}ln\frac{q_e}{C_e} \tag{15}$$

$$lnk_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{16}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{17}$$

where q_e is the amount of ions adsorbed per unit mass of activated carbon (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), T is the temperature (K) and R is the gas constant (8.314 J mol^{-1} K^{-1}) [286].

5. 0. Results and discussion

5. 1. Characterization of AC

In order to determine how the selected pesticides were adsorbed onto the activated carbon scanning electron microscopy (SEM) was utilized. (Details of the SEM are described in section 4.5.). Laksaci *et al.* (2017) [287] determined the morphology of ACs from coffee grounds was characterized by SEM images, which clearly indicates their heterogeneous surface and porous nature. The pores observed (µm range) act as channels for the microporous network of the adsorbent. Azouaou *et al.* (2010) [288] showed the structure of coffee grounds indicating that the coffee grounds had a porous and homogenous structure with deep pores. On the other hand, in the case of untreated coffee materials the surface was scraggy with a variety of cavities [27,289]. Xiaodong *et al.* (2013) [29] reported that the AC, which was prepared from spent coffee grounds, showed a lot of channels with an entrance size of several micrometers. These channels where micropores existed in guaranteed the fine gas diffusibility of activated carbon. El Messaoudi *et al.* (2016) [290] reported that the SEM images of date stones showed a significant change in the morphology of treated support, the examination of the morphology of date stones showed that the structure of treated support became microporous and irregular. Bouhamed, (2012) [291] studied that activated carbon prepared from date stones, the sorbent surface demonstrated after activation process a well-developed and uniform surface, forming orderly porous structure and a predominately microporous character which is responsible for the high developed surface area of this material.

5. 1. 1. Physical characterisation of exhausted coffee waste (SCG)

The scanning electron microscopy (SEM) equipped with an EDX attachment was used to examine the morphology and components of AC surface before and after the adsorption (Figure 5. 1). The results explained that the AC surface is irregular; a protrusion was created, and porous with various holes and channels. The macro- and mesopores were observed on the surface of the AC. The pore structure indicated the adsorption of carbendazim, linuron and isoproturon onto the surface of the adsorbent.

After adsorption, significant changes in surface morphology of AC were observed, since the pores were packed with selected pesticides.

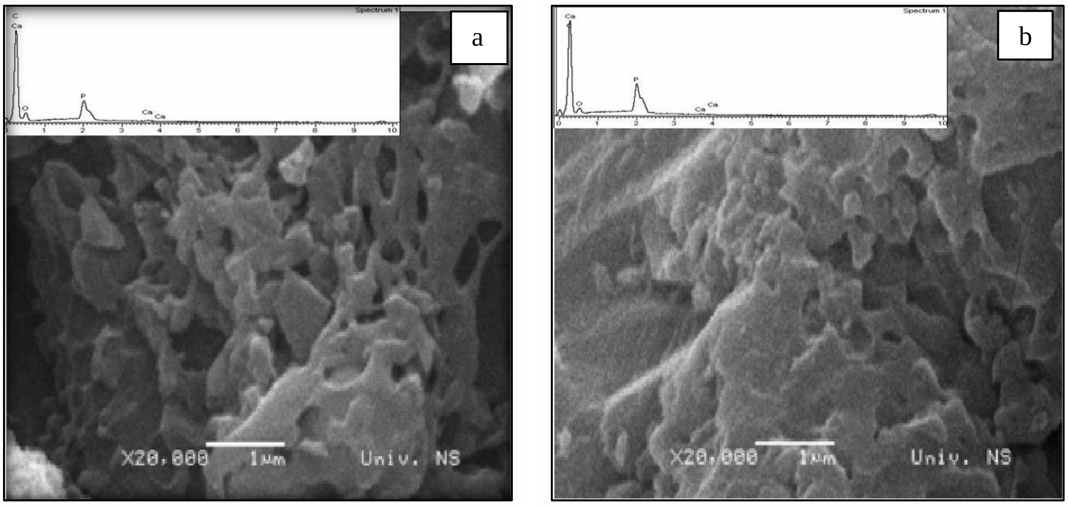


Figure 5. 1. (a). SEM micrograph of SCG surface before adsorption, (b). SEM micrograph of SCG surface after adsorption

5. 1. 2. Physical characterisation of date stones (DSAC)

Figure. 5. 2 (a, b and c), shows SEM micrographs of the raw DSAC residue and the resulting activated carbon prepared under the optimal conditions. For the date stones residue, the surface was quite smooth with pores, as shown in Figure. 5. 2 (a). After the activation process, the sorbent surface demonstrated a well-developed and uniform surface, forming an orderly porous structure and a predominately microporous character which is responsible for the highly developed surface area of this material Figure. 5.2 (b and c).

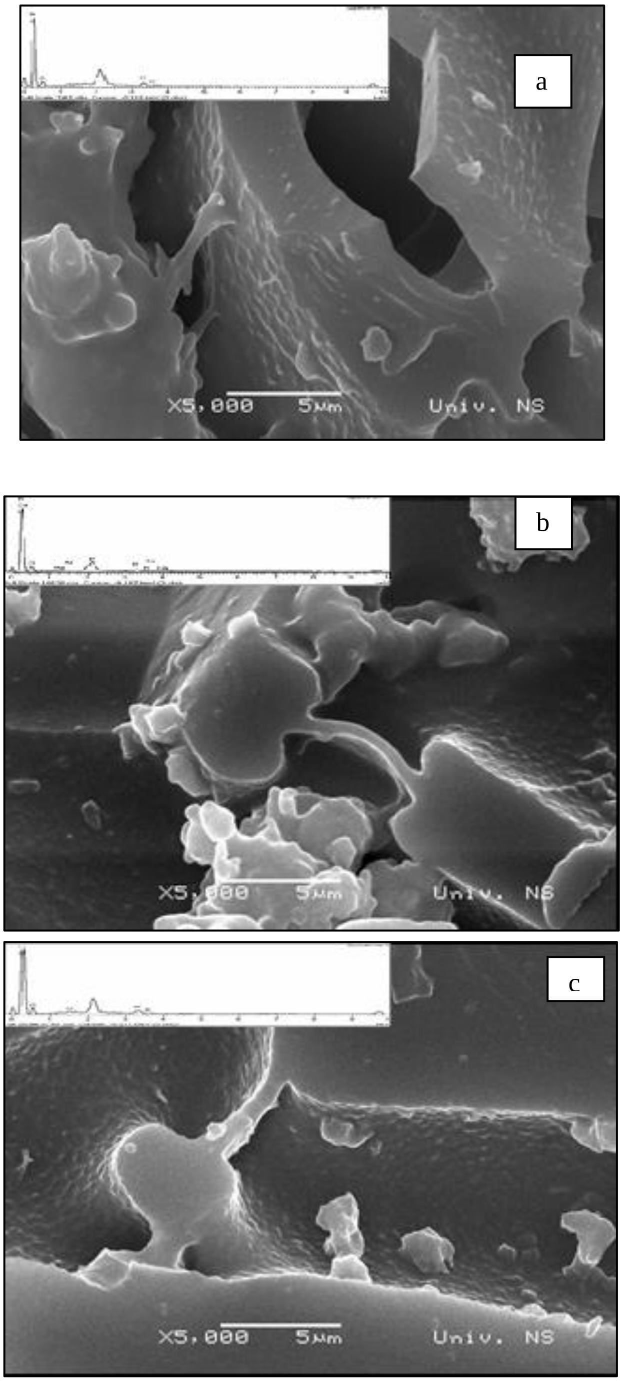
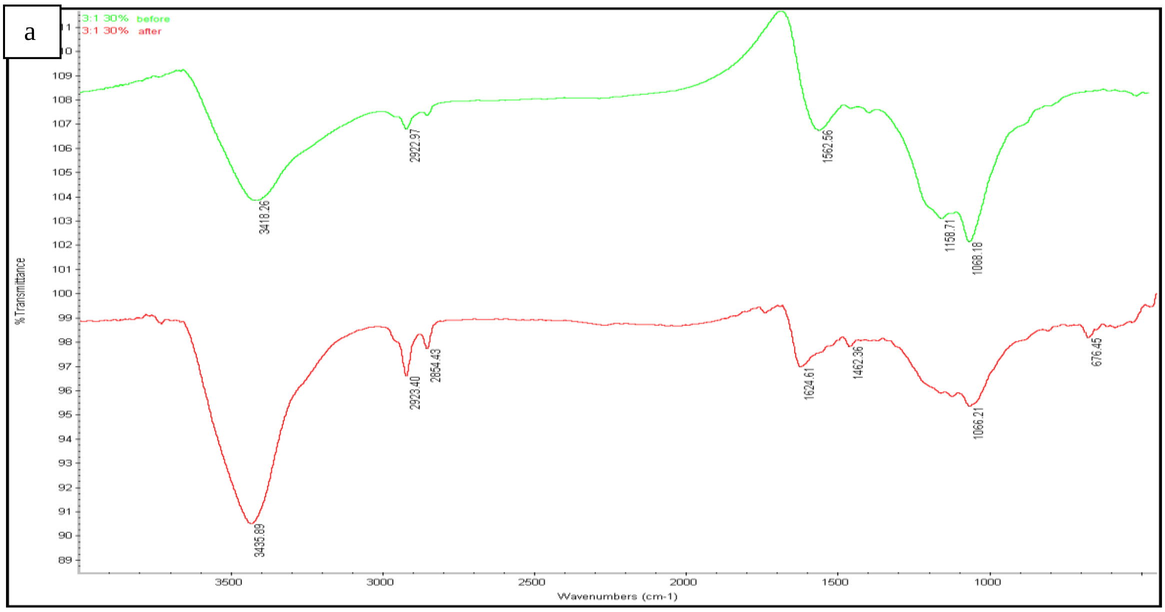


Figure 5. 2. SEM micrograph of DSAC surface before adsorption, (b). SEM micrograph of DSAC surface after adsorption of isoproturon, (c). SEM micrograph of DSAC surface after adsorption of (carbendazim, linuron and isoproturon).

5. 1. 3. The FTIR spectrum for (SCG)

The FTIR spectrum was used to get an understanding of the chemical structure and functional groups. FTIR spectrum of $SCG^{30\%}$ and $SCG^{50\%}$ is shown in (Figure 5. 3). The spectrum presents characteristic peaks that correspond to functional groups typical of AC. A broadband at 3418.6 cm^{-1} was attributed to the stretching vibration of hydroxyl functional groups including hydrogen bonding. The spectrum of pure AC indicated the presence of an O–H. The presence of the peak located around 2922.97 cm^{-1} corresponds to C–H vibrations in methyl and methylene groups. The band at 1562.56 cm^{-1} is ascribed to carbonyl C–O group which is affected by minor overlapping with C–C aromatic ring stretching vibration. The sharp band within 1158.71–1068.18 cm^{-1} is attributed to the C–O groups, which confirm the lignin structure of the SCG. In addition, the shoulder at 1068 cm^{-1} is attributed to the P– O –C bonds in the acidic phosphate esters, as well as the symmetric vibrations in the P–O–P chain. These bands are well defined as the H_3PO_4 impregnation ratio increases and absent in AC prepared.



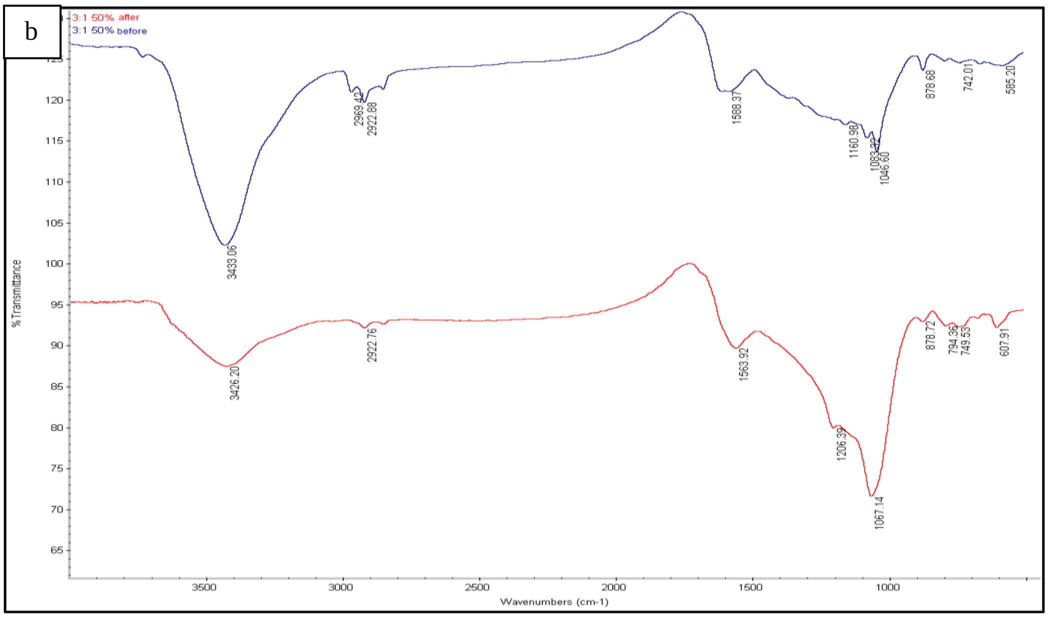
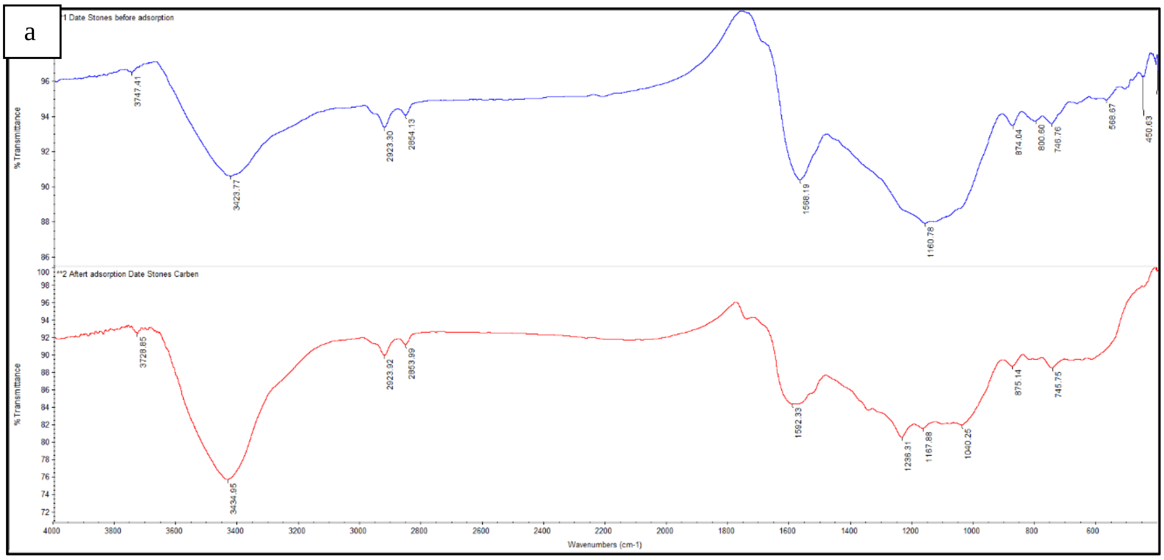
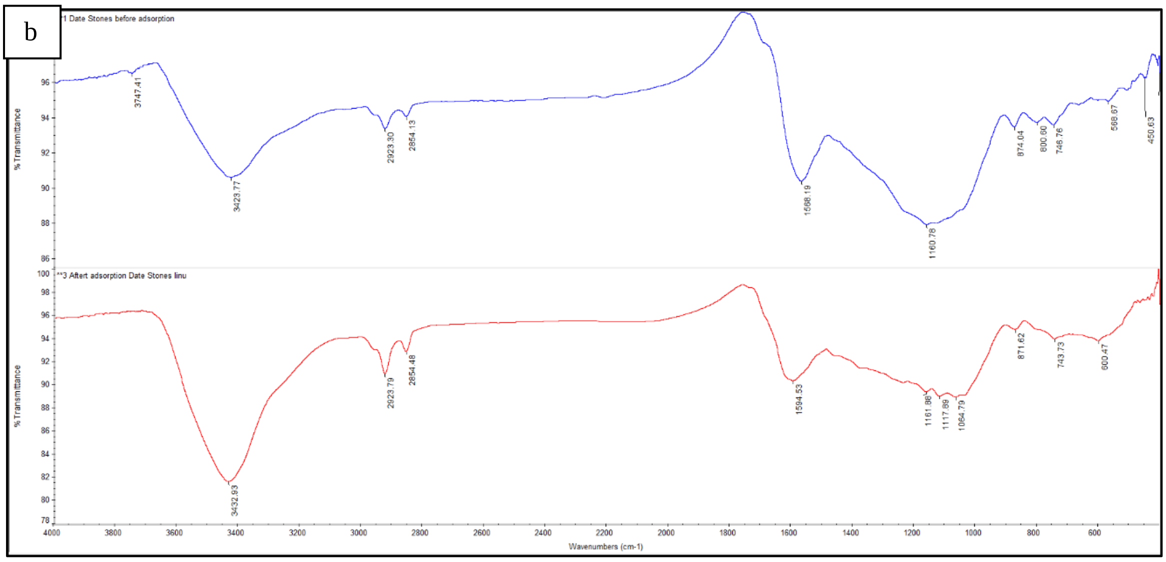


Figure 5. 3. FTIR spectrum of SCG before and after adsorption a. (3:1 $^{30\%}$***) b. (3:1*** $^{50\%}$***)***

5. 1. 4. The FTIR spectrum for (DSAC)

The FTIR is a significant method for qualitatively analysis of the adsorbents' distinctive functional groups. Fig. 5.4 display several functions which can also be observed in other carbons activated by the H_3PO_4 [292–294]. The FTIR analysis indicates the adsorption of carbendazim, linuron and isoproturon and their mixture onto DSAC exhibit a similar shape and the same functional groups. The wide band in the spectrum (3000 –3500 cm^{-1}) is attributed to the hydroxyl group O–H stretching mode with adsorbed water bending hydrogen. Bands (2900 – 2950 cm−1) are assigned to asymmetric and symmetric stretching vibrations of aliphatic bond –CH, –CH_2 and –CH_3 while the bands around 1580 cm^{-1} may be due to the presence of aromatic C = C ring stretching vibration. The bands at 2854 cm $^{-1}$ corresponds to the vibration of asymmetric and symmetric stretching C–H bands of cellulose [295]. The band at 1160.78 cm^{-1} could be attributed to esters (e.g. R–CO–O–R′), ethers (e.g. R–O–R′) or phenol groups [259]. A small shoulder at 1117.89 cm^{-1} and a relatively intense band at about 1040.25 cm^{-1} could be assigned to alcohol (R–OH) groups. This functional group is created as a consequence of the dehydration impact of H_3PO_4, potentially owing to the removal of H atom and OH groups from the aromatic rings during the impregnation and heat treatment phases. The peak at 1064 cm $^{-1}$ corresponds to the S–O elongation vibration [296].The band around 871.62 cm $^{-1}$ attributed to the C–H deformation in cellulose [297]. The peak at 874.04 cm^{-1} may be attributed to P– O– C aliphatic or aromatic stretching, P– O stretching in P= OOH or P–OH bending or P–O– P asymmetric stretching in polyphosphates. The peak at 1064.79 cm^{-1} may be due to a mixture of the P–O bond in the acid phosphate esters and the symmetric vibration of the polyphosphate chain P–O–P, whereas the band at 1160.78 cm^{-1} may be allocated to the stretching vibration of O–C in the P–O–C aromatic groups or to the hydrogen-bonded P=O phosphate or polyphosphate groups [298,299].





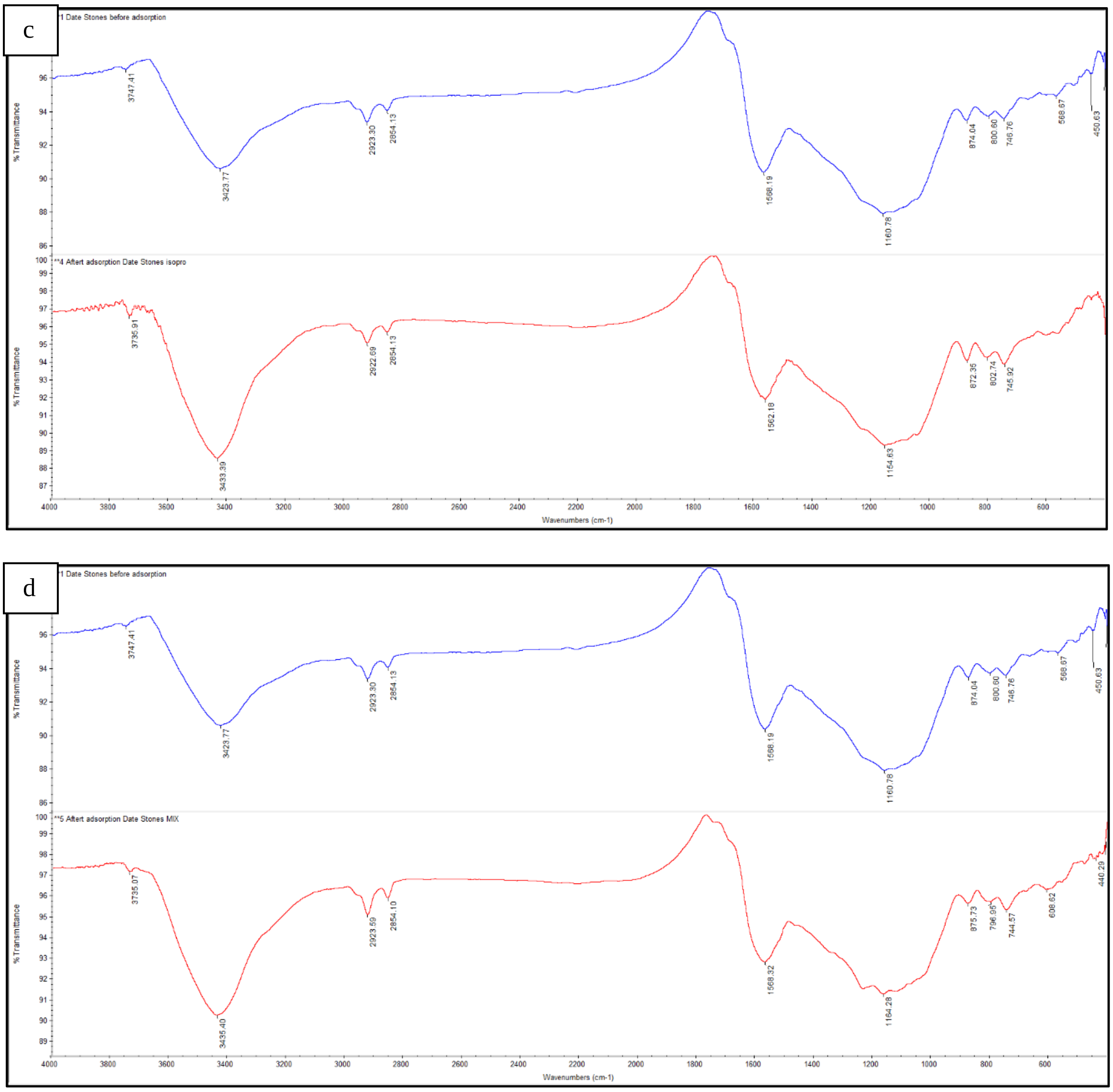


Figure 5. 4. FTIR spectrum of DSAC before and after adsorption a. carbendazim b. linuron c. isoproturon d. Mix

5. 1. 5. BET surface area of SCG and DSAC

It can be seen that SCG and DSAC have a highly developed BET surface area (803.422 and 307.450 m^2 g^{-1}) which the basic characteristic of ACs is. The BJH adsorption cumulative volume of pores for SCG and DSAC were 0.083 and 0.018 cm^3 g^{-1}. The total pore volume of SCG and DSAC were 0.423 and 0.1452 cm^3 g^{-1}, respectively.

5. 1. 6. Impact of H_3PO_4 concentration on SCG

The obtained results indicated that SCG was very good adsorbent for removal of selected pesticides (carbendazim, linuron and isoproturon). This research study demonstrated that high surface area of AC could be obtained by chemical activation of SCG with H_3PO_4. The release of moisture during carbonization of the H_3PO_4 treated sample, points out that H_3PO_4 is important agent which inhibited tar escape during carbonization.

The results of impregnation (H_3PO_4/coffee) are listed in Table 5. 1. The sample rate of the weight ratio was 3:1 where a concentration of H_3PO_4 at 30 % was optimum at pH of 5.00.

Table 5. 1. Influence of impregnation ratio H_3PO_4/coffee (w/w) on removal efficiency of carbendazim, linuron and isoproturon by adsorption ($C_\circ = 5$ mg L^{-1}, contact time = 30 min, Dosage of adsorbent = 3.00 g /1.50 L)

Impregnation ratio H_3PO_4/coffee (w/w)	Removal %	Yield	Weight loss (%)
$3{:}1^{30\%}$	94.44 ± 0.51	36.6	63.40

5. 1. 7. Impact of H_3PO_4 concentration on DSAC

The results of impregnation (H_3PO_4/date stones) are listed in Table 5. 2. The sample rate chosen of the weight ratio was 3:1, a concentration of H_3PO_4 at 30 % and pH 7.00. The main reason for the adoption of 30 % H_3PO_4 is that it is a low concentration and at the same time gave a high removal efficiency of the selected pesticides from the water medium as shown in Table 5. 2.

Table 5. 2. Influence of impregnation ratio H_3PO_4/ date stones (w/w) on removal efficiency of carbendazim, linuron and isoproturon by adsorption) $C_{\circ} = 5\ mg\ L^{-1}$, Cont. time = 90 min, Dosage of adsorbent = 2.5 g/ 1.25 L)

Impregnation ratio H_3PO_4/ date stones (w/w)	Removal %	Yield	Weight loss (%)
3:1$^{30\%}$	92.09 ± 0.51	34.92	65.08

5. 1. 8. Conclusions

The surface of the activated carbon prepared from coffee residue and date seeds changes before and after the adsorption process. It was noticed that there are channels before the process of adsorption and disappear after the process of adsorption of both adsorbents with the three selected pesticides. The reduction or disappearance of these channels indicates the successful process of adsorption of pesticides on these surfaces that were prepared from coffee residues and date seeds.

S_{BET} (m^2g^{-1}), Total pore volume (cm^3g^{-1}) and Mesopore volume (cm^3g^{-1}) of SCG and DSAC are shown in the Table (5. 3):

Table 5. 3. The textural properties of the synthesized SCG and DSAC

Parameter	**SCG**	**DSAC**
S_{BET} (m^2g^{-1})	803.422	307.450
Total pore volume (cm^3g^{-1})	0.423	0.1452
Mesopore volume (cm^3g^{-1})	0.083	0.018

Values related to SCG were greater than DSAC. This indicates that the surface area of the SCG is better for adsorption than the surface area of the DSAC. The removal rate was higher when using SCG than DSAC as it is shown in the Table 5. 1 and Table 5. 2.

5. 2. Effect of solution pH on adsorption

5. 2. 1. Effect of solution pH on adsorption (SCG)

The most important parameter of the adsorption process is the pH of a solution which influences the effectiveness and nature of the process. The pH of a solution affects the chemistry of selected pesticides, as well as the nature and activity of functional groups of the adsorption medium. The influence of pH on the SCG removal % for carbendazim, linuron and isoproturon was studied in the pH range from 3.0 to 10.0 (Figure 5. 5). The solutions of selected pesticides 5 mg L^{-1} were in contact with the adsorbent 1.0 g L^{-1} for carbendazim , 2.0 g L^{-1} for linuron for 30 min and and 1.5 g L^{-1} for isoproturon for 20 min at room temperature.

The results are shown in (Figure 5.5). It could be concluded that the removal efficiency of carbendazim changed slightly between deferent pH values. The highest removal was 95.83% at pH = 5.00. In contrast to this, there was a significant difference in the removal efficiency of linuron between deferent pH values. The highest removal efficiency of linuron was 92.45% at pH = 5.00. The highest removal efficiency for carbendazim and linuron observed at lower pH might be due to the higher concentration and mobility of H^+ ions in the solution. The surface of the AC was more positively charged, thus it was surrounded by hydroxonium ions, H_3O^+ and the electrostatic repulsive force between the selected pesticides and the charged surface. The highest removal efficiency of 91.83 % was for isoproturon was observed at pH=7.00.

On the other hand, the pHpzc of an SCG is an important characteristic that defines the pH at which the surface area has net electrical neutrality. The pHpzc of SCG was 8.40. At above pHpzc the surface of SCG is negatively charged and there is a strong electrostatic attraction between surface groups and selected pesticides. The value of pHpzc=8.40 of SCG suggested higher uptake of carbendazim, linuron and isoproturon Fig. 5. 6. Based on the results of pH effect on selected pesticides adsorption, as an optimum pH value for the further experiment for carbendazim, linuron, pH=5.00 was selected and pH=7.00 for isoproturon.

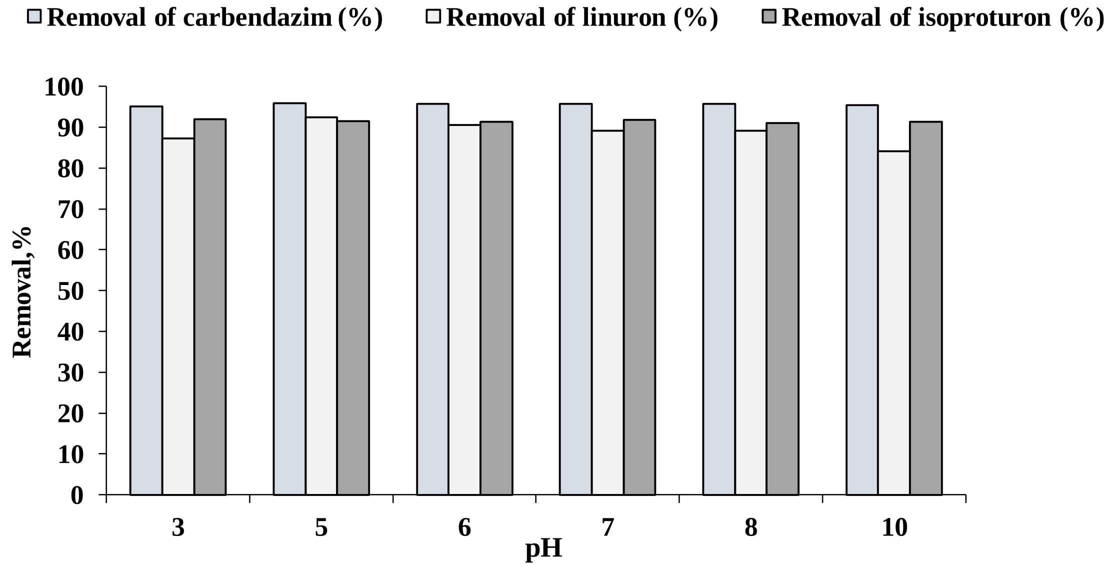


Figure 5. 5. Effect of pH on adsorption of carbendazim, linuron and isoproturon on SCG

5. 2. 2. Effect of solution pH on adsorption (DSAC)

The influence of pH on the DSAC removal, % for carbendazim, linuron and isoproturon was explored in the pH range from 3.0 to 10.0 (Figure 5. 6). The solutions of selected pesticides (5 mg L^{-1}) were in contact with the adsorbent (3 g L^{-1}) for 60 min at room temperature. The results of the removal percentage of carbendazim and linuron showed there is no significant difference ($P \leq 0.05$) between pH=5.00 to 8.00 and pH=3.00 to 8.00 at 60 min, respectively. The removal efficiencies of carbendazim, linuron and isoproturon at pH = 7.00 were 94.26, 95.37% and 90.03 %, respectively. The pH = 7.00 was selected as the optimum value. For carbendazim and linuron, the removal percentage values decreased slightly at the pH values higher than 7.00. In contrast, the removal percentage values of isoproturon changed from 90.03 % at pH 7.00 to 83.52 % at pH 10.00. Also, the adsorbent surface is affected by different pH values.

For any activated carbon, the surface functional groups and pH_{pzc} are essential characteristics as they indicate: the acidity/basicity of the adsorbent, the type of activated carbon (either H- or L-type), and the net carbon surface charge in solution. The acidic functionality of the DSAC surface is linked with oxygen-containing groups (e.g., carboxylic, anhydrides, lactones and phenols). The fundamental functional groups include oxygen-containing species such as the carbon basal plane system ketonic, pyronic, chromenic, and p-electron [300]. The surface charge of the DSAC was estimated by pH_{pzc} examination; the pH_{pzc} obtained was 8.60. The DSAC surface is loaded favorably below pH_{pzc} and charged negatively above pHpzc. Activated carbons with a pH_{PZC} higher than the pH of the solution, have positive surface charges. Therefore, there is a strong attraction between the adsorbent and adsorbate molecules. Generally, the value of pH_{PZC} is dependent on the presence of proton and hydroxyl groups on the surface of the DSAC sample. Consequently, the existence of acidic and/or fundamental impurities on the surface of DSAC samples may affect the quality of these materials.

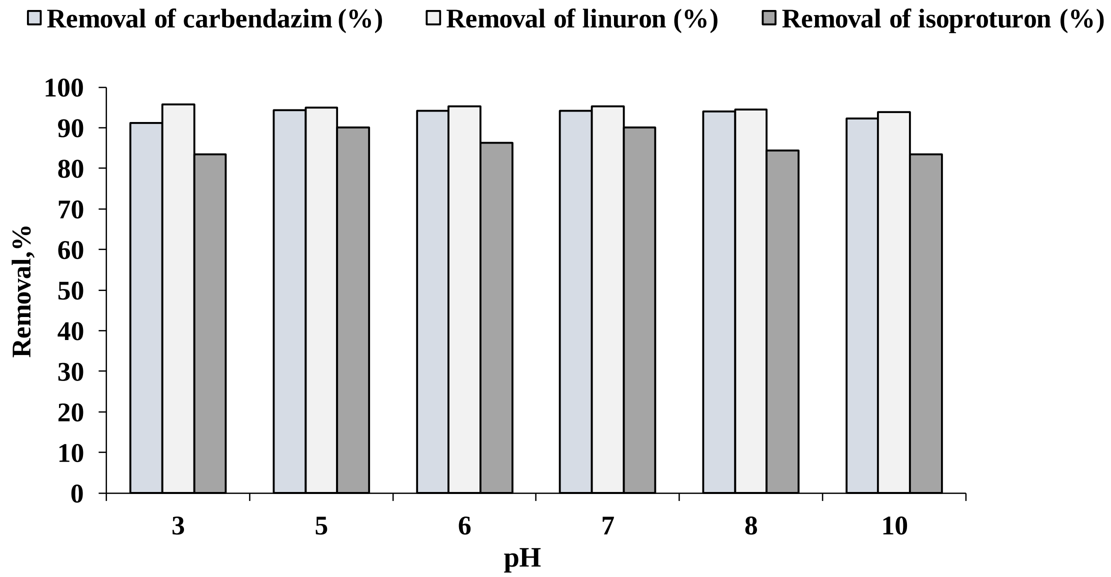


Figure 5. 6. Effect of pH on adsorption of carbendazim, linuron and isoproturon on DSAC

5. 2. 3. Effect of solution pH on adsorption Activated carbon (NORIT SA2)

Figure 5. 7 presented the effect of pH on the adsorption of carbendazim, linuron and isoproturon onto the Activated carbon (NORIT SA2). It can be seen from the figure 5. 7 that the removal percentage of selected pesticides depended on pH value strongly, and the maximum removal efficiency was obtained at pH = 7.00. The pH dependence of adsorption capacity could be explained in terms of the ionization of carbendazim, linuron and isoproturon and the protonation of functional group on the Activated carbon (NORIT SA2). The net charge on carbon surface is positive at a solution pH lower than that corresponding to pH_{PZC} and is negative at a solution pH higher than pH_{PZC}. Therefore, determining the pH_{PZC} for the carbon content is very crucial. The point of zero charge pH_{PZC} of the Activated carbon (NORIT SA2) was found to be 7.65. At pH 7.00, the removal of the selected pesticides was maximal. At $pH < pH_{PZC}$, the adsorbent has a positive surface charge and can act as an anion exchanger, while at $pH > pH_{PZC}$, the surface charge of the adsorbent is negative, which benefits for cations adsorption.

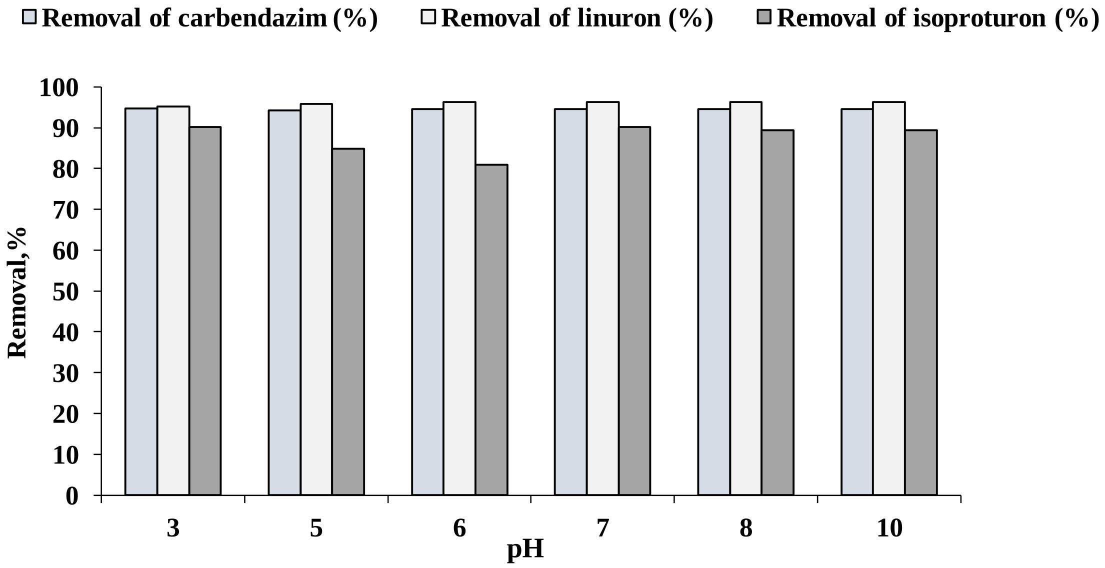


Figure 5. 7. Effect of pH on adsorption of carbendazim, linuron and isoproturon on Activated carbon (NORIT SA2).

5. 2. 4. Effect of solution pH on adsorption on Activated carbon (NORIT HYDRODARCO C)

pH is one of the critical parameters because it impacts the phenomenon of the sorbent surface charges, the degree of ionization and the speciation of sorbate species [301]. The adsorption of carbendazim, linuron and isoproturon were studied over the pH range of 3.00 – 10.00 and selected pesticides removals are shown in Figure 5. 8. Maximum removal percentage of carbendazim and linuron were achieved at pH 7.00, for isoproturon at pH 3.00. The influence of pH on the adsorption capacity removal efficiency of adsorbent can be attributed to the surface charges and (carbendazim, linuron and isoproturon) speciation in the solution.

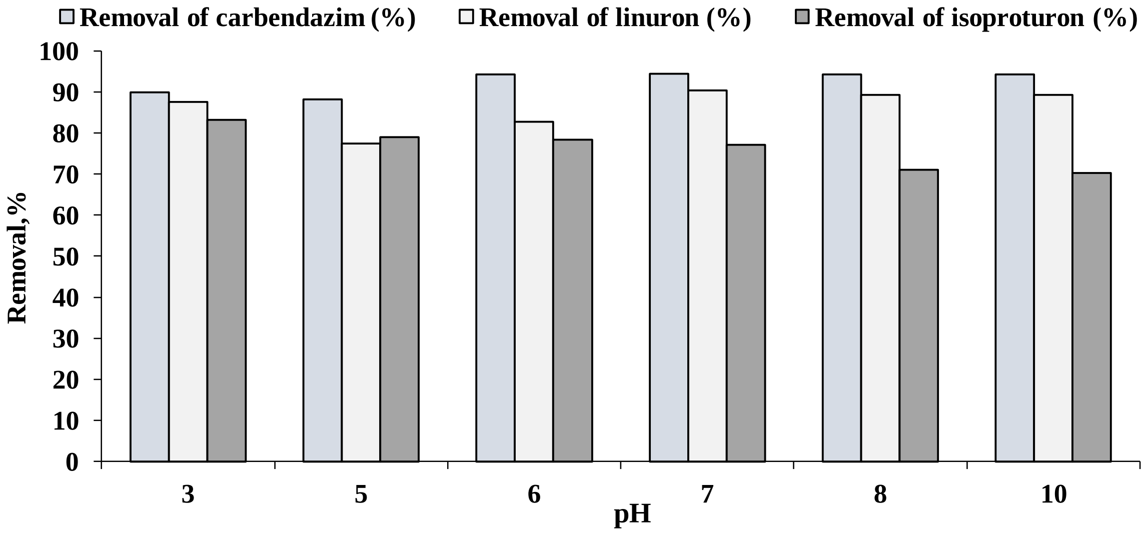


Figure 5. 8. Effect of pH on adsorption of carbendazim, linuron and isoproturon on Activated carbon (NORIT HYDRODARCO C)

5. 2. 5. Effect of solution pH on adsorption (Zeolite, type: ZSM-5)

It is well known that both the adsorbent and the adsorbate species in the solution are affected by the pH of the surface charge. (Figure 5. 9) shows the effects of pH on carbendazim, linuron and isoproturon adsorption by Zeolite, type: ZSM-5. Adsorbent, across the pH range 3.00 –10.00. The removal efficiency of carbendazim at pH 5.00 was 99.40 %, which indicate the optimum pH. It is evident from the figure 5.9 that the adsorption efficiencies of linuron and isoproturon reached the maximum values of 87.75 % and 92.55 % at acidic pH (3.00 and 5.00), respectively, but decreased gradually with the increase in pH.

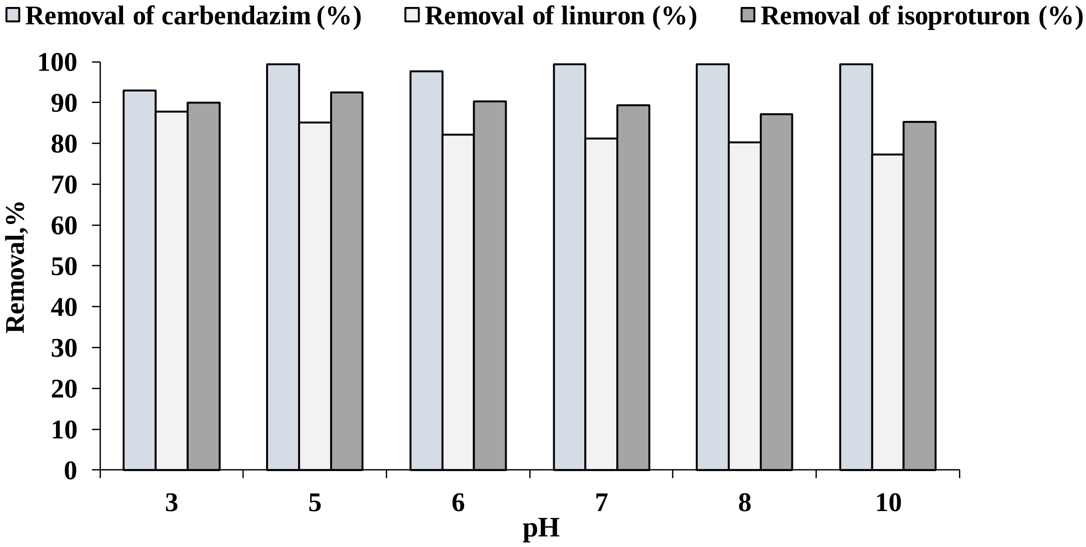


Figure 5. 9. Effect of pH on adsorption of carbendazim, linuron and isoproturon on (Zeolite, type: ZSM-5).

5. 2. 6. Conclusions

Table 5. 4 shows the best pH values that give the highest removal of carbendazim when using different adsorbents. It was observed that the optimum pH value = 5.00 when using SCG and Zeolite, type: ZSM-5, where the removal efficiency was 95.83 % and 99.40 %, respectively. pH = 7.00 was optimal when removing carbendazim using DSAC, Activated carbon (NORIT SA2) and Activated carbon (NORIT HYDRODARCO C) andthe removal efficiency was 94.26 %, 94.60 % and 94.37 %, respectively.

Table 5. 5 displays the optimum pH values that give the highest removal of linuron when using selected adsorbents. The optimum pH value = 5.00 when using SCG to remove linuron, pH value = 7.00 when using DSAC, Activated carbon (NORIT SA2)

and Activated carbon (NORIT HYDRODARCO C) to remove linuron and pH= 3.00 when using Zeolite, type: ZSM-5. The percentage of removal was shown in Table 5. 5.

The effect of pH values on the removal of the isoproturon was variable, Table 5. 6, pH = 7.00 when using SCG, DSAC and Activated carbon (NORIT SA2), pH = 3.00 when using Activated carbon (NORIT HYDRODARCO C) and pH = 5.00 when using Zeolite, type: ZSM-5.

Table 5. 4. Effect of pH values on the removal of the carbendazim

Adsorbent	pH	Removal of Carbendazim
SCG	5	95.83%
DSAC	7	94.26%
Activated carbon (NORIT SA2)	7	94.60%
Activated carbon (NORIT HYDRODARCO C)	7	94.37%
Zeolite, type: ZSM-5	5	99.40 %,

Table 5. 5. Effect of pH values on the removal of the linuron

Adsorbent	pH	Removal of Linuron
SCG	5	92.45%
DSAC	7	95.37%
Activated carbon (NORIT SA2)	7	96.25%
Activated carbon (NORIT HYDRODARCO C)	7	90.36%
Zeolite, type: ZSM-5	3	87.75%

Table 5. 6. Effect of pH values on the removal of the isoproturon

Adsorbent	pH	Removal of Isoproturon
SCG	7	91.83 %
DSAC	7	90.03 %
Activated carbon (NORIT SA2)	7	90.12%
Activated carbon (NORIT HYDRODARCO C)	3	83.21%
Zeolite, type: ZSM-5	5	92.55 %

5. 3. Influence of adsorption dosage

5. 3. 1. Influence of adsorption dosage (SCG)

Figure 5. 10 (a, b and c) depicts the removal efficiencies of carbendazim, linuron and isoproturon adsorbed by selected adsorbent dosages ranged from 77.73 to 97.65 %, from 21.50 to 91. 80 % and from 45.66% to 94.00%, respectively, with an increase in the mass of adsorbent from 0.2 to 2.4 g L^{-1} for carbendazim and linuron and from 0.2 to 4 g L^{-1} for isoproturon. After that, removal efficiencies reached a constant values probably indicated by higher number of binding sites available for sorption. Statistical analysis for carbendazim, linuron and isoproturon showed that there is a significant difference ($P \leq 0.05$) between selected SCG dosage at pH= 5.00 for carbendazim and linuron and pH= 7.00 for isoproturon at 30 min. Whereas no significant difference ($P \leq 0.05$) was between SCG dosages at 1.00, 2.00 and 2.40 g L^{-1} for carbendazim as well as linuron showed no significant difference ($P \leq 0.05$) just between SCG dosages at 2.00 and 2.40 g L^{-1}. Also, no significant difference ($P \leq 0.05$) is between SCG dosages at 3.00 and 4.00 g L^{-1} for isoproturon. The optimum chosen doses were 1.00, 2.00 and 3.00 g L^{-1} for carbendazim, linuron and isoproturon, respectively.

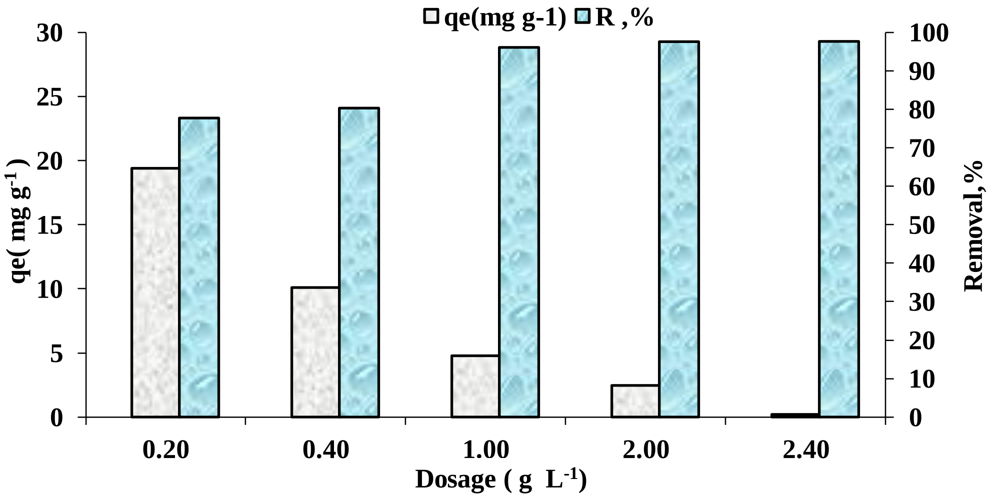


Figure. 5. 10 a. Influence of (SCG) dosage on the carbendazim adsorption process (C0 =5 mg L^{-1}, Contact time = 30 min, pH=5.00)

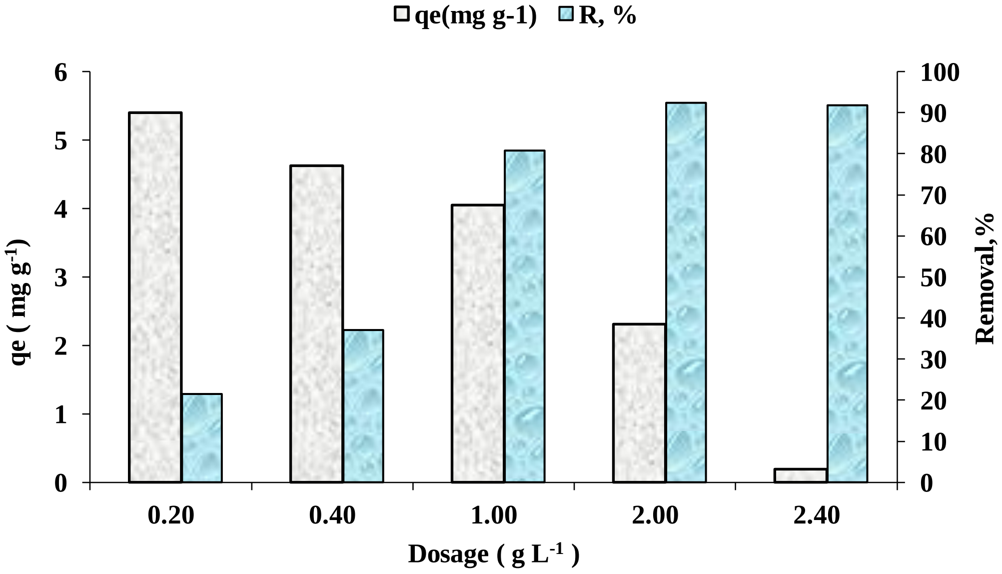


Figure. 5. 10b. Influence of (SCG) dosage on the linuron adsorption process (C$_0$ =5 mg L^{-1}, Contact time = 30 min, pH=5.00)

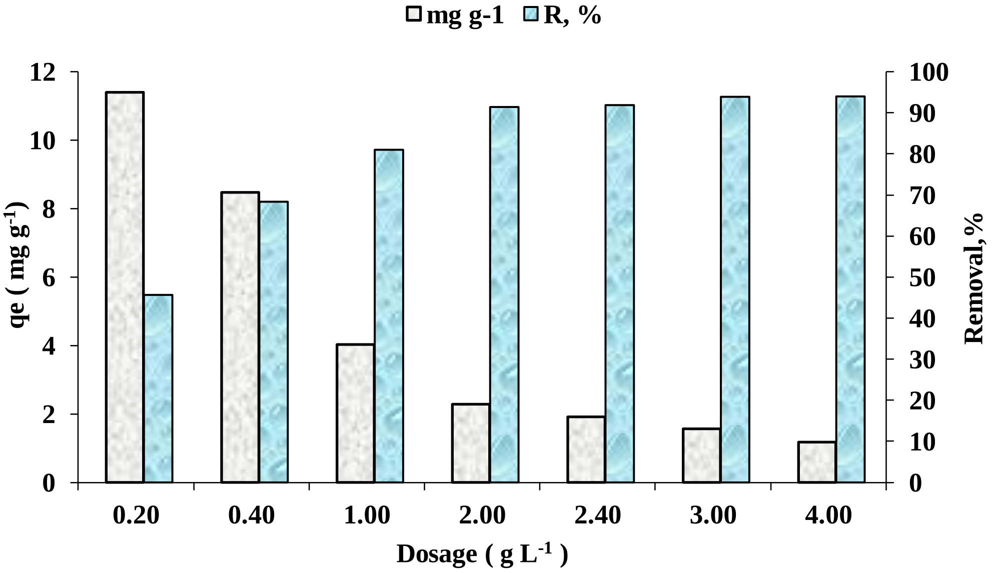


Figure. 5. 10 c. Influence of SCG dosage on the isoproturon adsorption process

(C_0 =5 mg L-1, Contact time = 30 min, pH=7.00)

Increased adsorbent dosage caused more adsorption sites which indicated that more adsorbate was attached to the surface. Further increase in SCG may not result in more effective adsorption due to the interference between binding sites of SCG doses. SCG was highly efficient in removing pesticides, such as linuron and carbendazim. Efficiency depends on the dosage of adsorbent used and varies by the type of contaminant.

5. 3. 2. Influence of adsorption dosage (DSAC)

The removal efficiencies of selected pesticides (carbendazim, linuron and isoproturon) by DSAC are shown in Figure 5. 11 (a, b and c). The removal efficiencies ranged from 67.80 to 93.99 %, from 87.15 to 95.98 % and from 54.00% to 88.25%, respectively, The mass of adsorbent from 1.00 to 4.00 g L^{-1} was used to study the influences of different mass on the removal of selected pesticides. The Statistical analysis was applied to determine the optimum mass, which gives the highest adsorption capacity or the highest removal percentage.

The Statistical analysis showed that there is a significant difference ($P \leq 0.05$) between selected DSAC dosage for carbendazim, linuron and isoproturon at pH= 7.00 and 60 min. The optimum chosen doses were 3.00, 2.00 and 3.00 g L^{-1} for carbendazim, linuron and isoproturon, respectively. An increase in the concentrations of DSAC from 1.00 to 4.00 g L^{-1} resulted in decrease of the adsorption capacity for carbendazim, linuron and isoproturon Figure 5.11 (a, b and c). Any additional increment in the concentration of DSAC up to 4.00 g L^{-1} did not result in a remarkable reducing in the adsorption capacity, for any of the selected pesticides investigated. The adsorption capacity for all three pesticides exhibits the same trend; it drops urs with the increase in the dosage of the DSAC dosages. The reduction in the adsorption capacity at a higher dosage of DSAC is attributed to the rise in BET surface area of the adsorbent, i.e. increment within the number of available adsorption sites to tie the ions whose concentration within the solution is steady. The negligible change in the removal efficiency of DSAC above 3.00g L^{-1} for (carbendazim and isoproturon) and above 2.00 g L^{-1} for linuron might be attributed to the presence of excess active sites on the DSAC surface, relative to the constant concentration of carbendazim, linuron and isoproturon in solution. The removal efficiency and adsorption capacity of carbendazim, linuron and isoproturon do not grow at higher doses of DSAC due to overlapping and aggregation, on another hand, the electrostatic refusal of the adsorbent particles, which results in a reduction of the effective DSAC surface area and the number of available active sites [302]. Moreover, the higher doses of the DSAC also reduce the efficiency of suspension mixing, causing a slow transfer of mass. All these perceptions are an agreement with the literature regarding the adsorption of ions by diverse activated carbons which were prepared from lignocellulosic materials.

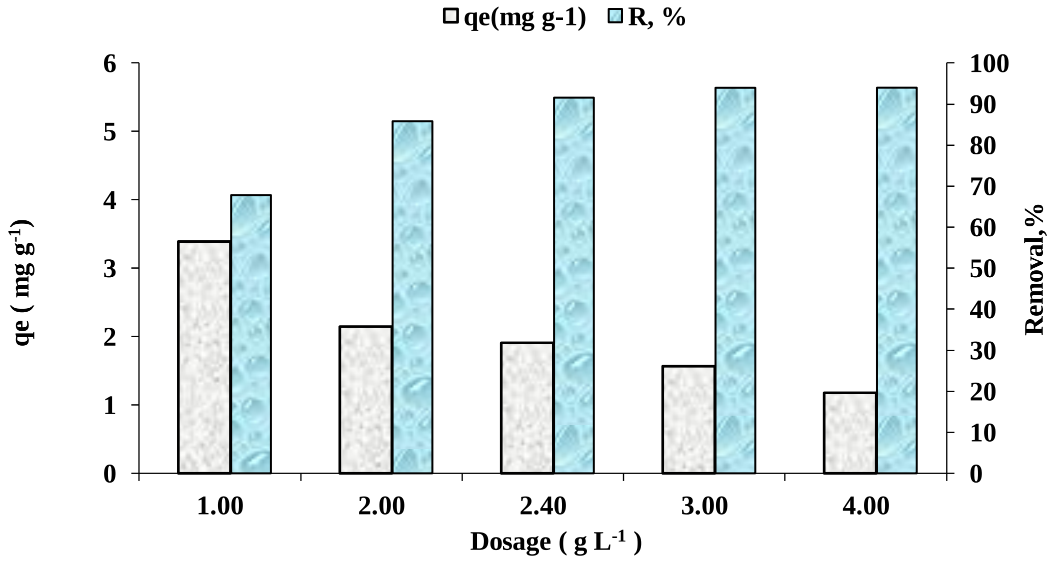


Figure 5. 11 a. Influence of (DSAC) dosage on the carbendazim adsorption process (C_0 =5 mg L^{-1}, Contact time = 60 min, pH = 7.00)

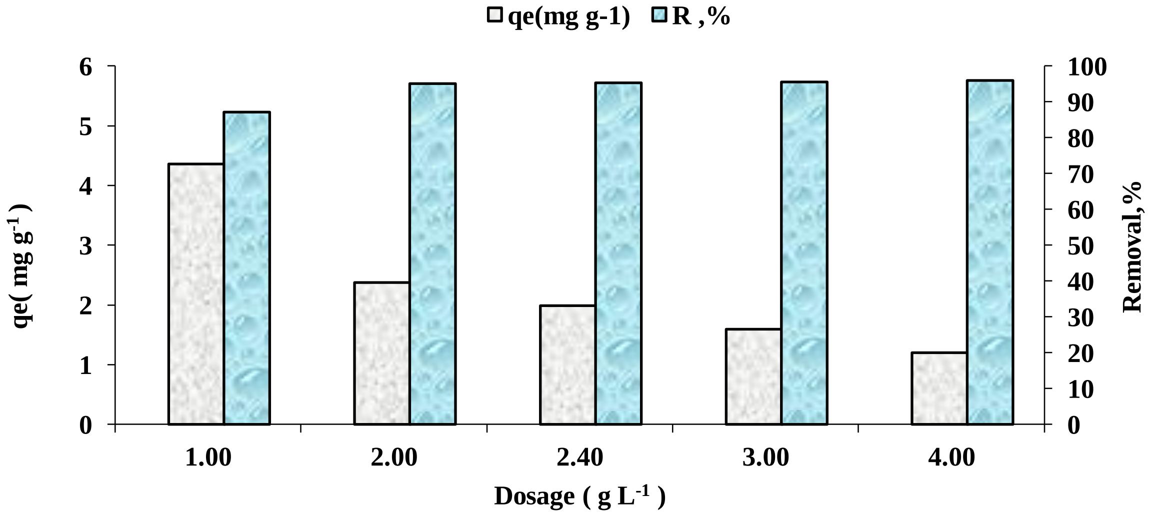


Figure 5. 11 b. Influence of (DSAC) dosage on the linuron adsorption process (C_0 =5 mg L^{-1}, Contact time = 60 min, pH = 7.00)

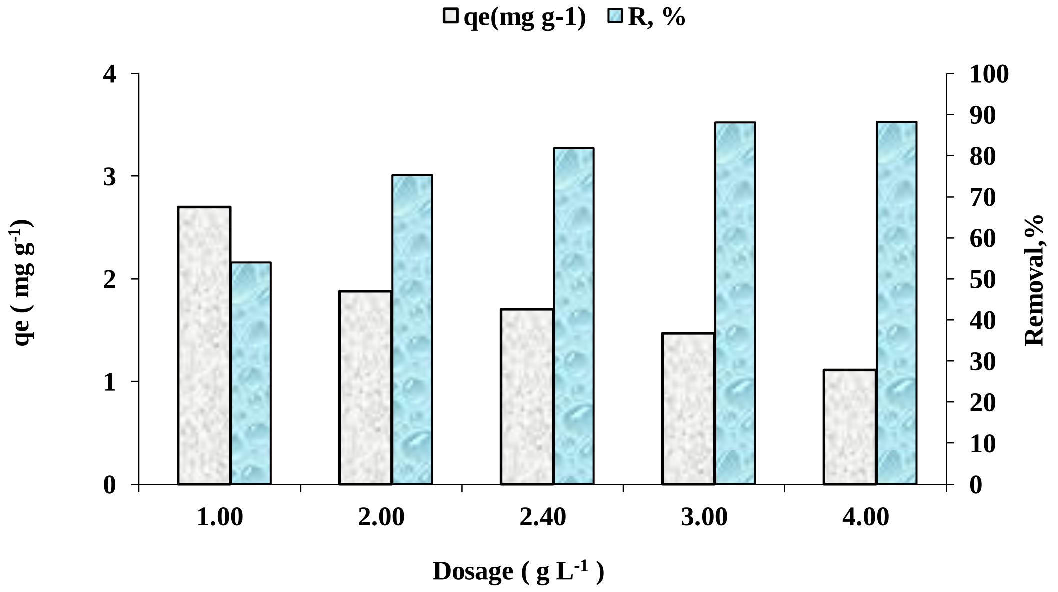


Figure 5. 11 c. Influence of (DSAC) dosage on the isoproturon adsorption process (C_o = 5 mg L^{-1}, Contact time = 60 min, pH = 7.00)

5. 3. 3. Influence of adsorption dosage Activated carbon (NORIT SA2)

Figure 5. 12 (a, b and c) shown the removal efficiencies of carbendazim, linuron and isoproturon by Activated carbon (NORIT SA2) ranged from 78.15 to 94.70%, from 94.80 to 96.25% and from 75.38 to 93.23%, respectively. Statistical analysis for carbendazim showed that there is a significant difference ($P \leq 0.05$) between selected Activated carbon (NORIT SA2) dosage at pH 7.00 and contact time at 60 min. No significant difference ($P \leq 0.05$) between Activated carbon (NORIT SA2) dosages at 0.10 and 0.24 g L^{-1}.

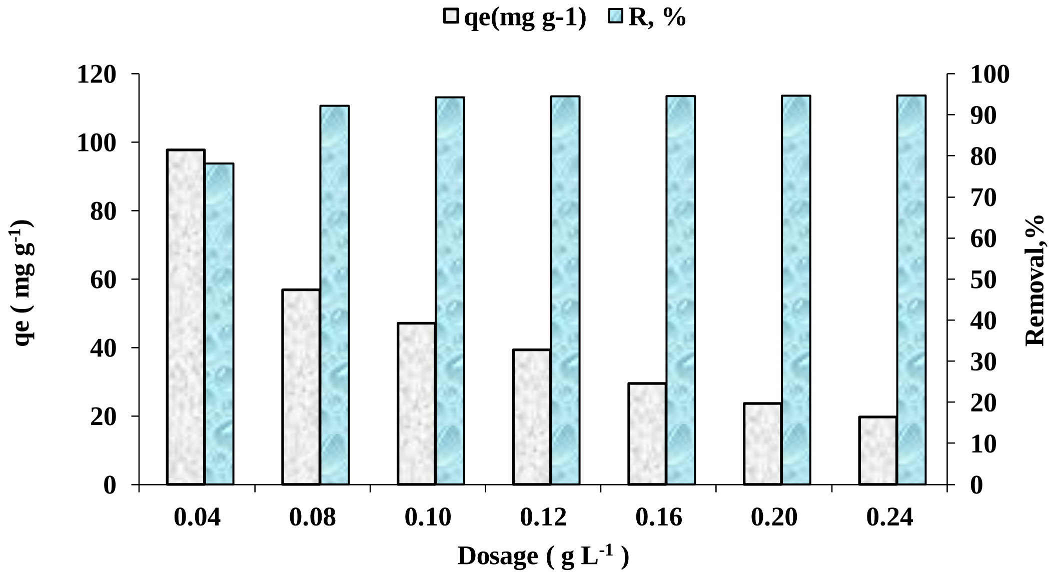


Figure 5. 12 a. Influence of (Activated carbon NORIT SA2) dosage on the carbendazim adsorption process (C_0 =5 mg L^{-1}, Cont. time = 60 min, pH = 7.00)

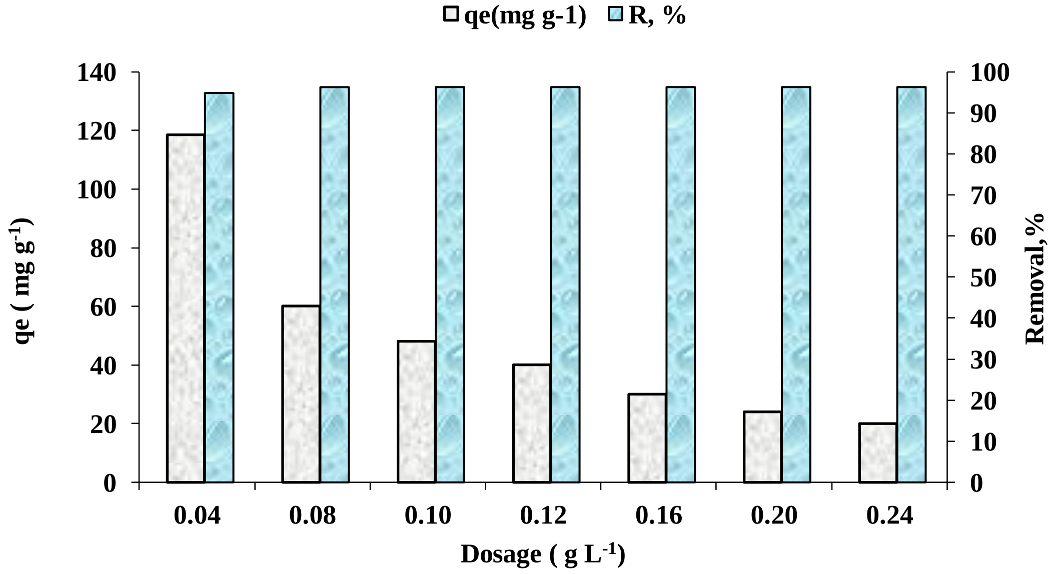


Figure 5. 12 b. Influence of (Activated carbon NORIT SA2) dosage on the linuron adsorption process (C_0 =5 mg L^{-1}, Cont. time = 30 min, pH = 7.00)

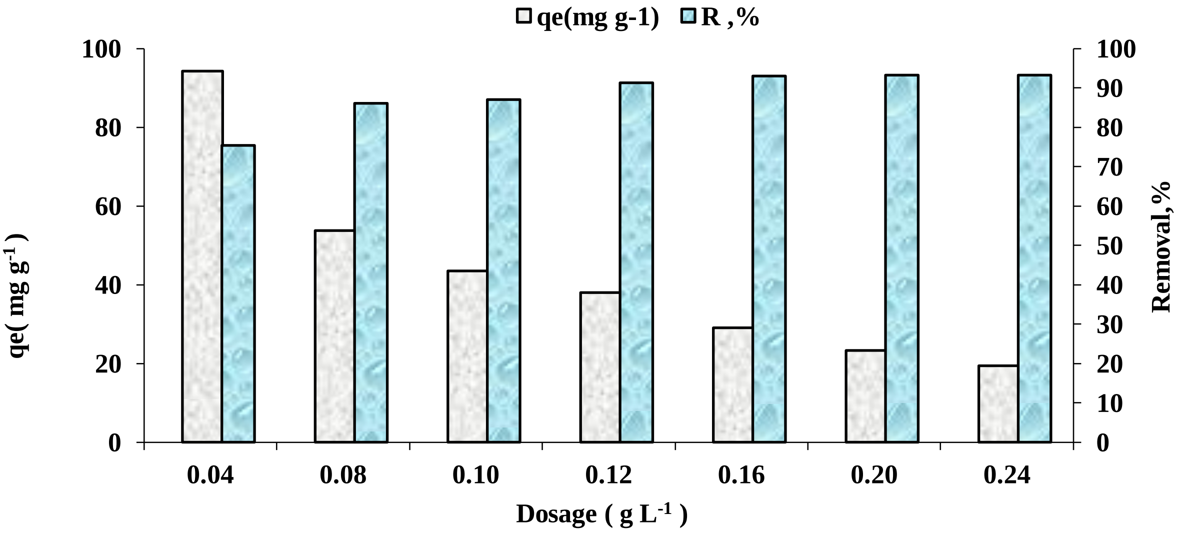


Figure 5. 12 c. Influence of (Activated carbon NORIT SA2) dosage on the isoproturon adsorption process (C_0 =5 mg L^{-1}, Cont. time = 30 min, pH = 7.00)

The dosage of 0.10 g L^{-1} of Activated carbon (NORIT SA2) was taken as an optimum mass. The statistical analysis for linuron and isoproturon indicated the dosages f 0.08 and 0.16 g L^{-1} for Activated carbon (NORIT SA2) at pH 7.00 and contact time at 30 min as optimum dosages, respectively. The adsorption capacities quickly reduced with the rise of adsorbent dosage from 0.04 to 0.08 g L^{-1} in all the cases, then the decrement is gradual, with the further growth of adsorbent dose to 0.24 g L^{-1}. The adsorption capacity of carbendazim, linuron and isoproturon decreased from 97.75 to 19.70 mg g^{-1}, from 118.50 to 20.04 mg g^{-1} and from 94.25 to 19.42 mg g^{-1}, respectively with the increment of adsorbent dosage. The low adsorption percentage can be ascribed to the truth that all the adsorbents have a limited numeral of active sites that would have reached saturation above a specific adsorbate concentration.

5. 3. 4. Influence of adsorption dosage of Activated carbon (NORIT HYDRODARCO C)

Figure 5. 13 (a, b and c) shown the removal efficiencies of carbendazim, linuron and isoproturon by Activated carbon (NORIT HYDRODARCO C) at different doses from

0.10 to 0.40 g L^{-1}. Statistical analysis for carbendazim shown that there is significant difference ($P \leq 0.05$) between selected Activated carbon (NORIT HYDRODARCO C) masses from 0.10 to 0.30 g L^{-1} at pH 7.00 and contact time of 60 min. No significant difference ($P \leq 0.05$) between Activated carbon (NORIT HYDRODARCO C) dosages at 0.30 and 0.40 g L^{-1} was observed. Dosage of 0.30 g L^{-1} was an optimum dosage. The results of statistical analysis for linuron and isoproturon showed the dosages 0.16 and 0.20 g L^{-1} at pH 7.00 , pH 3.00 and contact time of 30 min were an optimum dosages, respectively. It may be due to the overlapping of active sites at a higher dose. So, there was not any noticeable increase in the active surface area resulting due to the conglomeration of exchanger particles [303]. It is well evident from Figure 5.13 (a, b and c) that the removal of chosen pesticides increased with increment in the adsorbent dosage. It is evident that the removal of carbendazim, linuron and isoproturon ranged from 76.06 to 94.67 %, from 87.34 to 95.07 % and from 78.62 to 91.32 %, respectively. This is expected, since for a fixed initial solute concentration, increments in total adsorbent doses gives a higher surface area or adsorption sites and the adsorption potential raises. Various researchers have published similar results.

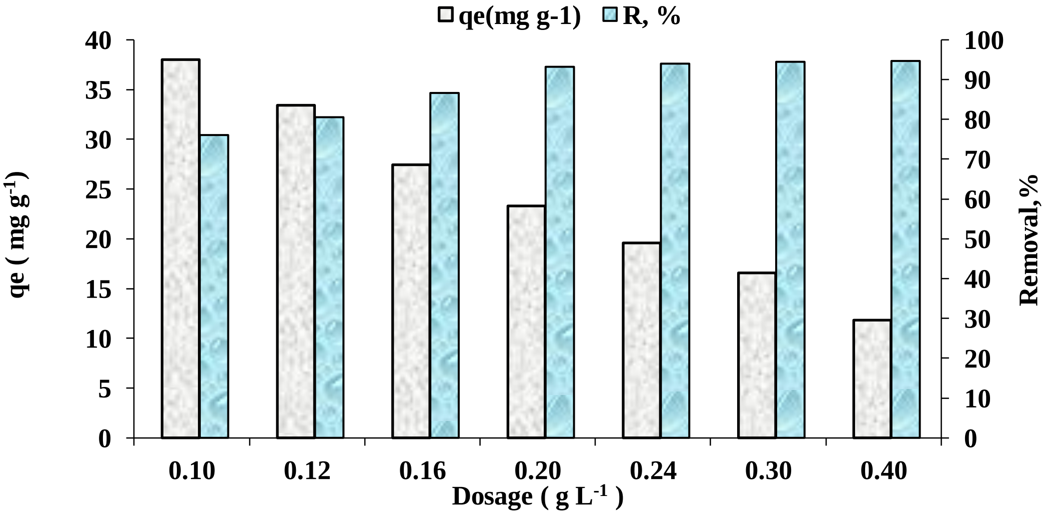


Figure 5. 13 a. Influence of (Activated carbon NORIT HYDRODARCO C) dosage on the carbendazim adsorption process (C_0 =5 mg L^{-1}, Cont. time = 60 min, pH = 7.00)

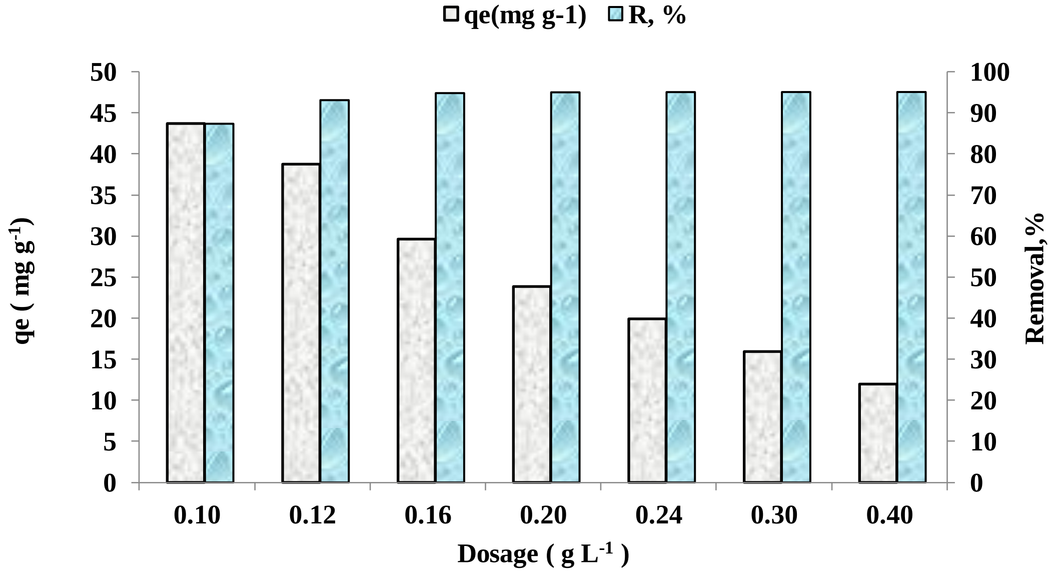


Figure 5. 13 b. Influence of (Activated carbon NORIT HYDRODARCO C) dosage on the linuron adsorption process (C_0 =5 mg L^{-1}, Cont. time = 30 min, pH = 7.00)

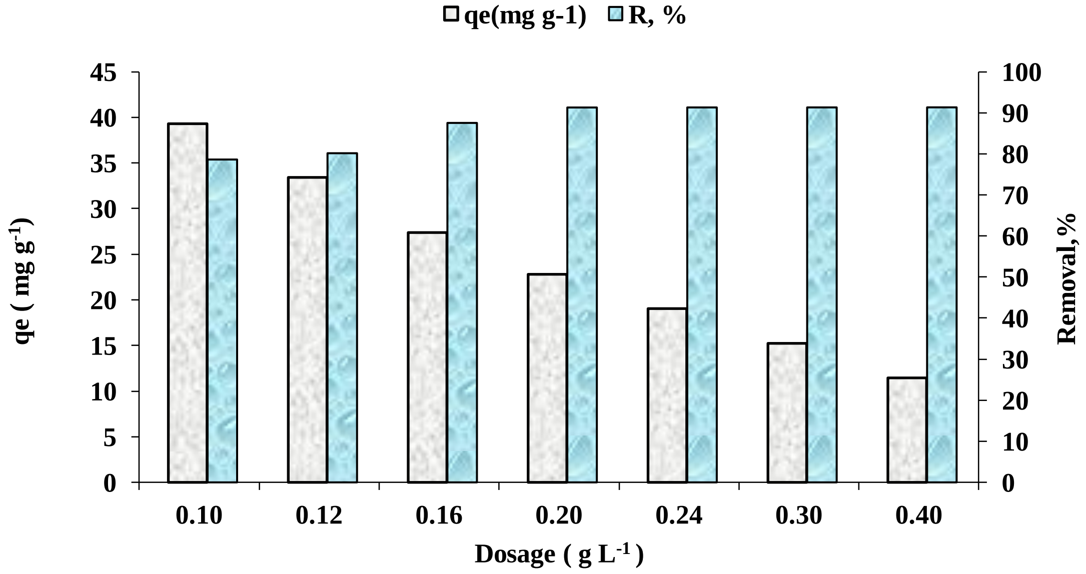


Figure 5. 13 c. Influence of (Activated carbon NORIT HYDRODARCO C) dosage on the isoproturon adsorption process (C_0 =5 mg L^{-1}, Cont. time = 30 min, pH = 3.00)

5. 3. 5. Influence of adsorption dosage (Zeolite, type: ZSM-5)

Figure 5. 14 (a, b and c) presented the removal percentage of carbendazim, linuron and isoproturon on Zeolite, type: ZSM-5 as adsorbent material. Adsorption experiments were carried out by adding various amounts of sorbents (1.00, 2.00, 2.40, 3.00, 4.00 and Figure 5.14 (a, b and c) showed the removal percentage of carbendazim, linuron and isoproturon on Zeolite, type: ZSM-5 as adsorbent material. Adsorption experiments were carried out by adding various amount of sorbents (1.00, 2.00, 2.40, 3.00, 4.00 and 5.00 g L^{-1}) for carbendazim and isoproturon and from (20.00, 30.00, 40.00, 50.00 and 60.00 g L^{-1}) for linuron. As noted there is a marked variation in dosage amounts used in removal carbendazim, linuron) and isoproturon. The removal efficiencies of carbendazim, linuron and isoproturon by Zeolite, type: ZSM-5 ranged from 92.63 to 99.43%, from 79.91 to 87.71% and from 75.40 to 92.54%, respectively.

Statistical analysis for carbendazim shown that there is no significant difference ($P \leq 0.05$) between Zeolite, type: ZSM-5 dosages at 2.00, 2.40, 3.00,4.00 and 5.00 g L^{-1} at pH 5.00 and contact time of 60 min. The dosage 2.00 g L^{-1} of Zeolite, type: ZSM-5 was taken as an optimum mass. The optimum mass for removal of linuron and isoproturon were 40.00 and 3.00 g L^{-1} at pH 3.00, pH 5.00 and contact time of 60 min, respectively. These results indicate that the removal percentage of selected pesticides raises with an increment in the adsorbent dosage from 1.00 to 5.00 g L^{-1} for carbendazim and isoproturon and from 20.00 to 60.00 g L^{-1} for linuron. These results were expected as with increased adsorbent dosage, the available sorption surface and availability of more adsorption sites rise, which results in more adsorbate attributed to the surfaces [304,305].

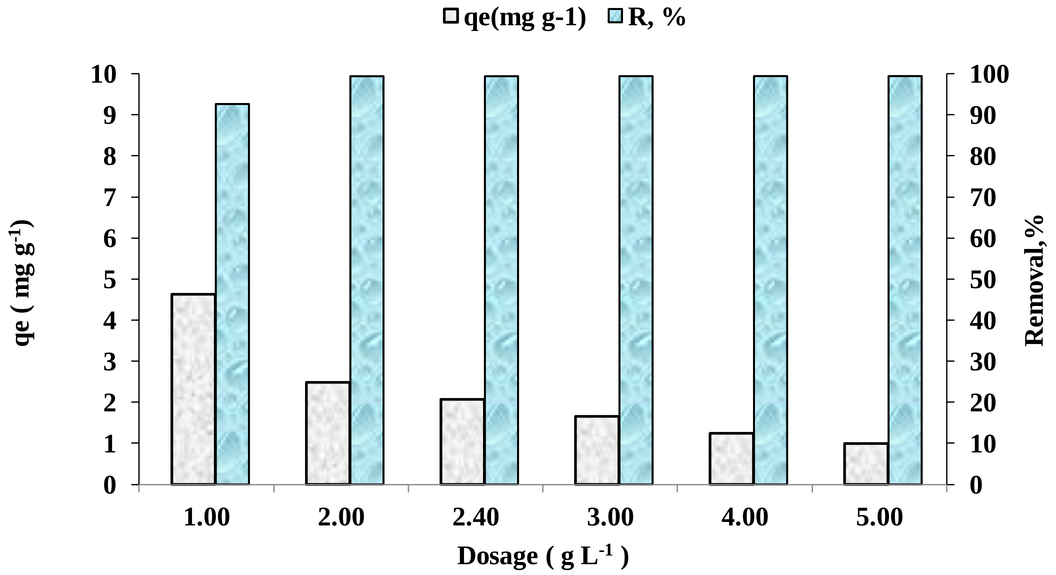


Figure 5. 14 a. Influence of (Zeolite, type: ZSM-5) dosage on the carbendazim adsorption process (C_0 = 5 mg L^{-1}, Cont. time = 60 min, pH = 5.00)

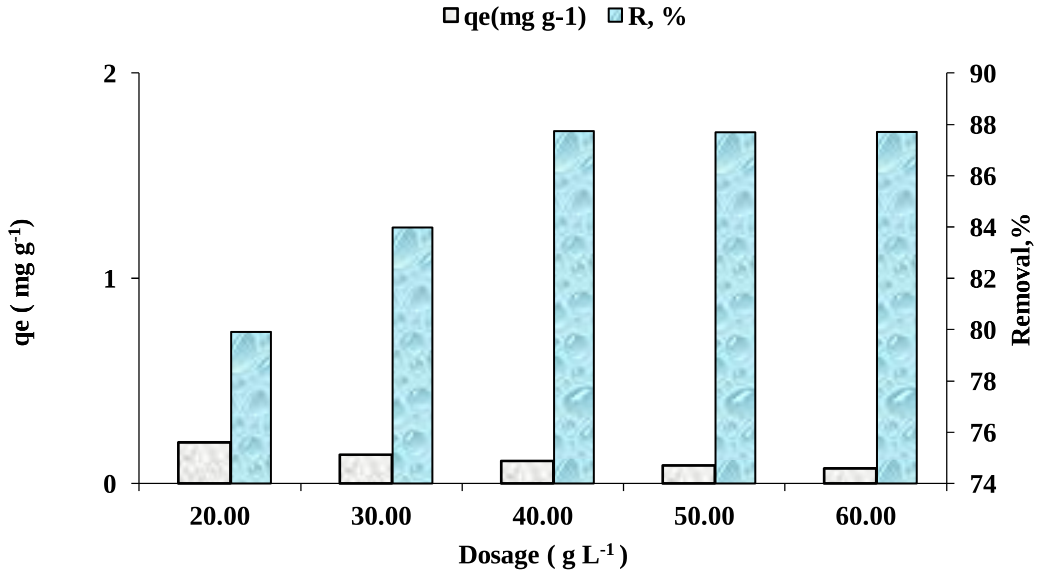


Figure 5. 14 b. Influence of Zeolite, type: ZSM-5 dosage on the linuron adsorption process (C_0 = 5 mg L^{-1}, Cont. time = 60 min, pH = 3.50)

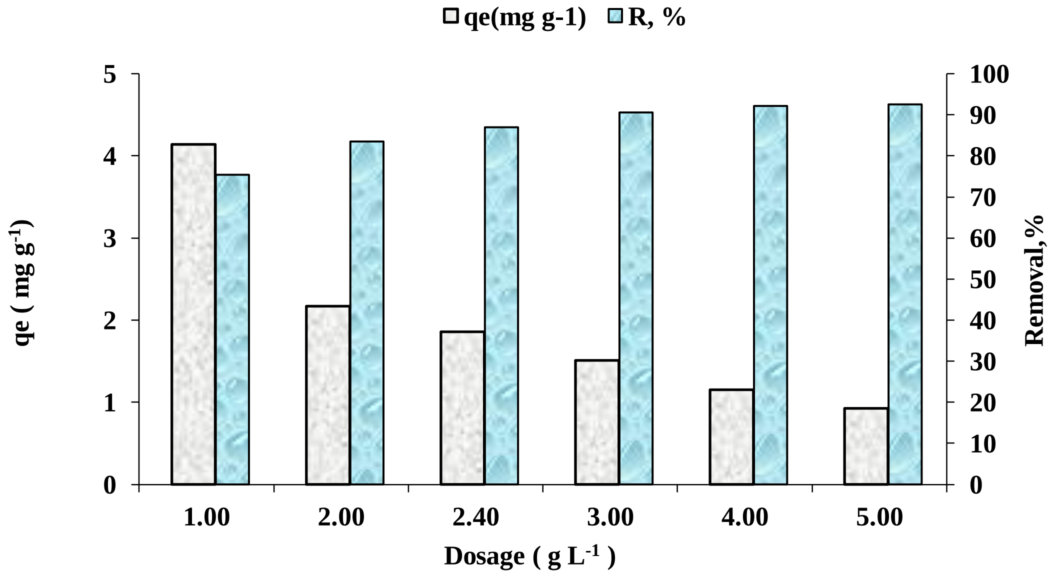


Figure 5. 14 c. Influence of (Zeolite, type: ZSM-5) dosage on the isoproturon adsorption process (C_0 = 5 mg L^{-1}, Cont. time = 60 min, pH = 5.00)

5. 3. 6. Conclusions

The study of influence of adsorbent dosages showed the difference in the optimum doses values among the selected adsorbents. Table 5. 7. Shows the optimum doses of adsorbents that gave the best removal of the selected pesticides. The lowest dose value was 0.08 (g L^{-1}) and the highest value was 40.00 (g L^{-1}). The lowest optimal doses used to remove selected pesticides were observed using adsorbents Activated carbon (NORIT SA2) and Activated carbon (NORIT HYDRODARCO C).

Table 5. 7. Comparison of optimum doses

Adsorbent	The optimal dose (g L^{-1}) in removal of carbendazim	The optimal dose (g L^{-1}) in removal of linuron	The optimal dose (g L^{-1}) in removal of isoproturon
SCG	1.00	2.00	3.00
DSAC	3.00	2.00	3.00
Activated carbon (NORIT SA2)	0.10	0.08	0.16
Activated carbon (NORIT HYDRODARCO C)	0.30	0.16	0.20
Zeolite, type: ZSM-5	2.00	40.00	3.00

5. 4. Influence of contact time

5. 4. 1. Influence of contact time (SCG)

Adsorption of carbendazim, linuron and isoproturon by SCG at various contact times in the solution with an initial carbendazim, linuron and isoproturon concentration of 5 mg L^{-1} is represented in Figure 5. 15 (a, b and c). It can be seen that the removal efficiency of carbendazim and linuron by adsorbents at 20 min was 95.13 and 92.13%, respectively at doses 1.00 and 2.00 g L^{-1} of SCG and pH value of 5.00. Also, the removal efficiency of isoproturon by adsorbents at 5.00 min was 93.02 % at dose 3.00 g L^{-1} of SCG and pH value of 7.00. Prolonging the contact time could not significantly improve carbendazim, linuron and isoproturon adsorption capacity.

Based on the statistical analysis, there is the slight significant difference in the removal efficiency ($P \leq 0.05$) between selected times (min) when the carbendazim and linuron were used. Figure 5. 15 (a, b) showed that the highest removal efficiencies were observed at 120 min which were 96.64 % and 93.22 %, while at 20 min were 95.13 % and 92.13 %, respectively. According to the relationship presented in Figure 5. 15 (a, b), there was a significant difference in the removal efficiency between the removal time at 20 min and 120 min. The removal time is crucial during the treatment. So, the removal efficiency at 20 min could be used for the future experiments. Figure 5.15 (c) has shown that the highest removal efficiency was observed at 90 and 120 min which was 94.30 % , while at 5.00 min was 93.02 %. The removal efficiency at 5.00 min could be used for the future experiments. The results point out that the sorption process is fast at the begining of the contact period, while it becomes slower near the equilibrium, due to the difficuties to sorb on remaining surface sites. It could be explained by the kinetic mechanisms of sorption. Actually, at the beginning of the process, surface reactions present the leading process, while near the equilibrium, intra-particle diffusion play an important role.

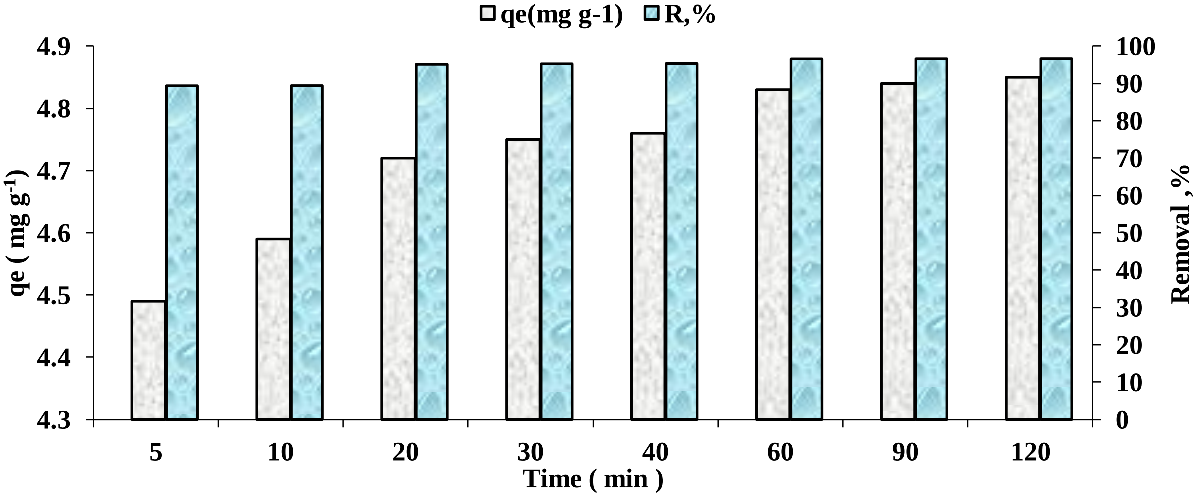


Figure 5. 15 a. Influence of contact time for carbendazim adsorption onto (SCG). ($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 1.00 g L^{-1}, pH= 5.00)

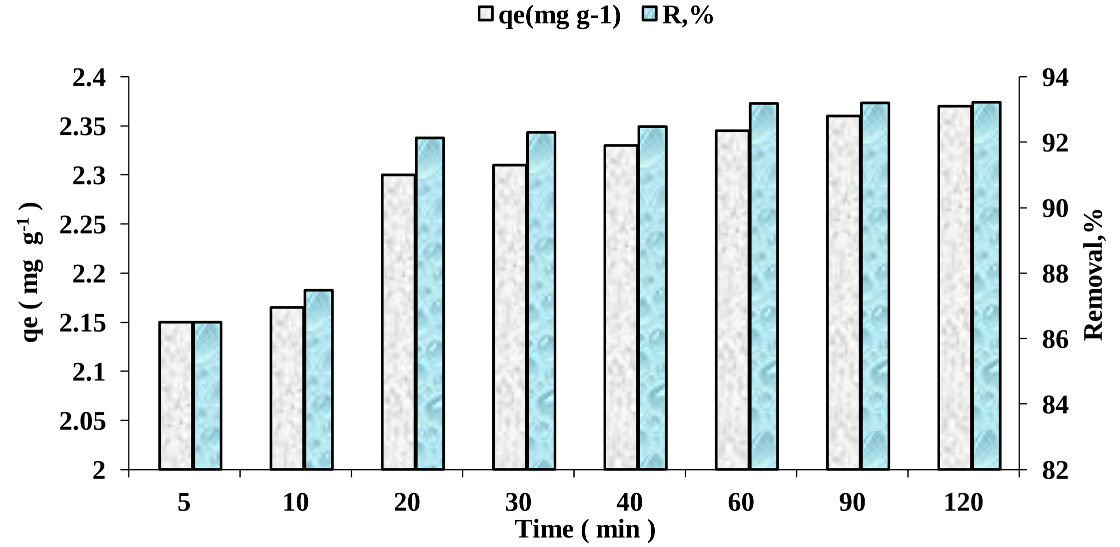


Figure 5. 15 b. Influence of contact time for linuron adsorption onto (SCG). ($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 2.00 g L^{-1}, pH= 5.00)

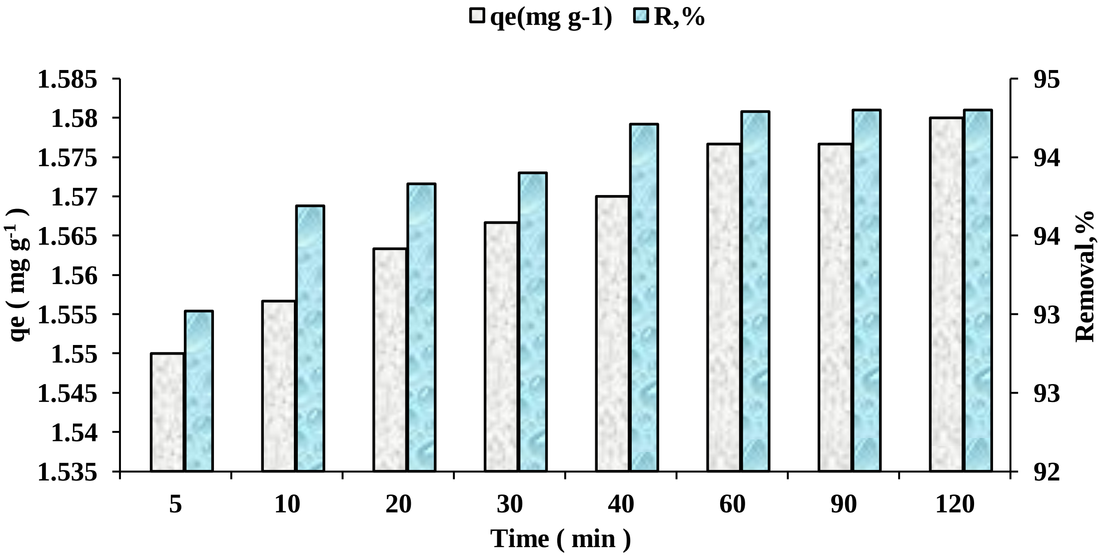


Figure 5. 15 c. Influence of contact time for isoproturon adsorption onto (SCG). ***($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)***

5. 4. 2. Influence of contact time (DSAC)

The contact time is a fundamental parameter in any transfer phenomena such as adsorption. The equilibrium adsorption capacity of carbendazim, linuron and isoproturon on DSAC was investigated to determine the time required to reach the equilibrium between adsorbent and selected pesticides solution (5 mg L^{-1}) and pH 7.00. Figure 5. 16 (a, b and c) presented the removal percentage of carbendazim, linuron and isoproturon increases from 22.20 to 94.14%, 82.51 to 95.11% and 33.63 to 91.81 % with increase in the contact time from 5.00 to 120 min. Based on the results it can be observed that the adsorption of selected pesticides occurs in two phases. The initial phase is fast due to the high concentration of free active sites on the DSAC surface, and due to the high initial concentration of pesticides. In the second phase, a reduction in the number of available

DSAC active sites and the reduction in residual concentrations of the pollutants occur. These two phenomena significantly reduce the rate of adsorption. Additionally, there is a possibility of the occurrence of the electrostatic repulsion on the surface due to the high amount of bounded cations [306]. During the first 10 min, the removal percentages of carbendazim, linuron and isoproturon were 84.47, 82.55 and 57.94%, respectively. After 10 min, it can be observed that the removal efficiency increase with the contact time until an equilibrium state is reached at 30, 40 and 90 min for carbendazim, linuron and isoproturon, respectively. Then, it increases slightly for the time period of 30 to 120, 40 to 120 and 90 to 120 min, respectively. This indicates that initial concentrations and different contact time played an important role in the adsorption of selected pesticides on DSAC. The assessment of the effect of contact time on the adsorption efficiency showed that after 30, 40 and 90 min there was no significant change in the adsorption rate. Accordingly, as the optimum contact times, 30, 40 and 90 min periods were chosen.

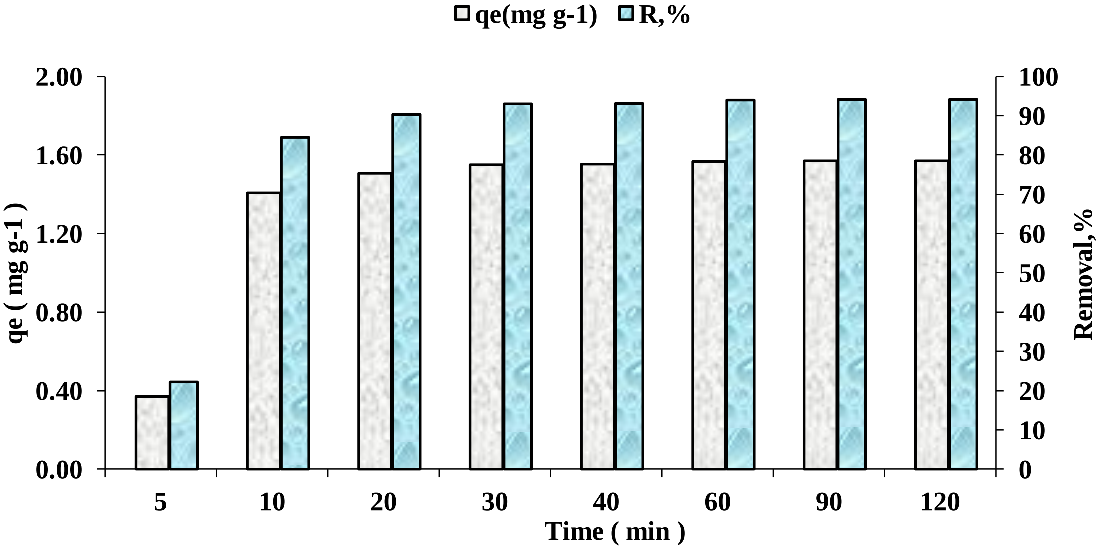


Figure 5. 16 a. Influence of contact time for carbendazim adsorption onto (DSAC). ($C_\circ$ = 5 mg L^{-1}, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

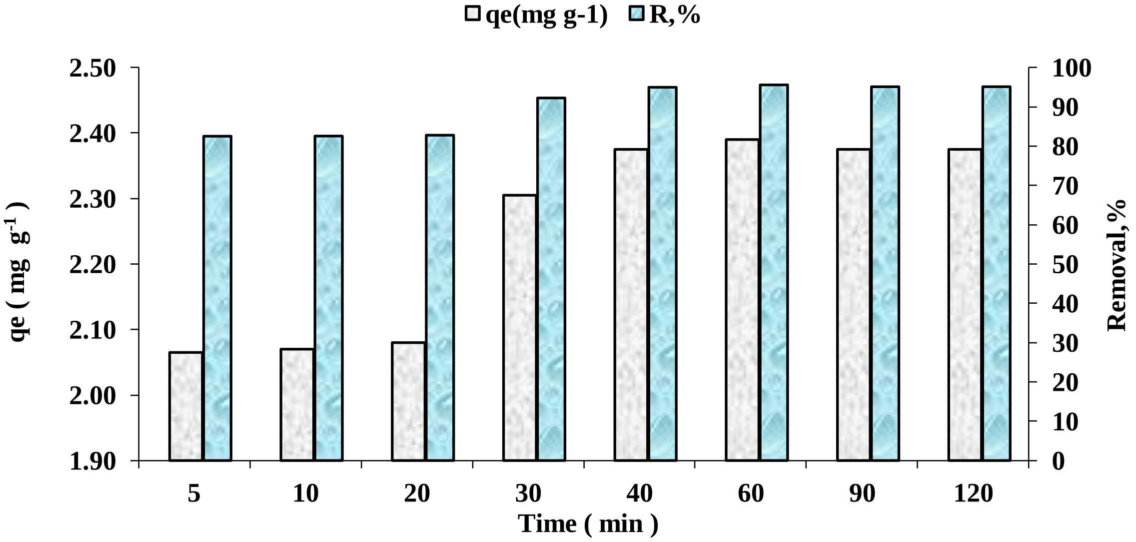


Figure 5. 16 b. Influence of contact time for linuron adsorption onto (SDAC).
($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 2.00 g L^{-1}, pH= 7.00)

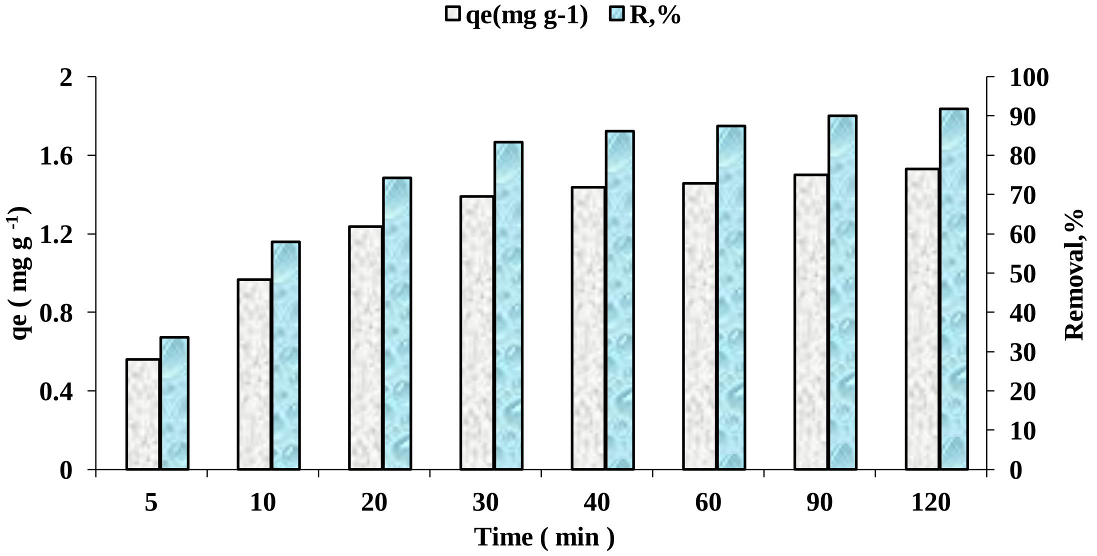


Figure 5. 16 c. Influence of contact time for isoproturon adsorption onto (DSAC).
($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

5. 4. 3. Influence of contact time of Activated carbon NORIT SA2

The effect of contact time on the Activated carbon (NORIT SA2) adsorption capacity for carbendazim, linuron and isoproturon were studied in the time range 5 – 120 min. The solutions of carbendazim, linuron and isoproturon of 5 mg L−1 were in contact with the adsorbent of 0.10, 0.08 and 0.16 g L-1 at pH 7.00, respectively. Contact time is unavoidably the basic parameter for all mass transfer phenomena, such as adsorption (Stawiński et al., 2017). Figure 5. 17 (a, b and c) shows that selected pesticides (carbendazim, linuron and isoproturon) adsorption is fast during the initial contact time and then slowly increases at higher contact time to reach the equilibrium at 60, 10 and 20 min where the removal percentage of carbendazim, linuron and isoproturon were 93.20%, 95.83% and 93.13%, respectively. Shaking and the concentration gradient on the active surface of the Activated carbon (NORIT SA2) might cause rapid adsorption at the beginning of the process. The assessment of the effect of contact time on the adsorption efficiency for carbendazim, linuron and isoproturon showed that after 60, 10 and 20 min, there was no significant change in the adsorption rate. Accordingly, as the optimum contact time, 60, 10 and 20 min period was chosen for further experiments.

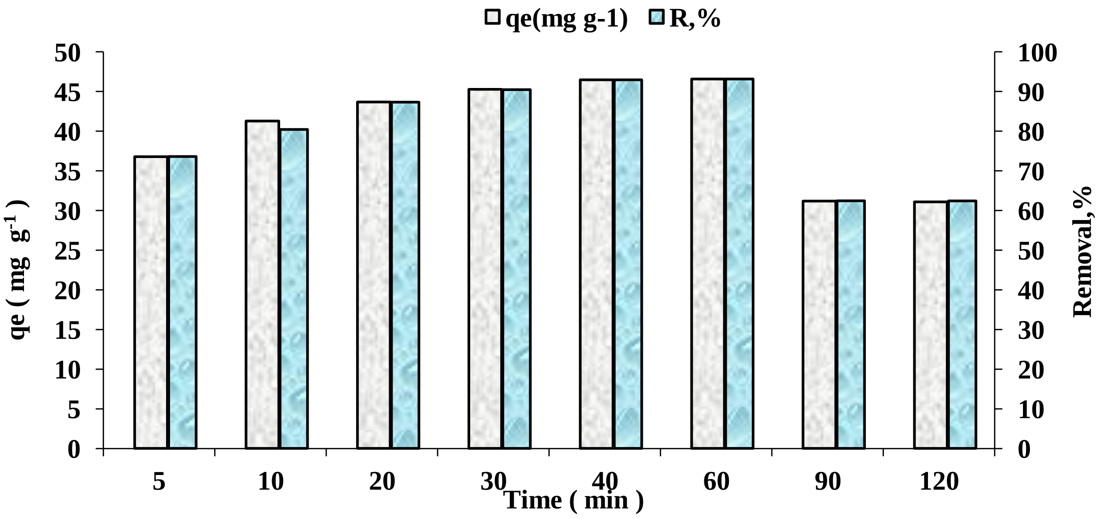


Figure 5. 17 a. Influence of contact time for isoproturon adsorption onto (DSAC).
($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

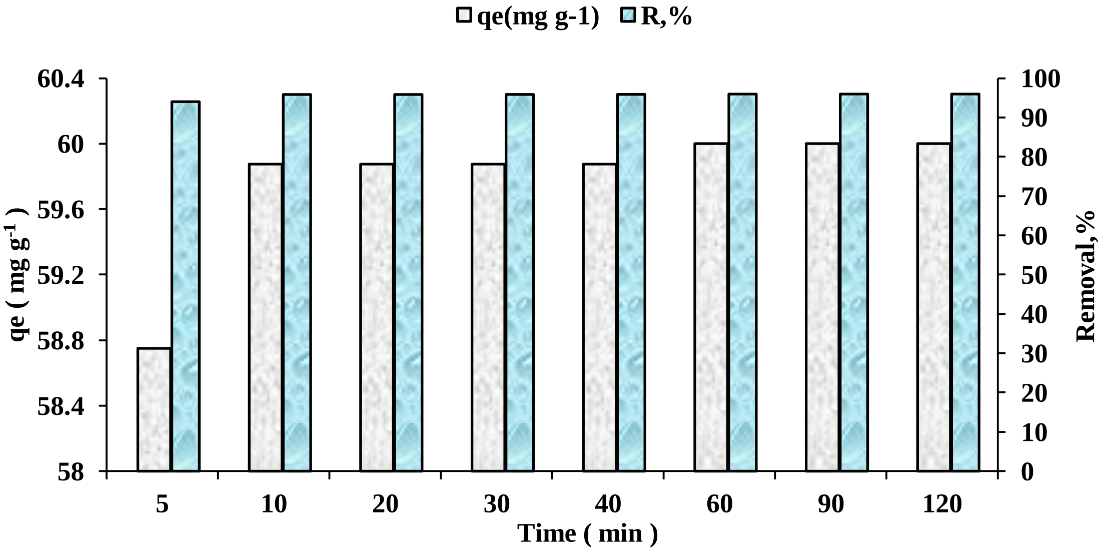


Figure 5. 17 b. Influence of contact time for linuron adsorption onto (Activated carbon (NORIT SA2)). ($C_\circ$ = 5 mg L^{-1}, Mass of adsorbent 0.08 g L^{-1}, pH= 7.00)

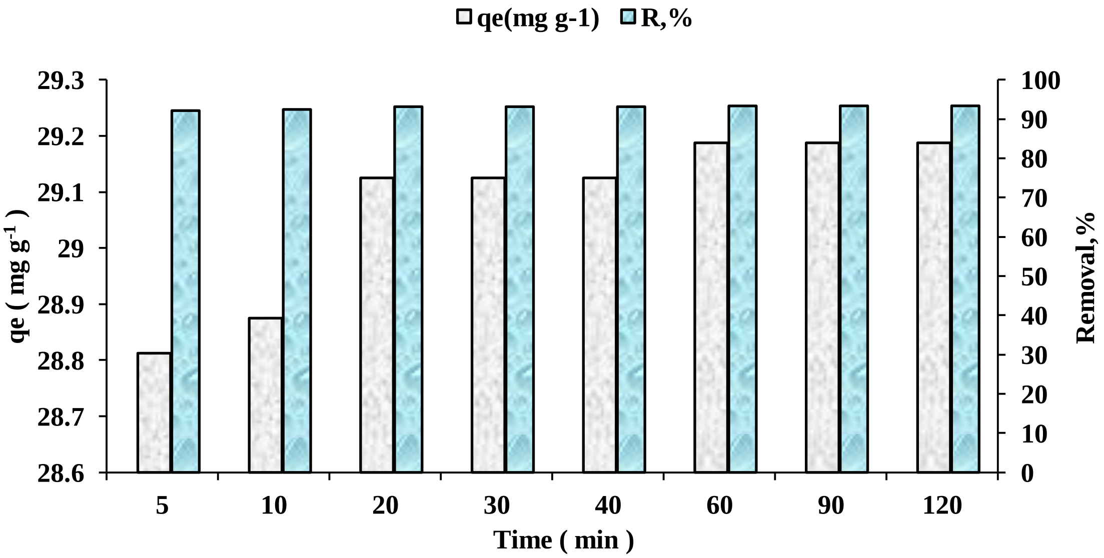


Figure 5. 17 c. Influence of contact time for isoproturon adsorption onto (Activated carbon (NORIT SA2)). ($C_\circ$ = 5 mg L^{-1}, Mass of adsorbent 0.16 g L^{-1}, pH= 7.00)

5. 4. 4. Influence of contact time of Activated carbon NORIT HYDRODARCO C

To establish an appropriate contact time between the Activated carbon (NORIT HYDRODARCO C) and selected pesticides (carbendazim, linuron and isoproturon) solution, sorption capacities and removal percentage of selected pesticides are measured as a function of time Figure 5. 18 (a, b and c). The results detect that the removal percentage and uptake of sorbate species are rapid at the initial stages of the contact period; then, it becomes slower near the equilibrium. Between these two stages of the uptake, the rate of sorption after the equilibrium is found to be nearly constant. The gained results confirm that a large number of empty surface sites are obtainable for sorption over the initial stage. With time, the remaining unoccupied surface sites are challenging to be occupied due to repulsive forces between the solute of selected pesticides on the solid and the bulk phases. It was noted that the time to reach equilibrium for carbendazim, linuron and isoproturon takes less than, 20, 5.00 and 30 min, respectively. The equilibrium time is relatively short as compared to others results in the literature [307,308]. The removal percentage of carbendazim, linuron and isoproturon increased from 86.77 to 94.47 %, 92.40 to 93.03 % and from 84.86 to 92.24 % with the selected pesticides concentration of 5 mg L^{-1} and pH of 7.00,7.00 and 3.00, respectively.

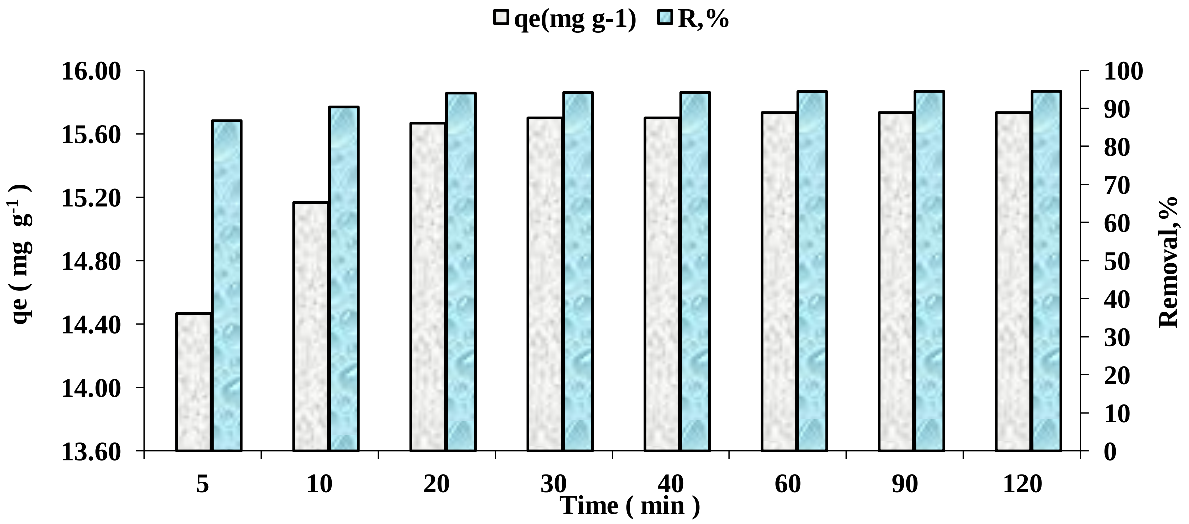


Figure 5. 18 a. Influence of contact time for carbendazim adsorption onto Activated carbon (NORIT HYDRODARCO C). ($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 0.30 g L^{-1}, pH= 7.00)

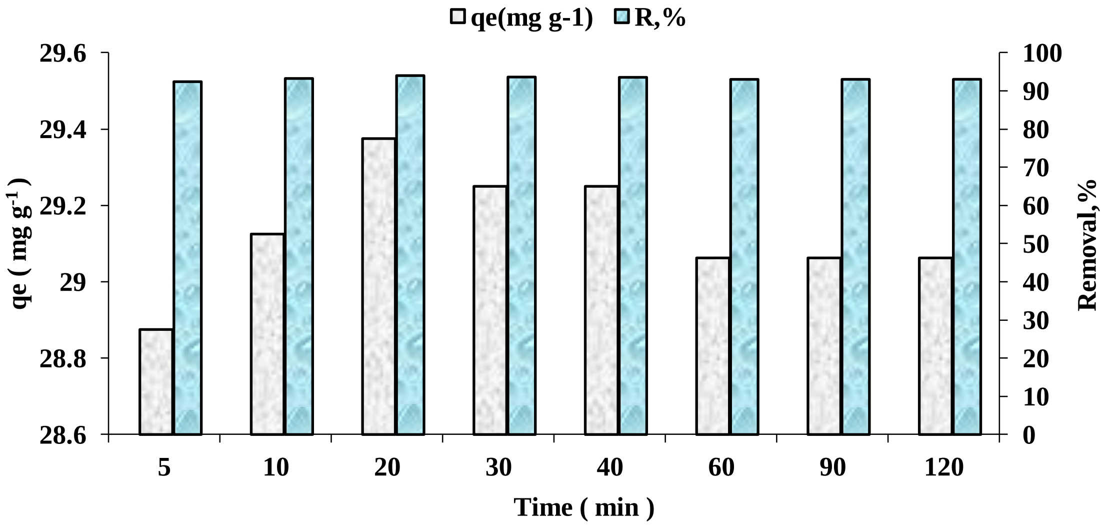


Figure 5. 18 b. Influence of contact time for linuron adsorption onto Activated carbon (NORIT HYDRODARCO C). ($C_\circ$ = 5 mg L^{-1}, Mass of adsorbent 0.16 g L^{-1}, pH= 7.00)

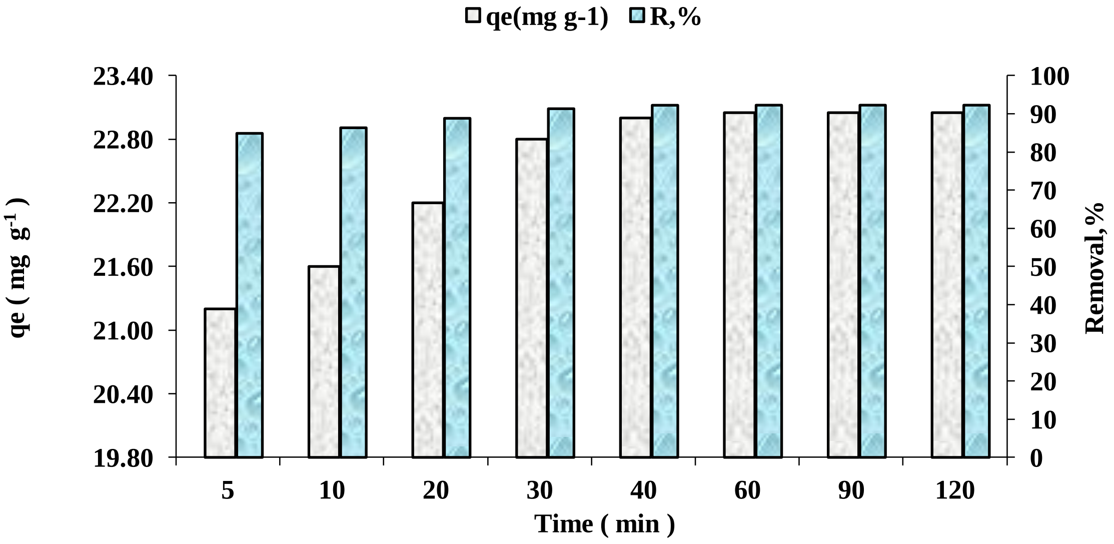


Figure 5. 18 c. Influence of contact time for isoproturon adsorption onto Activated carbon (NORIT HYDRODARCO C). ($C_\circ$ = 5 mg L^{-1}, Mass of adsorbent 0.20 g L^{-1}, pH= 3.00)

5. 4. 5. Influence of contact time (Zeolite, type: ZSM-5)

The removal of carbendazim, linuron and isoproturon pesticides as a function of contact time at different times was observed. The results are presented in Figure 5. 19 (a, b and c). As anticipated, the removal percentage growing with increase time until the equilibrium was reached between the amounts of adsorbate adsorbed on the adsorbent and that remained in solution. The removal increased rapidly as the contact time increased from 5.00 to 120 min. The adsorption process for carbendazim, linuron and isoproturon pesticides took 60 min to reach equilibrium at pH of 5.00, 3.00 and 5.00, respectively. This is confirmed by the results of the statistical analysis. The uptake of carbendazim, linuron and isoproturon pesticides increased gradually with increasing contact time, then is slightly stabilized at contact time of 60 min. High removal efficiencies for carbendazim, linuron and isoproturon were 99.45, 87.11 and 90.32 %, respectively at a contact time of 60 min. Hence, the contact time of 60 min was considered as optimum.

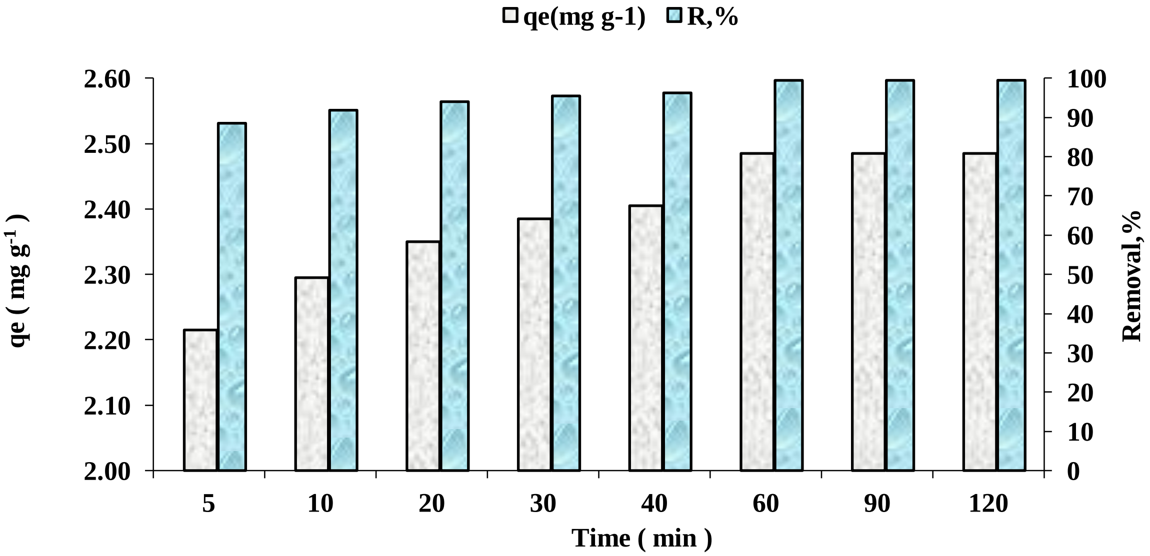


Figure 5. 19 a. Influence of contact time for isoproturon adsorption onto Activated carbon (NORIT HYDRODARCO C). ($C_{\circ}$ = 5 mg L^{-1}, Mass of adsorbent 0.20 g L^{-1}, pH= 3.00)

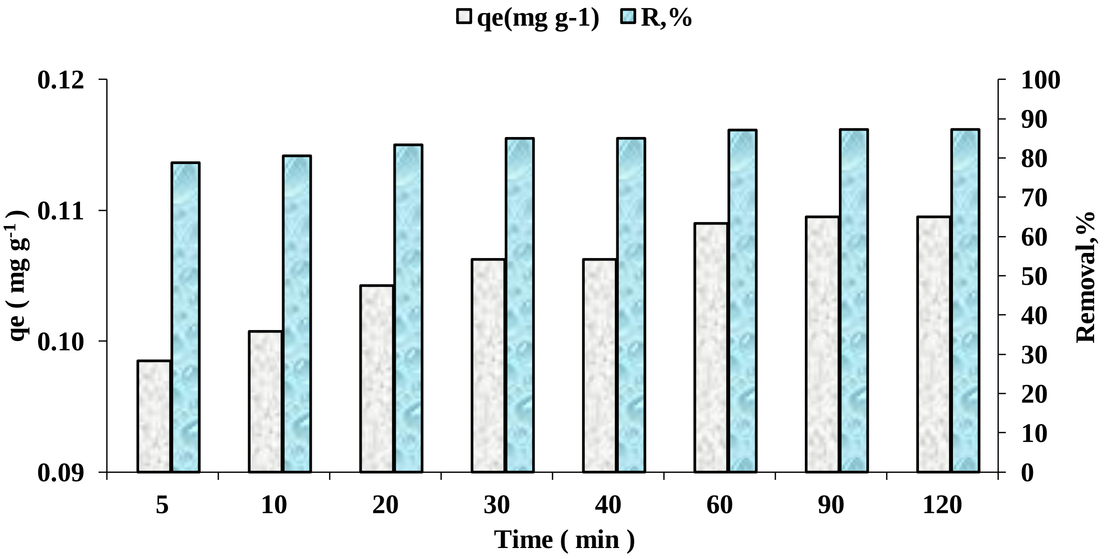


Figure 5. 19 b. Influence of contact time for linuron adsorption onto zeiolite. (C$_\circ$ = 5 mg L^{-1}, Mass of adsorbent 40.00 g L^{-1}, pH= 3.00)

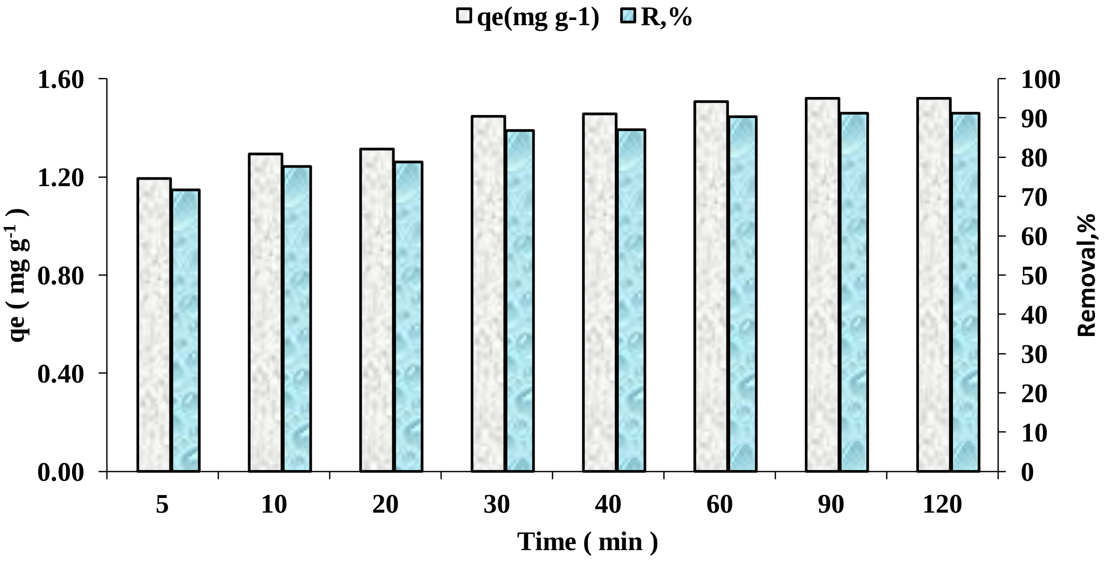


Figure 5. 19 c. Influence of contact time for isoproturon adsorption onto zeiolite. (C$_\circ$ = 5 mg L^{-1}, Mass of adsorbent 3.00 g L^{-1}, pH= 5.00)

5. 4. 6. Conclusions

Table 5. 8. shows the optimum Influence of contact time. The lowest optimum time was 5.00 min and the highest optimum time was 90.00 min. 5.00 min was enough to reach equilibrium to remove isoproturon using the SCG, this time is the fastest time to obtain equilibrium compared to other optimal times to remove the selected pesticides using the selected adsorbents.

Table 5. 8. Comparison of optimum time

Adsorbent	The optimal time (min) for removal of carbendazim	The optimal time (min) for removal of linuron	The optimal time (min) for removal of isoproturon
SCG	20.00	20.00	5.00
DSAC	30.00	40.00	90.00
Activated carbon (NORIT SA2)	60.00	10.00	20.00
Activated carbon (NORIT HYDRODARCO C)	20.00	5.00	30.00
Zeolite, type: ZSM-5	60.00	60.00	60.00

5. 5. Influence of initial concentration

5. 5. 1. Influence of initial concentration (SCG)

The influence of the initial concentration of carbendazim, linuron and isoproturon pesticides was studied at the following concentrations: 2, 4, 5, 6, 8, 10, 12 and 15 mg L^{-1}, whereas all other parameters were adjusted at optimum values: room temperature, pH of solution, mass of adsorbent and the time of contact.

The removal efficiencies of carbendazim, linuron and isoproturon pesticides by SCG were shown in Figure 5. 20 (a, b and c). The removal efficiencies of carbendazim, linuron and isoproturon raised from 52.69 to 99.32 %, from 78.32 to 92.38 % and from 58.97 to 95.70 %, respectively. The removal efficiencies were reduced when the concentrations of carbendazim, linuron and isoproturon were raised, as shown in Figure 5. 20 (a, b and c). A significant difference ($P \leq 0.05$) was observed between concentrations of carbendazim from 2 to 15 mg L^{-1}. There is no significant difference ($P \leq 0.05$) found between 5 and 6 mg L^{-1}. The highest removal efficiency of 99.32 % was registered at 2 mg L^{-1} when the dosage of SCG was 1.00 g L^{-1}, and pH value was 5.00, while contact time was 20 min. Based on the linuron concentrations of 2, 4, and 5 mg L^{-1} higher removal efficiency was observed. The statistical analysis has shown that there is no significant difference ($P \leq 0.05$) in the removal efficiency between those concentrations and also between concentrations of 6, 8, and 10 mg L^{-1} respectively. There is a significant difference ($P \leq 0.05$) between concentratios of 2, 4, 5 mg L^{-1} and 6, 8, 10, 12, 15 mg L^{-1}. It was observed that the concentration of 2 mg L^{-1} possessed the highest removal efficiency when the pH value was 5.00 and the contact time was 20 min, while the dosage of SCG was 2.00 g L^{-1}.

Figure 5. 20 (c) explained the adsorption of isoproturon onto SCG. It is clear that the adsorption capacity increased with increasing of initial isoproturon concentration, but when it relates to the efficiency of pesticide removal from the solution, the situation was reversed. Concentration of 2 mg L^{-1} possessed the highest removal efficiency when the pH value was 7.00 and the contact time was 5.00 min, while the dosage of SCG was 3.00 g L^{-1}.

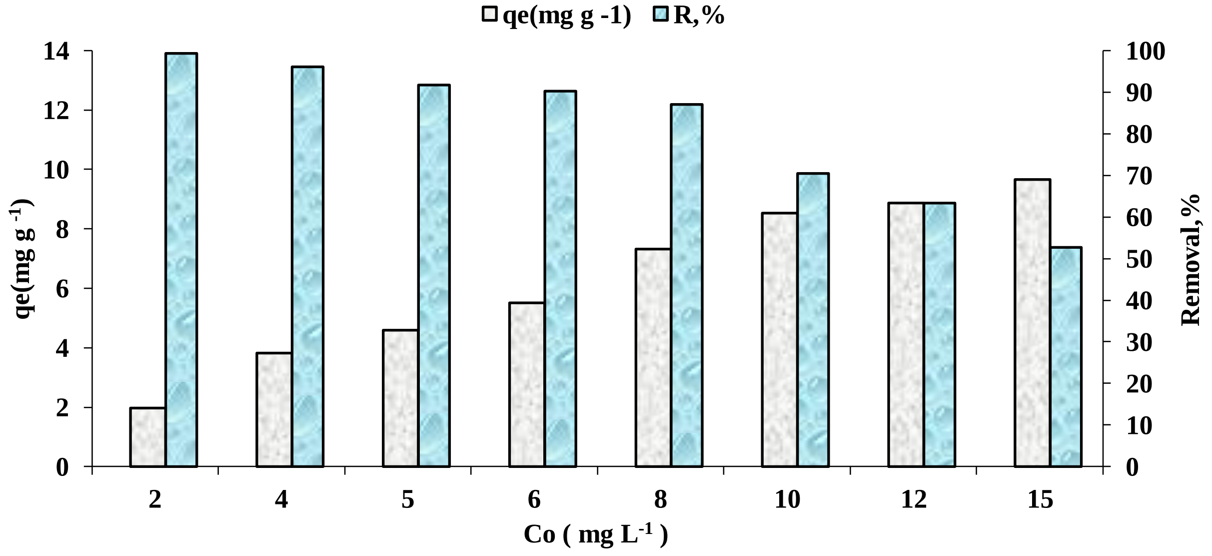


Figure 5. 20 a. Influence of the carbendazim concentration in the adsorption process. (Cont. time = 20 min, Mass of adsorbent 1.00 g L^{-1}, pH= 5.00)

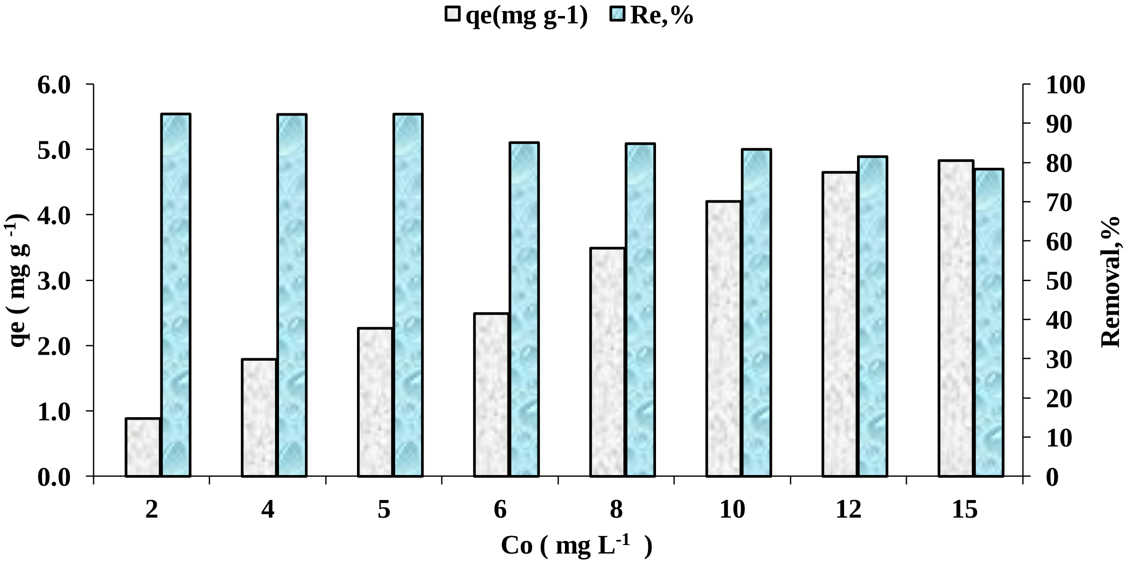


Figure 5. 20 b. Influence of the linuron concentration in the adsorption process. (Cont. time = 20 min, Mass of adsorbent 2.00 g L^{-1}, pH= 5.00)

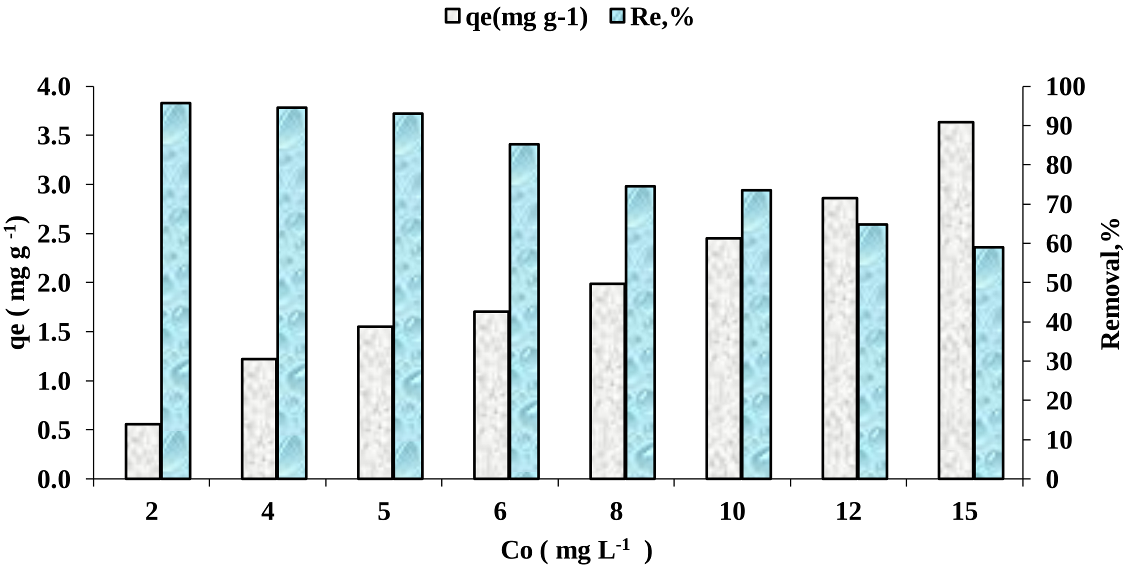


Figure 5. 20 c. Influence of the isoproturon concentration in the adsorption process. (Cont. time = 5.00 min, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

However, at higher initial concentrations of carbendazim, linuron and isoproturon there are fewer available adsorption sites of the SCG and the removal percentages of selected pesticides are decreased. These results are in a good agreement with the results achieved for selected pesticides adsorption on the other adsorbents, as previously outlined by Leite *et al.* (2013) and Tsai *et al.* (2013) [309,310]. The raised initial concentration of carbendazim, linuron and isoproturon lead to competitive adsorption at a constant number of available active sites [311,312]. Figure 5. 20 (a, b and c) shows that the amount of carbendazim, linuron and isoproturon adsorbed on SCG increased with the initial concentration of selected pesticides. At the initial concentration of 15 mg L^{-1}, the adsorption maximum is reached at 9.66, 4.83 and 3.63 mg g^{-1}, for carbendazim, linuron and isoproturon, respectively.

5. 5. 2. Influence of initial concentration of pesticides adsorption on DSAC

Initial adsorbate concentration of carbendazim, linuron and isoproturon pesticides onto DSAC was investigated at various initial concentrations, from 2 to 15 mg L^{-1} (at pH 7, DSAC doses 3.00, 2.00 and 3.00 g L^{-1}, room temperature 25 ± 1 ˚C and contact time 30, 40 and 90 min), respectively.

The effect of the initial concentrations of carbendazim, linuron and isoproturon pesticides on adsorption is presented in Figure 5. 21 (a, b and c). With a rise in the initial concentration of carbendazim, linuron and isoproturon, adsorption capacity also growing, which is likely due to the increased concentration gradient between the selected pesticides and the DSAC. The Figure 5. 21 (a, b and c) shown that the adsorption capacities were high when the initial carbendazim, linuron and isoproturon concentration was 15 mg L^{-1}. The adsorption capacities for carbendazim, linuron and isoproturon were 4.46, 7.07 and 4.50 mg g^{-1} onto DSAC, respectively. This is due to the limited availability of active adsorption sites on the DSAC surface. Adsorption capacity increases with an increase in initial concentration due to the increased probability of cavity collisions with active centers or functional groups. In a solution with high initial concentrations, rapid saturation of functional groups on the surface of activated carbon occurs [313].

The removal efficiency of carbendazim, linuron and isoproturon pesticides decreased from 96.05 % to 80.61 %, from 96.78% to 85.32% and from 94.67% to 83.95%, respectively, when the carbendazim, linuron and isoproturon concentrations increased from 2 to 15 mg L^{-1}. The removal efficiency was high on the lowest initial selected pesticides concentration. The percentage of carbendazim, linuron and isoproturon adsorption decreases with increasing initial carbendazim, linuron and isoproturon concentrations. The raised initial concentration of carbendazim, linuron and isoproturon lead to competitive adsorption at a constant numeral of available active sites [311,312].

In terms of engineering, the impact of the initial concentrations of pesticides is a significant parameter because the water contaminated with pesticides contains wide range of concentrations. Based on the known amount of concentrations of pesticides existing in the water contaminate, optimal process conditions are defined in which the selected pollutant will be separated by increasing or decreasing the mass of activated carbon or contact time, and thus optimally the adsorption process of pesticides.

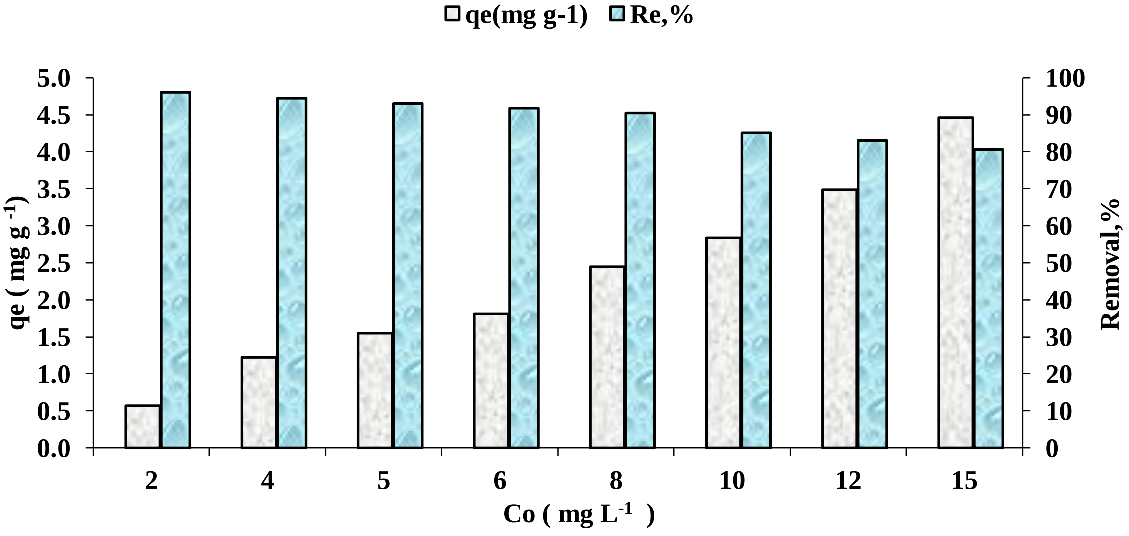


Figure 5. 21 a. Influence of the carbendazim concentration in the adsorption process. (Cont. time = 30 min, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

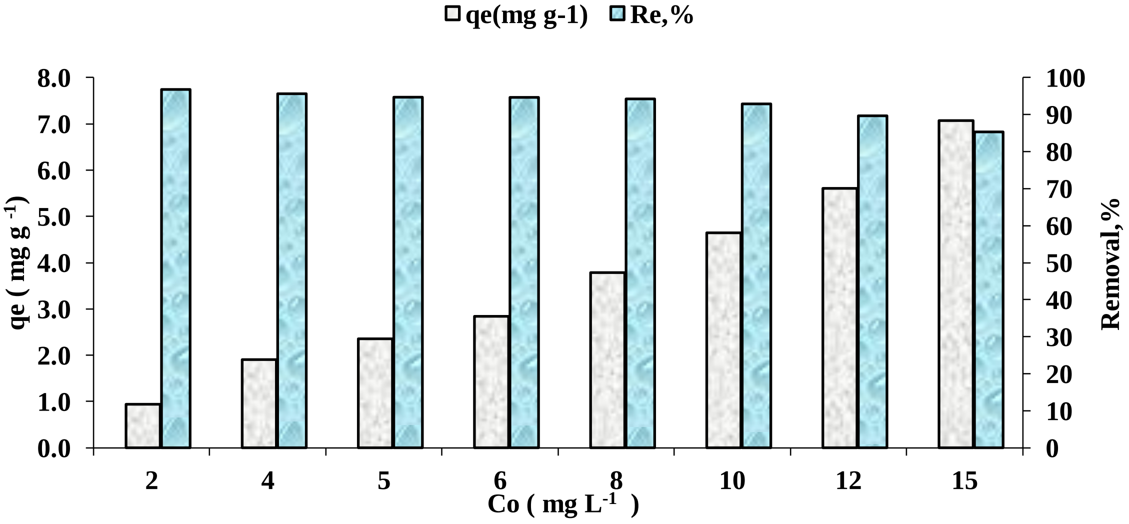


Figure 5. 21 b. Influence of the linuron concentration in the adsorption process. (Cont. time = 40 min, Mass of adsorbent 2.00 g L^{-1}, pH= 7.00)

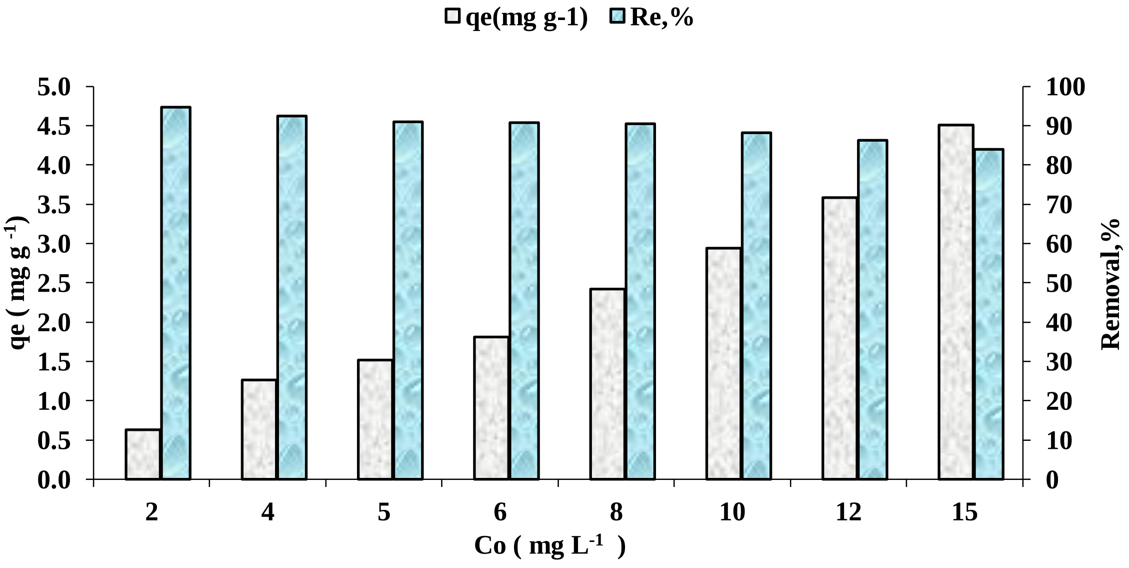


Figure 5. 21 c. Influence of the isoproturon concentration in the adsorption process. (Cont. time = 90 min, Mass of adsorbent 3.00 g L^{-1}, pH= 7.00)

5. 5. 3. Influence of initial concentration of pesticides adsorption on Activated carbon NORIT SA2

It was evident that in case the initial concentration is increased then the adsorption capacity at equilibrium increases, too (Figure 5.22 (a, b and c)). The adsorption capacity increases from 18.70 to 123.90 mg g^{-1} for carbendazim, from 24.00 to 177.25 mg g^{-1} for linuron and from 7.50 to 87.69 mg g^{-1} for isoproturon when the initial concentration is expanded from 2 to 15 mg L^{-1}. This phenomenon may be due to a bigger mass exchange driving constrain and increased number of collision between selected pesticides particles and activated carbon (NORIT SA2) [314]. In common, raising the concentration of adsorbate increases the adsorption rate independently of the nature of adsorbent surface such as textural properties and surface functionalities. High concentrations increase the availability of mesopores for selected pesticides atoms, as well as interactions at solid–liquid interface [315,316].

The removal efficiency of carbendazim, linuron and isoproturon pesticides was diminished from 93.97 % to 73.67 %, from 98.58 % to 87.65 % and from 96.07 % to 81.18%, respectively, when the carbendazim, linuron and isoproturon concentration expanded from 2 to 15 mg L^{-1} at (pH 7, DSAC doses 0.10, 0.08 and 0.16 g L^{-1}, room temperature 25 ± 1 ˚C and contact time 60, 10 and 200 min), respectively.

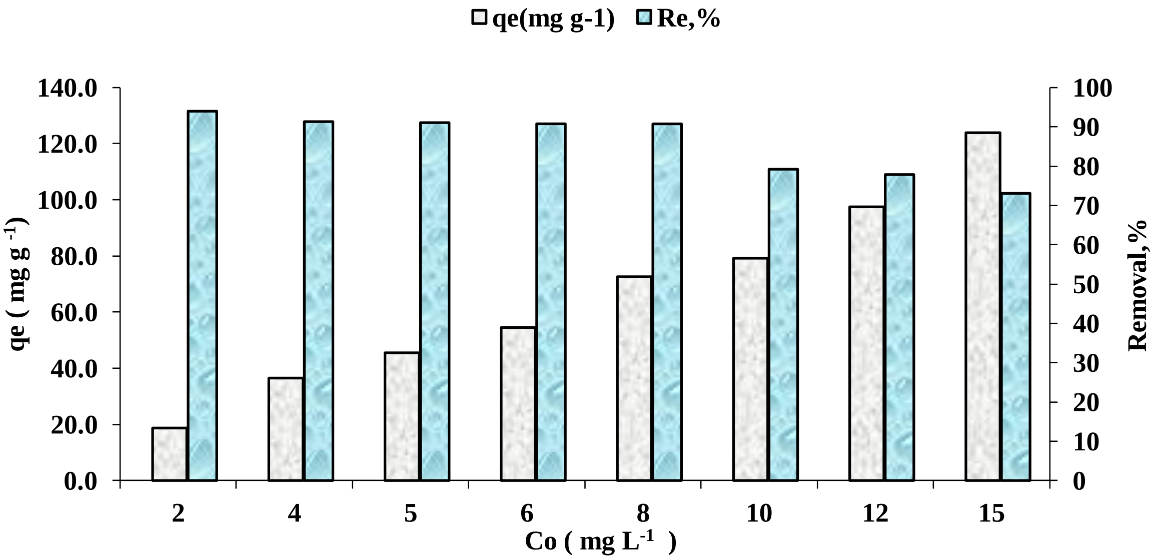


Figure 5. 22 a. Influence of the carbendazim concentration in the adsorption process. (Cont. time = 60 min, Mass of adsorbent 0.10 g L^{-1}, pH= 7.00)

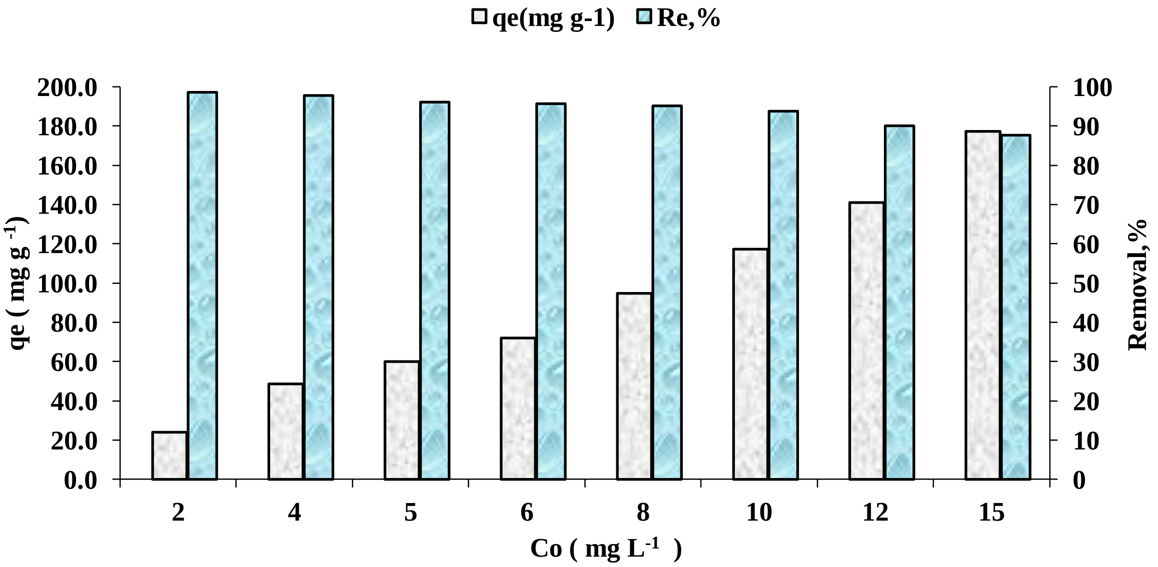


Figure 5. 22 b. Influence of the linuron concentration in the adsorption process. (Cont. time = 10 min, Mass of adsorbent 0.08 g L^{-1}, pH= 7.00)

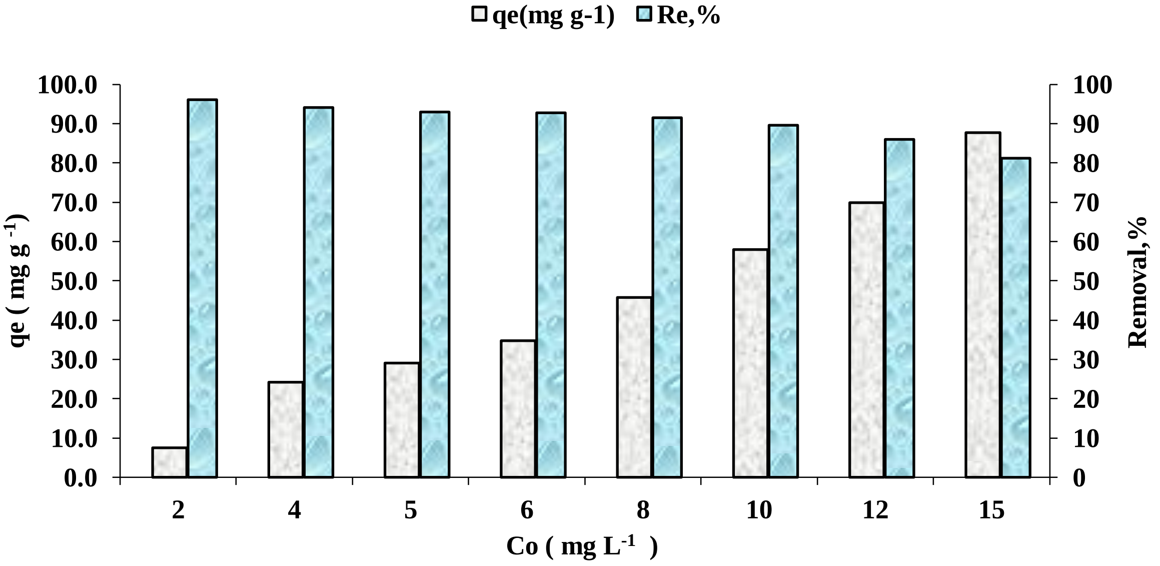


Figure 5. 22 c. Influence of the isoproturon concentration in the adsorption process. (Cont. time = 20 min, Mass of adsorbent 0.16 g L^{-1}, pH= 7.00)

5. 5. 4. Influence of initial concentration (Activated carbon (NORIT HYDRODARCO C))

The initial concentration of carbendazim, linuron and isoproturon are driving force for mass exchange between the liquid and strong stage (diffusion parameter), as well as for chemical bonding of ions to active centers (kinetic parameter). The influence of the initial concentration of chosen pesticides was examined at different concentrations: 2, 4, 5, 6, 8, 10, 12 and 15 mg L^{-1}, while keeping all other parameters for carbendazim, linuron and isoproturon at exemplary values: 25.0 ± 1 ˚C, pH 7.00, 3.00 and 7.00, Activated carbon (NORIT HYDRODARCO C) doses 0.30, 0.16 and 0.20 g L^{-1}, and the contact time 20, 30 and 20 min, respectively. When the initial concentration of carbendazim, linuron and isoproturon within the show arrangements increases, the percentage removal for selected pesticides diminishes. The graph in Figure 5.23 (a, b and c) display that the removal efficiency is elevated at the initial concentration of carbendazim, linuron and isoproturon of 2 mg L^{-1}, and the lowest at the initial concentration of 15 mg L^{-1}. A comparison of the chart in Figure 5.23 (a, b and c) detected that the grade of decrease in removal efficiency is almost similar for carbendazim, linuron and isoproturon. In the case of linuron and isoproturon, an increase in the initial concentration after 8 mg L^{-1} leads to a higher decline in the efficiency level. Solutions that contain lower concentrations of carbendazim, linuron and isoproturon are eligible to reach the equilibrium faster to the active centers that are considerably more than the ions present in solution. Figure 5.23 (a, b and c) illustrates that the amount of carbendazim, linuron and isoproturon adsorbed on activated carbon (NORIT HYDRODARCO C) raises with the initial concentration of chosen pesticides. At the initial concentration of 15 mg L^{-1} the adsorption maximum is reached at 45.10, 61.95 and 78.31 mg g^{-1}, for carbendazim, linuron and isoproturon, respectively.

Figure 5.23 (a, b and c) shows the decreasing in removal efficiency of carbendazim, linuron and isoproturon with increasing of the initial concentration from 2 to 15 mg L^{-1}. The removal efficiencies decreased from 96.08 to 83.63 %, 95.12 to 72.08 % and 97.07 to 73.69 %, respectively.

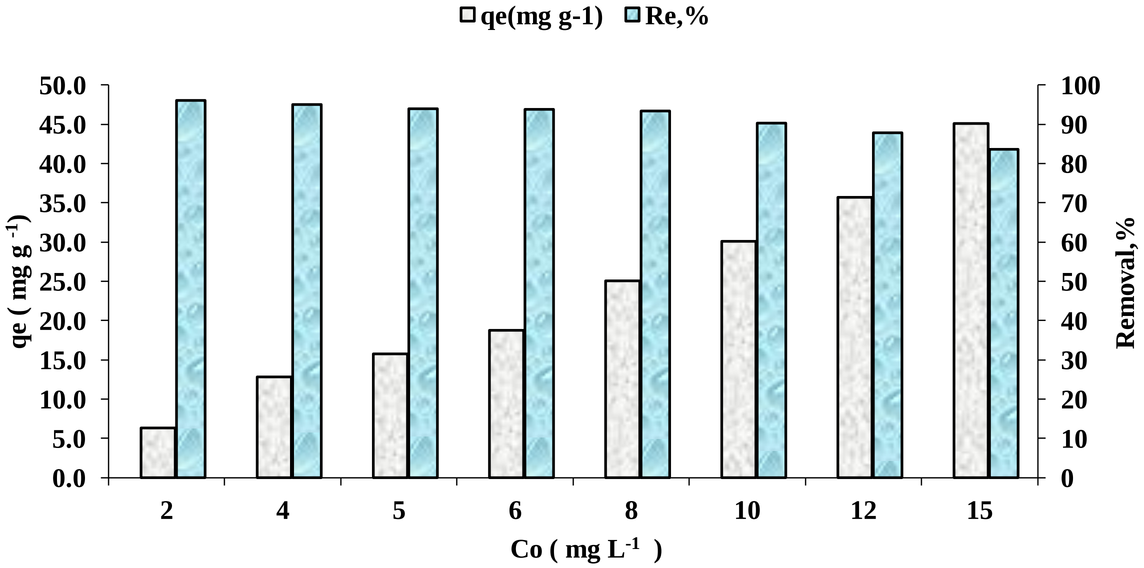


Figure 5. 23 a. Influence of the carbendazim concentration in the adsorption process. (Cont. time = 20 min, Mass of adsorbent 0.30 g L^{-1}, pH= 7.00)

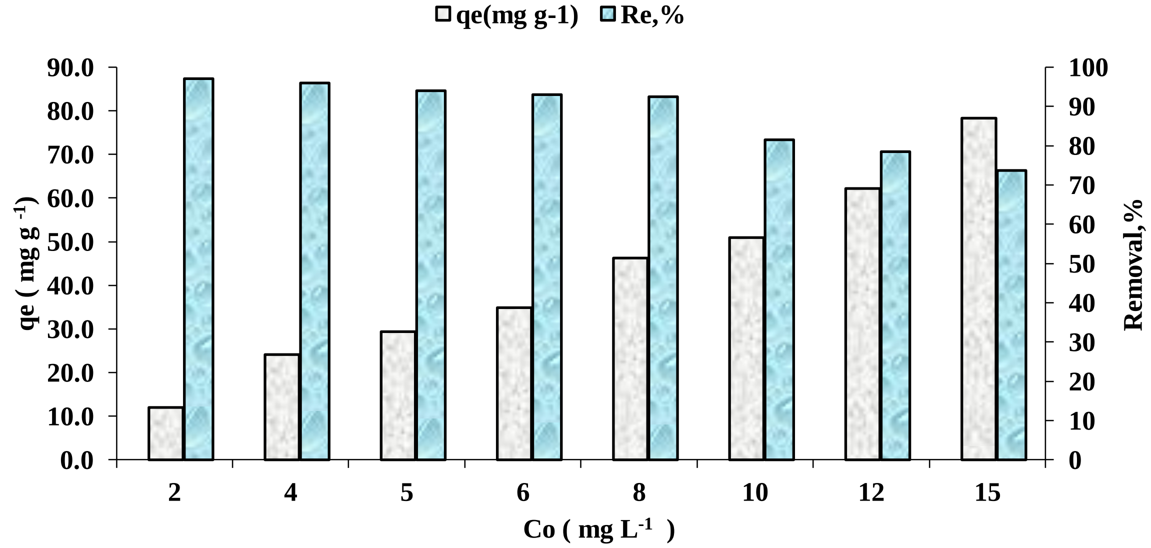


Figure 5. 23 b. Influence of the linuron concentration in the adsorption process. (Cont. time = 20 min, Mass of adsorbent 0.16 g L^{-1}, pH= 7.00)

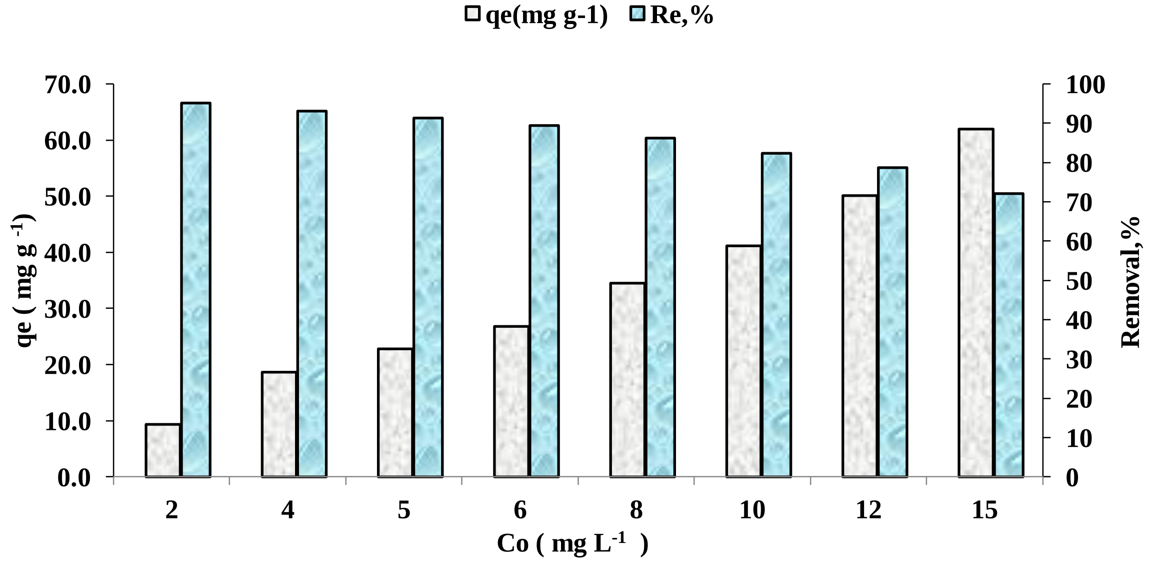


Figure 5. 23 c. Influence of the isoproturon concentration in the adsorption process. (Cont. time = 30 min, Mass of adsorbent 0.20 g L^{-1}, pH= 3.00)

5. 5. 5. Influence of initial concentration (Zeolite, type: ZSM-5)

The initial concentration of carbendazim, linuron and isoproturon in the solution is significant parameter as the pesticides concentration changes over a broad range in industrial effluents. Fig. 5.24 (a, b and c) describes the alteration in adsorption trends of Zeolite, type: ZSM-5 with variation in the initial concentration of adsorbate (carbendazim, linuron and isoproturon) in the solution and at optimal experimental conditions pH = 5.00, 3.00 and 5.00, adsorbent dose 2.00, 40.00 and 3.00 g L^{-1}, contact time 60 min and temperature 25.0 ± 1 °C, respectively. The adsorption behavior in the figure indicates the decreasing trend of carbendazim, linuron and isoproturon adsorption on Zeolite, type: ZSM-5. Removal efficiencies ranged from 99.95 % to 64.28 %, from 89.50 % to 69.91 % and from 94.77 % to 70.28 % as the initial carbendazim, linuron and isoproturon concentration increased from 2 to 15 mg L^{-1}, respectively. The adsorption capacity values increased continuously with the increase of initial carbendazim, linuron and isoproturon concentration from 1.00 to 6.28 mg L^{-1}, from 0.038 to 0.30 mg L^{-1} and from 0.62 to 4.03 mg L^{-1}, respectively. At lower initial concentrations of selected pesticides, sufficient adsorption sites are available for adsorption of carbendazim, linuron and isoproturon. At higher concentrations, relatively less available sites induced a reduction in adsorption of carbendazim, linuron and isoproturon on the Zeolite, type: ZSM-5 surface.

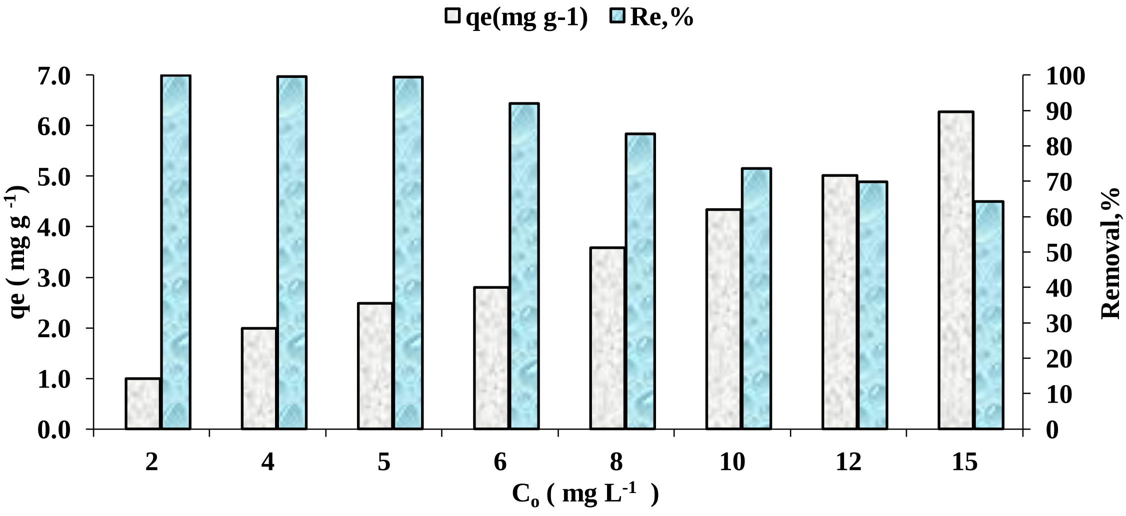


Figure 5. 24 a. Influence of the carbendazim concentration in the adsorption process. (Cont. time = 60 min, Mass of adsorbent 2.00 g L^{-1}, pH= 5.00)

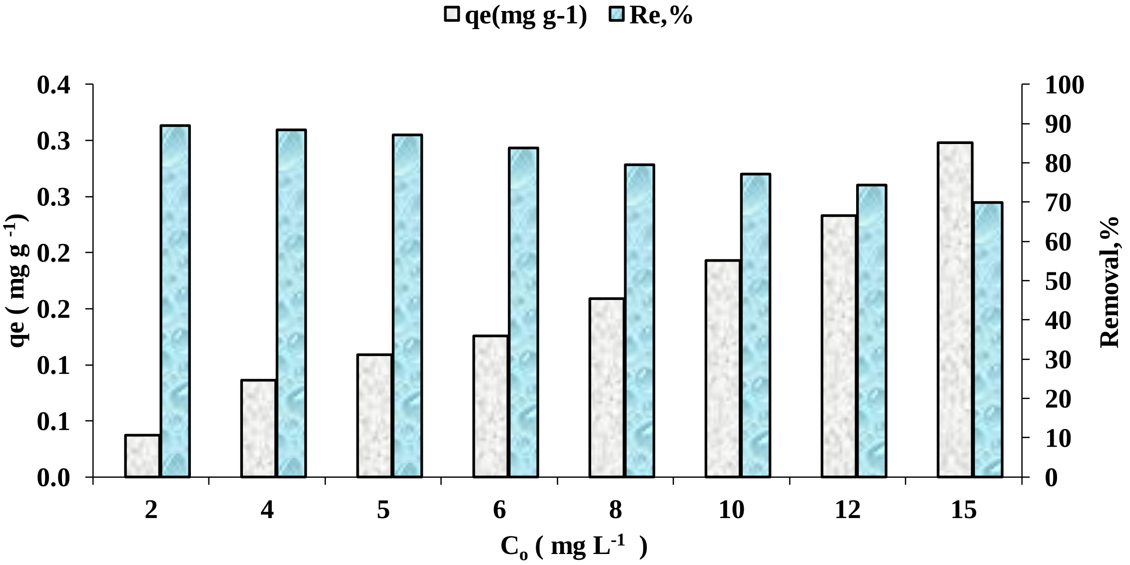


Figure 5. 24 b. Influence of the linuron concentration in the adsorption process. (Cont. time = 60 min, Mass of adsorbent 40.00 g L^{-1}, pH= 3.00)

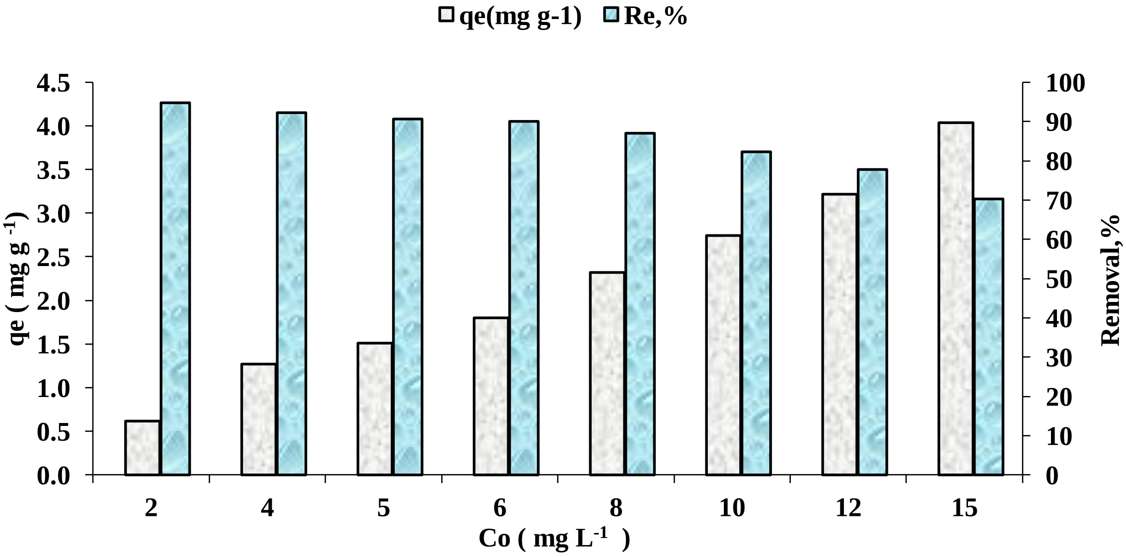


Figure 5. 24 c. Influence of the isoproturon concentration in the adsorption process. (Cont. time = 60 min, Mass of adsorbent 3.00 g L^{-1}, pH= 5.00)

5. 5. 6. Conclusions

It can be concluded that the lower concentrations of the selected pesticides effect on the higher removal. On the contrary, the higher concentrations of the studied pesticides effect on the lower removal rate.

5. 6. Modeling of adsorption isotherms

5. 6. 1. Modeling of adsorption isotherms (SCG)

The experimental data are evaluated by Langmuir, Freundlich and Temkin isotherm models. Obtained results are summarized in Table 5. 3 along with the linear correlation coefficients (*r*), residual root mean square error (RMSE) and Chi-square ($\chi 2$) tests. As it can be seen in Figure I. 1 (a, b, c), Figure I. 2 (a, b, c) and I. 3 (a, b, c), isotherms are subsequently linearly fitted. Based on the obtained correlation coefficients (r) (Table 5. 3) the fit of carbendazim, linuron and isoproturon with three isotherm models (Langmuir, Freundlich and Temkin. Experimental results for carbendazim, linuron and isoproturon can be described well with Langmuir, Freundlich and Temkin adsorption models ($r > 0.900$). It can be concluded that the aforementioned describes the sorption isotherm of carbendazim, linuron and isoproturon adequately onto AC developed from SCG.

The smallest values of RMSE and χ^2 and the greatest values of (r) were obtained with Freundlich model for carbendazim among the three isotherms. All selected pesticides were fitted very well with the Langmuir, Freundlich and Temkin isotherms. For linuron the best fitting isotherm corresponded to Langmuir isotherm and the χ^2 was a lowest with Temkin isotherms. The Langmuir adsorption isotherm is based on the model which was developed assuming monolayer coverage of the adsorbent surface. According to the Langmuir model, a significant adsorption capacity for carbendazim and linuron was achieved: 11.918 mg $g^{-1}$and 5.834 mg g^{-1}, respectively. This result is consistent with the Langmuir isotherm hypothesis which assumes that the adsorption takes place only at specific localized sites on the surface and the surface is energetically homogeneous, the theoretical and experimental maximum adsorption capacities are in good agreement.

On the other hand, constant K_f, which is the adsorption capacity and the parameter n, which reflects the degree of deviation from the linearity of adsorption. If the value of n = 1, the adsorption follows a linear function; for values n < 1, the adsorption is unfavorable, and if n > 1, the adsorption is favored. Freundlich coefficient n values achieved the condition of n > 0, for favorable adsorption. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent. This leads to the conclusion that the surface of SCG is made of small heterogeneous patches configurations which are favorable for adsorption phenomenon. In this study, the obtained values for n are higher than 1, and, accordingly, the adsorption is favoured. Adsorption affinity for binding of carbendazim and linuron on SCG is high.

Table 5. 9. Isotherm constants of the Langmuir, Freundlich and Temkin models for carbendazim, linuron and isoproturon uptake by SCG

	Isotherm model	**Parameters**		
		Carbendazim	Linuron	Isoproturon
$q_{max,exp}$ (mg $g^{-1)}$		11.400	4.830	3.630
Langmuir	q_{max} (mg g^{-1})	11.990	5.834	4.154
	K_L (L mg^{-1})	29.411	6.269	3.014
	r	0.991	0.985	0.915
	RMSE	1.183	0.215	0.368
	χ^2	15.120	6.580	3.575
Freundlich	K_f	7.402	2.700	1.661
	$1/n$	0.363	0.514	0.459
	r	0.993	0.919	0.864
	RMSE	1.196	0.777	0.305
	χ^2	0.220	1.017	0.637
Temkin	B (J L^{-1})	1.969	1.331	0.807
	A	55.423	9.982	10.485
	r	0.975	0.958	0.909
	RMSE	0.643	0.369	0.344
	χ^2	1.309	0.372	0.713

5. 6. 2. Modeling of adsorption isotherms (DSAC)

The calculated parameters summarize correlation coefficients (*r*) and error functions (Table 5. 4). The graphical representation of these models is shown in Figure I. 4 (a, b, c), Figure I. 5 (a, b, c) and Figure I. 6 (a, b, c). The lowest RMSE and $\chi 2$ values and the highest (*r*) values were acquired with Temkin model for carbendazim and with Freundlich model for linuron and isoproturon among the three isotherms, respectively. The experimental outcomes can be well described with the adsorption models Freundlich and Temkin (r > 0.900). For all three selected pesticides, the Langmuir isotherm has reduced correlation coefficients, except isoproturon, the value of (*r*) was 0.853. The Freundlich model is compatible with the adsorption on an energetically heterogeneous surface where the adsorbed molecules interact with each other, point out the type of physical adsorption. The correlation coefficients for the adsorption of linuron and isoproturon are higher in the Freundlich's model, compared to the Temkin's model. For this reason, the interpretation of the Freundlich's constants was accepted in this study: The adsorption capacity which described by constant K_f, and reflects the degree of deviation from the linearity of adsorption which depicted by n. If the value of n = 1, the adsorption follows a linear function, the adsorption is unfavorable for values n < 1, and if n > 1, it favors adsorption [317]. In the current study, the values acquired for n are higher than one and, consequently, the adsorption is favored and the adsorption affinity for binding of linuron and isoproturon on DSAC is high.

On the other side, higher values of the correlation coefficients ($r = 0.975$) and lowest RMSE= 4.766 and $\chi^2 = 0.576$ were obtained with Temkin model for carbendazim among the three isotherms. Shows excellent linearity regardless of the maximum capacity of adsorption used to calculate the coverage area.

Table 5. 10. Isotherm constants of the Langmuir, Freundlich and Temkin models for carbendazim, linuron and isoproturon uptake by DSAC

	Isotherm model	**Parameters**		
		Carbendazim	Linuron	**Isoproturon**
$q_{max,exp}$ (mg $g^{-1)}$		4.460	7.070	4.510
Langmuir	q_{max} (mg g^{-1})	10.780	29.585	25.906
	K_L (L mg^{-1})	3.501	9.225	14.992
	r	0.475	0.575	0.853
	$RMSE$	0.538	1.399	1.631
	χ^2	28.760	126.738	144.157
Freundlich	K_f	2.658	7.414	2.958
	$1/n$	0.806	0.905	0.678
	r	0.902	0.984	0.980
	$RMSE$	0.458	0.414	0.259
	χ^2	0.783	0.304	0.258
Temkin	B (J L^{-1})	1.622	2.751	1.289
	A	6.043	9.874	10.932
	r	0.934	0.954	0.916
	$RMSE$	0.397	0.544	0.443
	χ^2	0.576	0.974	1.270

5. 6. 3. Modeling of adsorption isotherms (Activated carbon (NORIT SA2))

Adsorption isotherm defines how adsorbed molecules distribute between the liquid and solid stages when the process of adsorption reaches an equilibrium state [318]. Analyzing the isothermic adsorption information by fitting them into distinct isothermic models is a significant step in finding the appropriate model that can be used for the design method. The adsorption isotherms of carbendazim, linuron and isoproturon on the Activated carbon (NORIT SA2) at room temperature (25 ± 2 ˚C) were shown in Figure I. 7 (a, b, c), Figure I. 8 (a, b, c) and Figure I. 9 (a, b, c), respectively. The isotherm models of Langmuir, Freundlich and Temkin were used to portray the adsorption of the equilibrium, respectively.

Table 5. 5 summarized the correlation coefficients (r) and the constants from the three isotherm models. The significance of mathematical adsorption isotherms modelling is linked to the likelihood of acquiring distinctive adsorption process

coefficients that are usually compared to the coefficients obtained for different pesticide/adsorbent structures. Langmuir, Freundlich and Temkin models have been equipped with adsorption information to assess which is more relevant. Experimental findings demonstrate the most excellent description of the method of adsorption by the Freundlich model for selected pesticides. The amount adsorbed rises as the pesticide solution concentration rises, according to the Freundlich equation. By comparing each pesticide's adsorption conduct, the most considerable k_f value for linuron (185.600 mg g^{-1}) was noted. And that for all the pesticides investigated, the Freundlich isotherm exponent 1/n was comparable with a value close to one, this shows a linear rise from the concentration of adsorption to the concentration of equilibrium. The peak multilayer adsorption capability assessed by the Freundlich equation is between 21.79 to 114.10, 30.35 to 160.98 and 11.91 to 92.5 mg g^{-1} for carbendazim, linuron and isoproturon, respectively. This shows the higher effectiveness of activated carbon (NORIT SA2) in the removal of pesticides.

Table 5. 11. Isotherm constants of the Langmuir, Freundlich and Temkin models for carbendazim, linuron and isoproturon uptake by Activated carbon (NORIT SA2)

Isotherm model		**Parameters**		
		Carbendazim	Linuron	**Isoproturon**
$q_{max,exp}$ (mg $g^{-1)}$		123.900	177.250	83.750
Langmuir	q_{max} (mg g^{-1})	140.845	312.500	182.000
	K_L (L mg^{-1})	153.846	370.370	101.010
	r	0.942	0.878	0.804
	RMSE	1.157	1.589	2.639
	χ^2	362.485	1275.307	818.448
Freundlich	K_f	67.189	185.600	64.595
	1/n	0.552	0.717	0.766
	r	0.966	0.974	0.977
	RMSE	10.667	9.311	6.447
	χ^2	11.688	8.368	6.545
Temkin	*B* (J L^{-1})	30.671	55.463	28.010
	A	11.461	17.478	9.806
	r	0.945	0.953	0.936
	RMSE	9.880	13.790	7.549
	χ^2	12.696	17.651	53.223

5. 6. 4. Modeling of adsorption isotherms (Activated carbon (NORIT HYDRODARCO C))

The isotherms adsorption parameters acquired as well as the (r) and constants are displayed in Table 5. 6. The graphical representation of these models is shown in Figure I. 10 (a, b, c), Figure I. 11 (a, b, c) and Figure I. 12 (a, b, c). The (r), which defines the fit of a data collection, disclosed that the Freundlich isotherm model better described the adsorption of both carbendazim and isoproturon on Activated carbon (NORIT HYDRODARCO C) than the Langmuir model. Moreover, in describing the equilibrium information, the reduced Chi-square (χ^2) tests values verified the suitability of the Freundlich model. The better alignment with the Freundlich model indicates that the activated carbon (NORIT HYDRODARCO C) absorption of carbendazim and isoproturon may involve multilayer adsorption with interactions between the pesticide molecules and the heterogeneous nature of the Activated carbon (NORIT HYDRODARCO C) surface. Besides, the values of n acquired for carbendazim, and isoproturon adsorption on activated carbon (NORIT HYDRODARCO C) was higher than 1, indicating favorable adsorption. However, the Langmuir model also gave significant results with (r) values above 0.95. The Langmuir monolayer adsorption capacities of 60.970, 78.740 and 78.160 mg g^{-1} were obtained for carbendazim, linuron and isoproturon, respectively. Comparison of the adsorption capacities of Activated carbon (NORIT HYDRODARCO C) illustrates higher adsorption in the case of linuron and isoproturon than for carbendazim. This could be attributed to the smaller molecular size of linuron and isoproturon which can easily penetrate the pores of the Activated carbon (NORIT HYDRODARCO C) than the carbendazim molecules and stronger attachment of linuron and isoproturon to the Activated carbon (NORIT HYDRODARCO C) surface. Temkin model gives the values of correlation coefficient higher than 0.95, which indicates the fit of the Temkin model with the absorption of selected pesticides also.

Table 5. 12. Isotherm constants of the Langmuir, Freundlich and Temkin models for carbendazim, linuron and isoproturon uptake by Activated carbon (NORIT HYDRODARCO C)

	Isotherm model	**Parameters**		
		Carbendazim	Linuron	**Isoproturon**
$q_{max,exp}$ (mg g^{-1})		45.100	78.310	61.950
Langmuir	q_{max} (mg g^{-1})	60.970	78.740	78.160
	K_L (L mg^{-1})	79.360	166.660	70.422
	r	0.954	0.961	0.952
	RMSE	1.024	0.954	1.320
	χ^2	182.996	165.308	217.500
Freundlich	K_f	33.98	48.261	33.876
	1/n	0.620	0.446	0.566
	r	0.972	0.958	0.987
	RMSE	2.729	6.210	2.662
	χ^2	2.368	6.713	1.626
Temkin	B (J L^{-1})	12.530	16.024	15.732
	A	15.180	25.578	10.979
	r	0.968	0.953	0.958
	RMSE	2.926	5.848	4.475
	χ^2	2.871	5.486	6.169

5. 6. 5. Modeling of adsorption isotherms (Zeolite, type: ZSM-5)

Table 5. 7 summarizes the results of all three isotherms under the current research. Isotherm's best fit was chosen based on the largest correlation coefficient (r) value which describing the isotherm's fitness to the experimental information.

Figure I. 13 (a, b, c), Figure I. 14 (a, b, c) and Figure I. 15 (a, b, c) displays the appropriate experimental information for linear isotherm models. For carbendazim, it can be observed from Figure 37 (a) that Langmuir isotherm fitted better than the other two isotherms, for linuron it can be observed from Figure 38 (c) that Temkin isotherm fitted better than the other two isotherms. For isoproturon, the values of correlation coefficient (r) were similar (r = 0.96) for three isotherm models. For three pesticides the Freundlich parameter (1/n) was found to be less than one, which also indicated a Langmuir isotherm [319]. Table 5. 7 lists the comparison of maximum monolayer adsorption capacity of carbendazim, linuron and isoproturon onto Zeolite, type: ZSM-5. The Zeolite, type: ZSM-5 in this work had a relatively small adsorption capacity 5.892, 0.880 and 4.790 mg g^{-1} for carbendazim, linuron and isoproturon, respectively.

Table 5. 13. Isotherm constants of the Langmuir, Freundlich and Temkin models for carbendazim, linuron and isoproturon uptake by Zeolite, type: ZSM-5

	Isotherm model	**Parameters**		
		Carbendazim	Linuron	**Isoproturon**
$q_{max,exp}$ (mg $g^{-1)}$		6.280	0.300	4.040
Langmuir	q_{max} (mg g^{-1})	5.892	0.880	4.790
	K_L (L mg^{-1})	26.595	0.125	4.995
	r	0.966	0.421	0.965
	RMSE	1.034	0.020	0.363
	χ^2	2.784	0.072	5.050
Freundlich	K_f	4.238	0.111	2.212
	$1/n$	0.243	0.804	0.515
	r	0.928	0.909	0.960
	RMSE	0.493	0.021	0.198
	χ^2	0.796	0.037	0.222
Temkin	B (J L^{-1})	0.701	0.108	0.962
	A	550.59	3.404	12.961
	r	0.913	0.948	0.961
	RMSE	0.600	0.024	0.276
	χ^2	0.915	0.036	0.360

5. 7. Adsorption Kinetics

To design a quick and efficient model, adsorption rate studies are conducted. To comprehend the mechanism of adsorption, such as chemical mass transfer response, an appropriate model is needed. The three kinetic models were applied, the pseudo-first-order, pseudo-second-order and intraparticle diffusion.

5. 7. 1. Adsorption Kinetics of (SCG)

The results of three kinetic models: pseudo-first order and pseudo-second order model summarized in the Table 5. 8 and Figure 5. 25 (a, b). The calculated q_e values, obtained by pseudo-first order model, were not meaningful, and they were very low in comparison with the experimental results. It has been proposed that the pseudo-second order model has a strong correlation r = 0.999 between t and t/q_t for the adsorption kinetics of selected pesticides on SCG. It can be seen in Figure 5. 25 (b), the theoretical q_e values obtained by the pseudo-second order model are close to the experimental results. All these observations suggest that the adsorption of carbendazim, linuron and isoproturon on SCG occurs according to the mechanism of the second order reaction, that the bonding process is, in no small extent, kinetically controlled, and that it belongs to chemisorption processes. It can be concluded from the results that carbendazim, linuron and isoproturon adsorption behaviors on SCG could be better explained by the pseudo-second order model, proposing that strong chemical forces at the surface are caused by exchanging electrons.

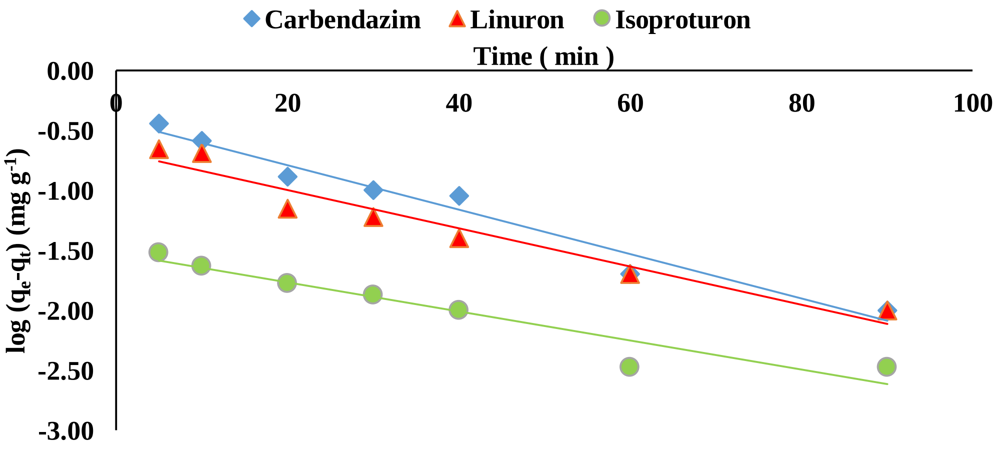


Figure 5. 25 a. Pseudo-first order kinetics plot of Carbendazim, Linuron and Isoproturon onto SCG

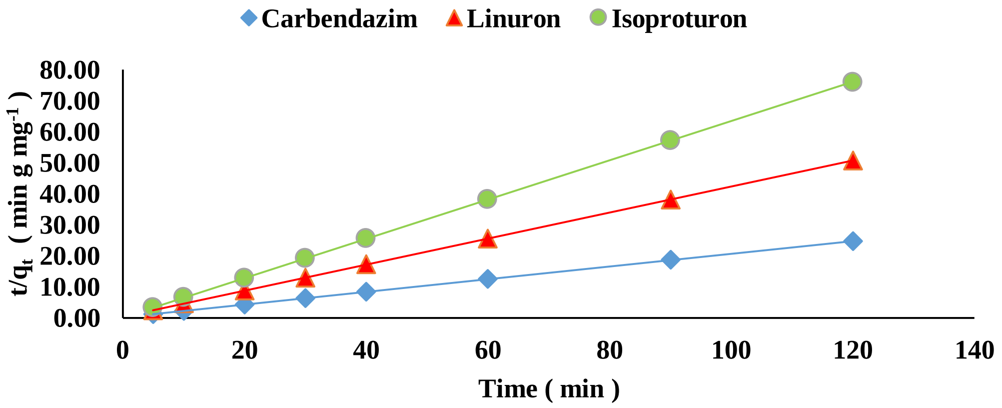


Figure 5. 25 b. Pseudo-second order kinetics plot of Carbendazim, Linuron and Isoproturon onto SCG

Table 5. 14. Kinetic parameters for the adsorption of carbendazim, linuron and isoproturon onto (SCG)

		Carbendazim	Linuron	Isoproturon
q_e, *exp* (mg g^{-1})		4.850	2.370	1.580
Pseudo-first order	q_e (mg g^{-1})	0.379	0.208	0.030
	K_1 (min^{-1})	0.042	0.036	0.028
	r	0.983	0.970	0.957
Pseudo-second order	q_e (mg g^{-1})	4.892	2.383	1.582
	K_2 (g mg^{-1}.min^{-1})	0.233	0.499	3.040
	r	0.999	0.999	0.999

5. 7. 2. Adsorption Kinetics (DSAC)

Adsorption kinetics phenomena are essential to understand adsorption reaction mechanisms [320]. The applicability of the three models was verified. The plot of log (q_e-q_t) versus t for pseudo-first order and of t/q_t versus t for pseudo-second order models. Table 5. 9 and Figure 5. 26 (a, b) summarized the correlation coefficients r, the rate constants k_1 and k_2 obtained from the slopes of the respective linear plots are provided. From the results, it can be seen that the adsorption of carbendazim, linuron and isoproturon did not follow well the equation of pseudo-first order. The correlation coefficients were high / better for the pseudo-second order model (implying that this adsorption scheme best considers a pseudo-second-order model). Also, $q_{e,exp}$ and q_e values determined from the pseudo-second order model were close.

Observations show that DSAC adsorption of carbendazim, linuron and isoproturon happens as a second-order reaction and that the pesticides bonding process is largely kinetically controlled and a method of chemisorption [321]. The literature also revealed similar results, i.e. Drin (aldrin, dieldrin and endrin) pesticides removal from aqueous solutions using acid-treated date stones [225]. El Bakouri *et al*.(2009) [225] also noted the effective implementation of the pseudo-second order model to describe the experimental kinetic information of adsorption by date seeds of drin pesticides.

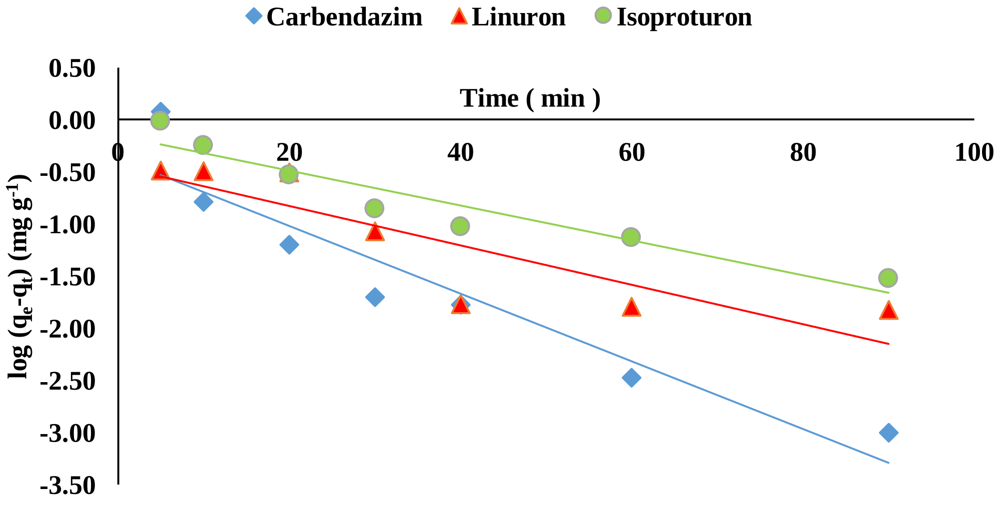


Figure 5. 26 a. Pseudo-first order kinetics plot of Carbendazim, Linuron and Isoproturon onto DSAC.

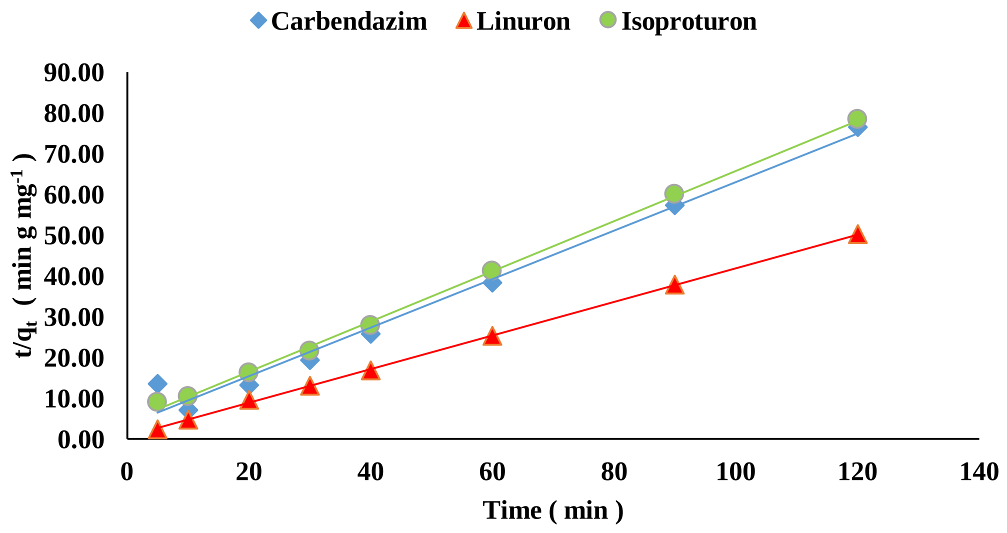


Figure 5. 26 b. Pseudo-second order kinetics plot of Carbendazim, Linuron and Isoproturon onto DSAC

Table 5. 15. Kinetic parameters for the adsorption of carbendazim, linuron and isoproturon onto (DSAC)

		Carbendazim	Linuron	Isoproturon
q_e, *exp* (mg g^{-1})		1.570	2.390	1.530
Pseudo-first order	q_e (mg g^{-1})	0.428	0.356	0.701
	K_1 (min^{-1})	0.075	0.044	0.038
	r	0.947	0.874	0.951
Pseudo-second order	q_e (mg g^{-1})	1.678	2.423	1.622
	K_2 (g mg^{-1}.min^{-1})	0.102	0.252	0.091
	r	0.992	0.999	0.999

5. 7. 3. Adsorption Kinetics (Activated carbon (NORIT SA2))

Kinetic reaction models were used to define the adsorption frequency and likely adsorption mechanism Comparison of adsorption rate constants, the estimated q_e, and the coefficients of correlation is presented in Table 5. 10 and Figure 5. 27 (a, b). Clearly, pseudo-second-order kinetics best define carbendazim, linuron and isoproturon pesticides adsorption here. For this model, the calculated q_e values are very similar to the experimental $q_{e,\ exp}$. For carbendazim, linuron and isoproturon pesticides, the correlation coefficients of pseudo-second order kinetic models were r = 0.999. The k_2 constant is the time-scaling factor, i.e. the time required for the system to achieve an equilibrium state is short when its value is high [322].

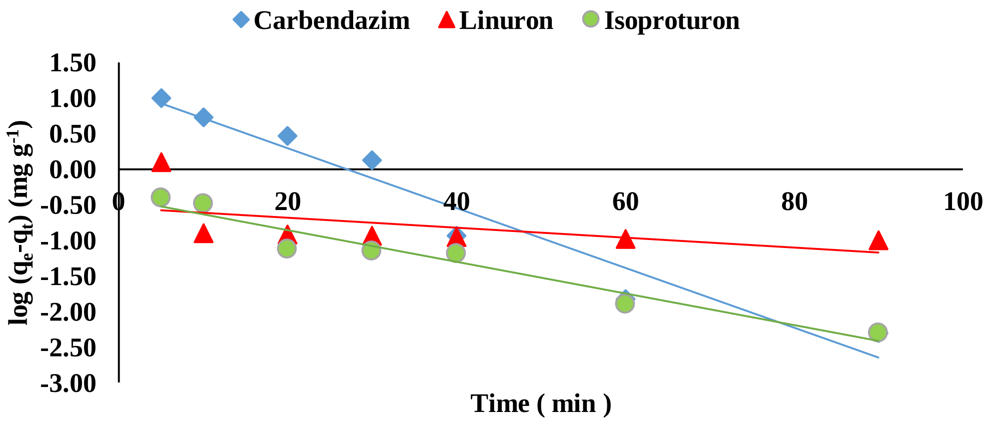


Figure 5. 27 a. Pseudo-first order kinetics plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT SA2).

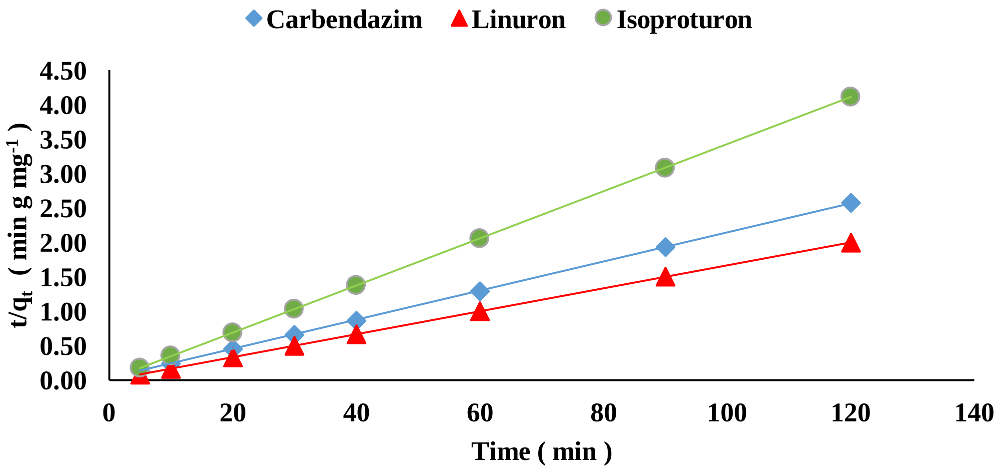


Figure 5. 27 b. Pseudo-second order kinetics plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT SA2)

Table 5. 16. Kinetic parameters for the adsorption of carbendazim, linuron and isoproturon onto (Activated carbon (NORIT SA2))

		Carbendazim	Linuron	Isoproturon
q_e, *exp* (mg g^{-1})		46.615	60.000	29.200
Pseudo-first order	q_e (mg g^{-1})	13.667	0.284	0.383
	K_1 (min^{-1})	0.096	0.016	0.051
	r	0.972	0.531	0.971
Pseudo-second order	q_e (mg g^{-1})	47.170	59.880	29.239
	K_2 (g $mg^{-1}.min^{-1}$)	0.017	0.254	0.377
	r	0.999	0.999	0.999

5. 7. 4. Adsorption Kinetics (Activated carbon (NORIT HYDRODARCO C))

In general, the pseudo-second order r values of the kinetic model was = 0.999 (Figure 5. 28 (b)) and the pseudo-second order calculated q_e values were very close to the experimental $q_{e,\ exp}$ values. These findings indicate that sorption of carbendazim, linuron and isoproturon pesticides followed the second-order reaction and suggest that the method of rate control may involve chemical sorption involving valence forces by sharing or exchanging electrons between sorbent and sorbate [321,323]. The constant reaction rate K_2 depends (in large part) on the operating conditions and is related to how fast equilibrium is reached, i.e. when it is relatively high, the time required to achieve equilibrium is relatively short . In this study, the initial sorption rates obtained with the carbendazim, linuron and isoproturon pesticides were 0.230, 0.646 and 0.055 (g $mg^{-1}.min^{-1}$) (Table 5. 11), respectively. It was suggested that the fast removal was accountable for ion-exchange and surface-sorption responses (e.g. surface complexation) with acid functional groups (amines, carboxyl and hydroxyl).

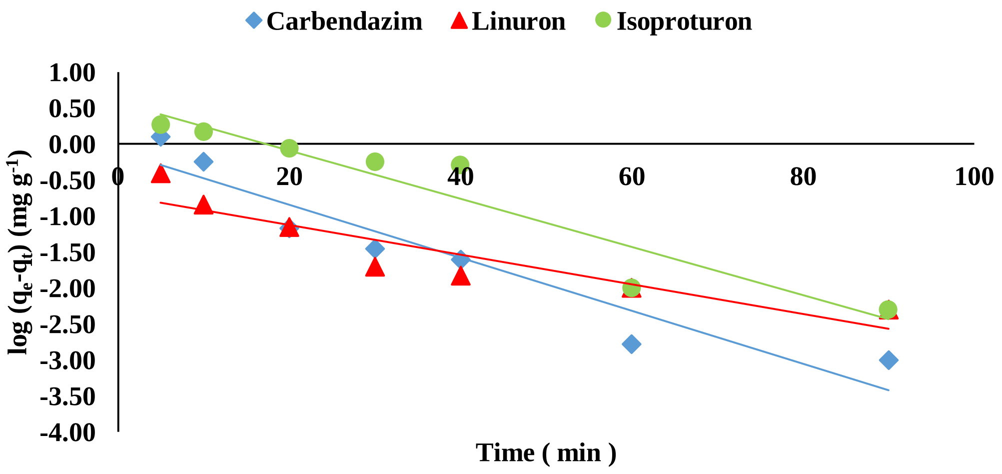


Figure 5. 28 a. Pseudo-first order kinetics plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT HYDRODARCO C)

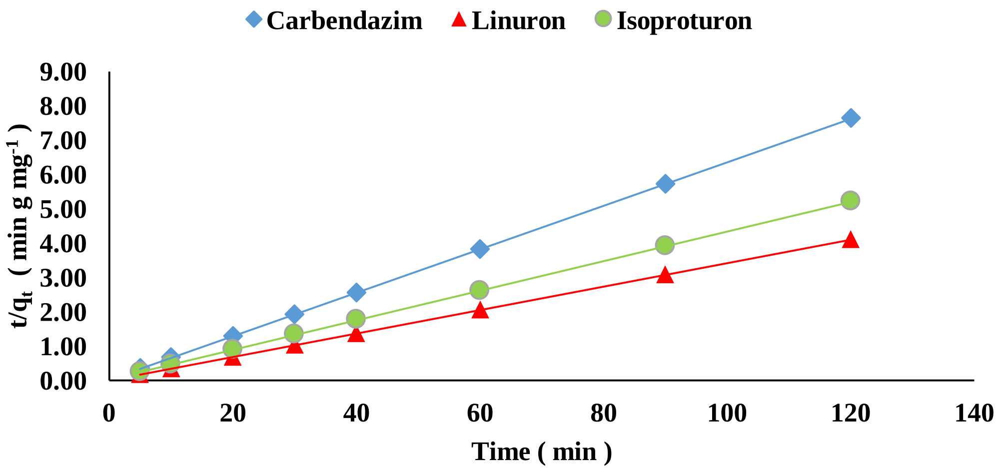


Figure 5. 28 b. Pseudo-second order kinetics plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT HYDRODARCO C)

Table 5. 17. Kinetic parameters for the adsorption of carbendazim, linuron and isoproturon onto (Activated carbon (NORIT HYDRODARCO C))

		Carbendazim	Linuron	Isoproturon
q_e, *exp* (mg g^{-1})		15.735	29.270	23.060
Pseudo-first order	q_e (mg g^{-1})	0.780	0.195	3.778
	K_1 (min^{-1})	0.084	0.047	0.077
	r	0.952	0.912	0.953
Pseudo-second order	q_e (mg g^{-1})	15.772	29.325	23.201
	K_2 (g $mg^{-1}.min^{-1}$)	0.230	0.646	0.055
	r	0.999	0.999	0.999

5. 7. 5. Adsorption Kinetics (Zeolite, type: ZSM-5)

The values of q_e and sorption rate constant k_1 of carbendazim, linuron and isoproturon pesticides on Zeolite, type: ZSM-5 which Obtained from the pseudo-first order are determined from the plot of log (q_e_ q_t) against t Figure 5. 29 (a). The calculated q_e values are discovered not in agreement with the experimental values. This indicates that the sorption of carbendazim, linuron and isoproturon pesticides does not follow pseudo-first order kinetic. The first-order model's inefficiency to match the kinetic information may be due to a limit layer controlling the start of the sorption process [324]. This is also compatible with most literature-reported instances. For the pseudo-second order, the constant adsorption rate k_2 and the capacity of adsorption q_e of carbendazim, linuron and isoproturon pesticides were calculated from the slopes and intercepts of t/q_t plots against t Figure 5. 29 (b). The findings are shown in Table 5. 12. It can be seen that the calculated coefficient of correlation r is very close to unity and that the calculated q_e values are in agreement with experimental values. These results indicate that the pseudo-second order model portrays more properly the sorption kinetic of the researched scheme than the pseudo-first order model.

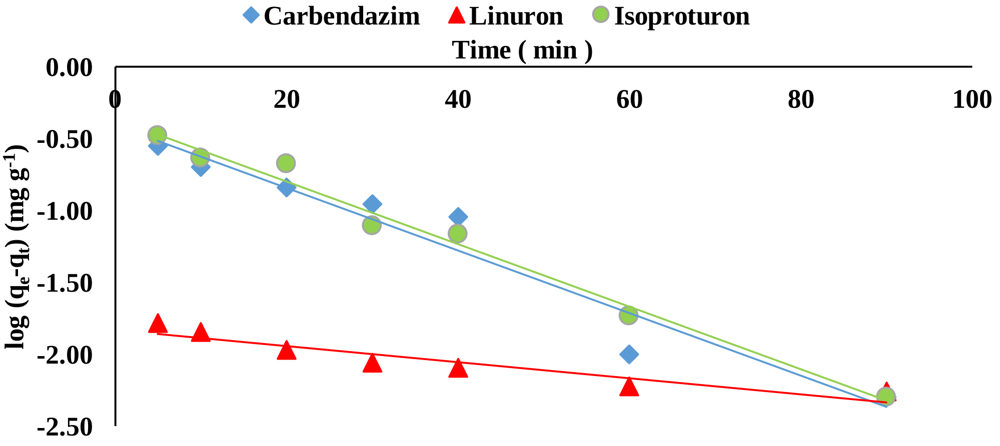


Figure 5. 29 a. Pseudo-first order kinetics plot of Carbendazim, Linuron and Isoproturon onto Zeolite, type: ZSM-5.

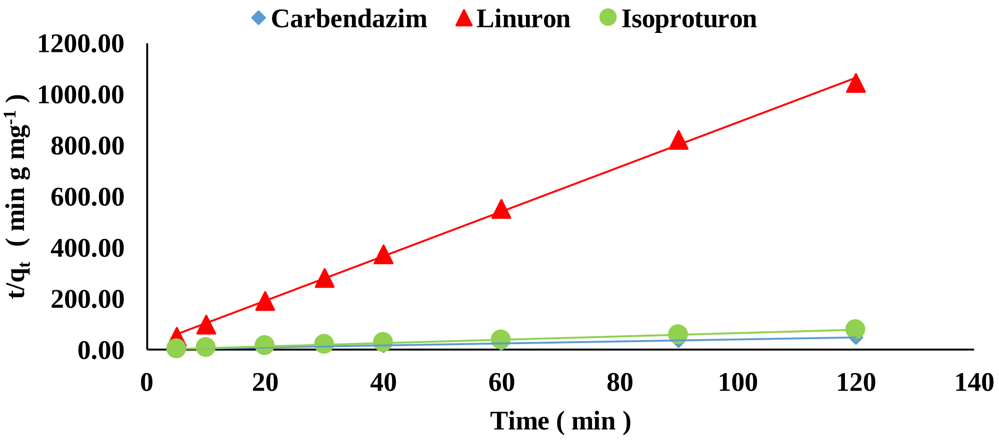


Figure 5. 29 b. Pseudo-second order kinetics plot of Carbendazim, Linuron and Isoproturon onto Zeolite, type: ZSM-5.

Table 5. 18. *Kinetic parameters for the adsorption of carbendazim, linuron and isoproturon onto (Zeolite, type: ZSM-5)*

		Carbendazim	Linuron	Isoproturon
q_e, *exp* (mg g^{-1})		2.495	0.115	1.525
Pseudo-first order	q_e (mg g^{-1})	0.392	0.015	0.432
	K_1 (min^{-1})	0.05	0.013	0.050
	r	0.971	0.941	0.993
Pseudo-second order	q_e (mg g^{-1})	2.520	0.115	1.555
	K_2 (g mg^{-1}.min^{-1})	0.322	4.212	0.275
	r	0.999	0.999	0.999

5. 8. Intraparticle diffusion model of adsorbents

Since the diffusion model is presented on the same graph for each pesticide, the multilinearity of the results is difficult to perceive. Large variations in the q_t value spread the graph on the y-axis, and three stages in the adsorption process are hard to notice. Figure 5. 30 (a, b, c, d and e) and Table 5. 13 show that for the process of adsorption of carbendazim, linuron and isoproturon pesticides on adsorbents (SCG, DSAC, Activated carbon (NORIT SA2), Activated carbon (NORIT HYDRODARCO C) and Zeolite, type: ZSM-5, three rates of diffusion are essential: the movement of adsorbents through the diffusion boundary layer, intra-particle diffusion and equilibrium achievement. The initial process is the external surface adsorption, followed by the adsorption stage in which intraparticle diffusion is the rate-limiting. The final process is the equilibrium state where intraparticle diffusion slows down since low adsorbate concentrations left in the solution.

The intraparticle diffusion model, it should be noted that, although the model predicts to do so, q_t versus $t_{1/2}$ lines of this model do not pass from the origin. For this model, the information is compelled to move from the origin, even lower coefficients of regression are acquired. For the current adsorption information, therefore, the intraparticle diffusion model does not appear to be effectively applied.

Based on these results, it was concluded that the adsorption of selected pesticides by selected adsorbents is a complex combination of surface chemisorption processes and that the most important control steps are the diffusion of boundary layers and the diffusion of intraparticle.

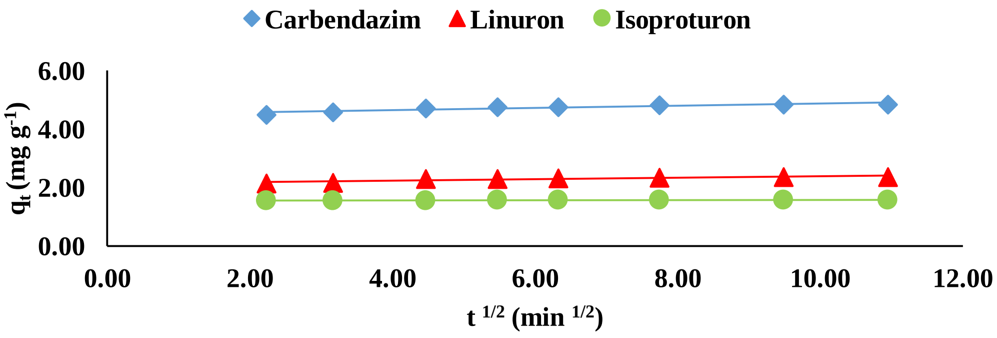


Figure 5. 30 a. Intraparticle diffusion plot of Carbendazim, Linuron and Isoproturon onto SCG

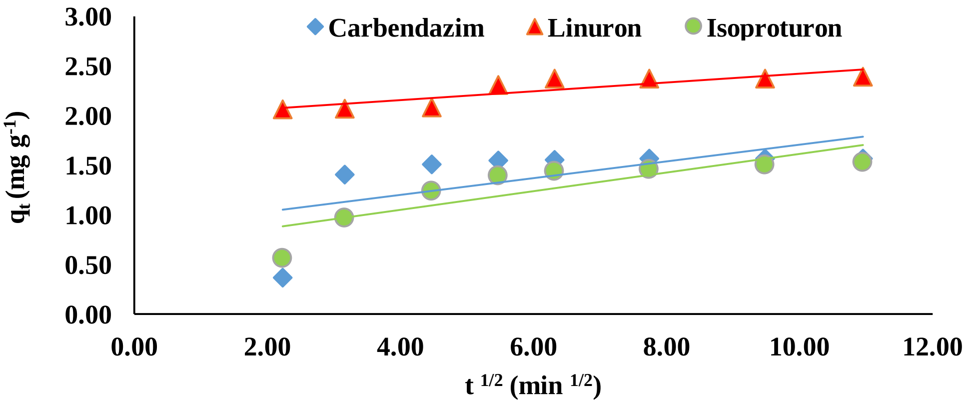


Figure 5. 30 b. Intraparticle diffusion plot of Carbendazim, Linuron and Isoproturon onto DSAC

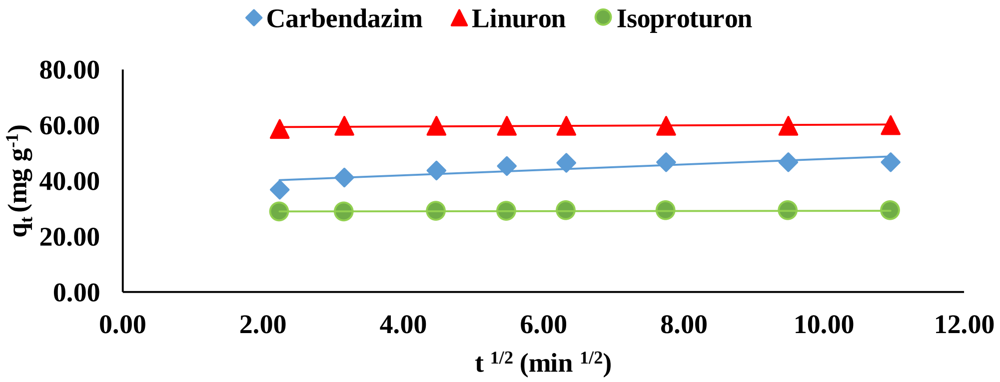


Figure 5. 30 c. Intraparticle diffusion plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT SA2)

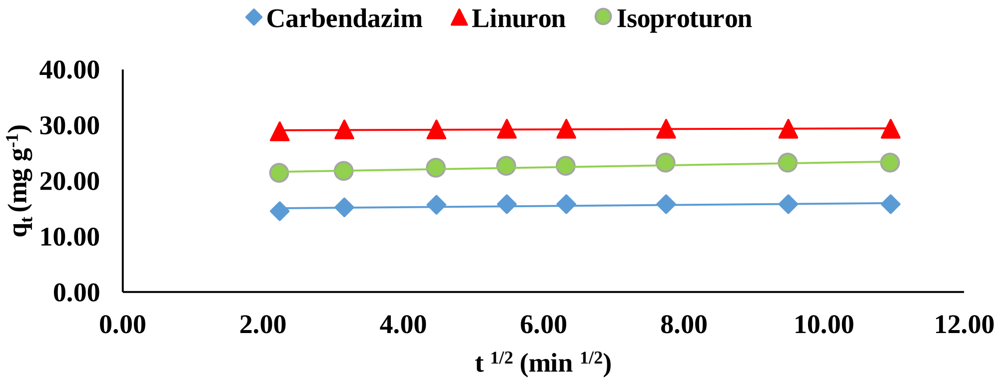


Figure 5.30 d. Intraparticle diffusion plot of Carbendazim, Linuron and Isoproturon onto Activated carbon (NORIT HYDRODARCO C)

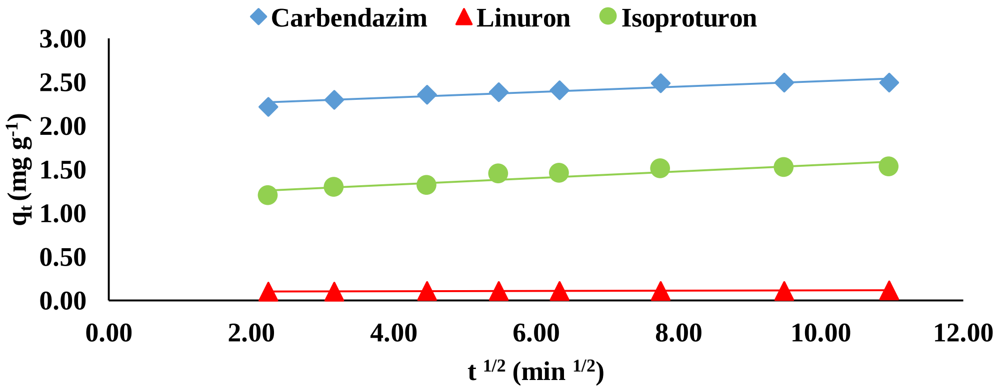


Figure 5.30 e. Intraparticle diffusion plot of Carbendazim, Linuron and Isoproturon onto Zeolite, type: ZSM-5

Table 5. 19. Intraparticle diffusion model for the adsorption of carbendazim, linuron and isoproturon onto adsorbents

		Carbendazim	Linuron	Isoproturon
Intraparticle diffusion of SCG		0.038	0.024	0.003
		4.489	2.135	1.546
		0.908	0.880	0.961
Intraparticle diffusion of DSAC	K_i (mg g^{-1} $min^{-1/2}$)	0.084	0.438	0.093
	C (mg g^{-1})	0.861	1.980	0.676
	r	0.616	0.867	0.842
Intraparticle diffusion of AC (NORIIT SA2)	K_i (mg g^{-1} $min^{-1/2}$)	0.959	0.080	0.042
	C (mg g^{-1})	38.201	59.257	28.882
	r	0.823	0.596	0.838
Intraparticle diffusion of AC (NORIT HYDRODARCO C)	K_i (mg g^{-1} $min^{-1/2}$)	0.108	0.033	0.214
	C (mg g^{-1})	14.815	28.981	21.066
	r	0.719	0.742	0.927
Intraparticle diffusion of Zeolite, type: ZSM-5	K_i (mg g^{-1} $min^{-1/2}$)	0.031	0.001	0.037
	C (mg g^{-1})	2.192	0.095	1.172
	r	0.948	0.974	0.918

5. 9. Thermodynamic approach

Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$) were calculated from Van't Hoff plots ln K_L versus $1/T$

for carbendazim, linuron and isoproturon onto SCG, DSAC, Activated carbon (NORIT SA2), Activated carbon (NORIT HYDRODARCO C) and Zeolite, type: ZSM-5 at different temperatures (298, 308 nd 318 K) Figure I. 16 (a, b, c, d and e).

The temperature effects the adsorption mechanism and the diffusion of molecules in the pores of the adsorbent materials [325]. Results were presented in Table 5. (14, 15, 16, 17 and 18). The negative values for $\Delta H°$ indicate the exothermic nature of the adsorption, which explains the decrease of pesticides adsorption efficiency as the temperature increased. The values for $\Delta H° < 20$ kJ mol^{-1} confirm that the physisorption is dominant process on the surface of adsorbents. The physical adsorption is usually characterized by weak Van der Waals bonds. The positive values for $\Delta S°$, indicate increasing randomness at the solid/liquid interface during pesticides adsorption onto the adsorbents. The negative values for $\Delta G°$ show the spontaneity of the adsorption process which is thermodinamically favorable.

Table 5. 20. Thermodynamic parameters for adsorption of carbendazim, linuron and isoproturon onto SCG

Pesticide	Temperature (K)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})
Carbendazim	298	-2.037	20.23	-8.06
	308			-8.27
	318			-8.47
Linuron	298	-12.596	26.27	-20.42
	308			-20.69
	318			-20.95
Isoproturon	298	-12.128	27.68	-20.38
	308			-20.65
	318			-20.93

Table 5. 21. Thermodynamic parameters for adsorption of carbendazim, linuron and isoproturon onto DSAC

Pesticide	Temperature (K)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})
Carbendazim	298	-13.760	30.30	-22.79
	308			-23.09
	318			-23.39
Linuron	298	-35.210	95.53	-63.68
	308			-64.63
	318			-65.59
Isoproturon	298	-13.718	32.25	-23.33
	308			-23.65
	318			-23.97

Table 5. 22. Thermodynamic parameters for adsorption of carbendazim, linuron and isoproturon onto (Activated carbon (NORIT SA2))

Pesticide	Temperature (K)	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
Carbendazim	298	-0.707	44.66	-14.014
	308			-14.461
	318			-14.908
Linuron	298	-10.891	12.16	-14.515
	308			-14.636
	318			-14.758
Isoproturon	298	-3.326	28.24	-11.743
	308			-12.025
	318			-12.308

Table 5. 23. Thermodynamic parameters for adsorption of carbendazim, linuron and isoproturon onto Activated carbon (NORIT HYDRODARCO C))

Pesticide	Temperature (K)	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
Carbendazim	298	-4.367	21.89	-10.890
	308			-11.109
	318			-11.328
Linuron	298	-3.575	53.81	-19.612
	308			-20.150
	318			-20.688
Isoproturon	298	-8.043	62.14	-26.560
	308			-27.181
	318			-27.803

Table 5. 24. Thermodynamic parameters for adsorption of carbendazim, linuron and isoproturon onto (Zeolite, type: ZSM-5)

Pesticide	Temperature (K)	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
Carbendazim	298	-41.404	109.16	-73.934
	308			-75.026
	318			-76.118
Linuron	298	-29.806	80.31	-53.737
	308			-54.540
	318			-55.343
Isoproturon	298	-64.932	215.22	-129.069
	308			-131.221
	318			-133.374

5. 10. Desorption and regeneration research

5. 10. 1. Desorption and regeneration studies of SCG

Desorption experiments were performed in order to explore the possibilities for the reuse and recovery of SCG. The results in Figure 5. 31 and Figure II. 1 (a, b, c) depicts that after three adsorption-desorption cycles (C1, C2 and C3), the desorption efficiency was 100% for all of the investigated samples. The pyrolysis at 500 ˚C was enough to degrade carbendazim, linuron and isoproturon.

The adsorption of carbendazim changed from 96.00% to 81.23% during three cycles Figure II. 1 (a). In contrast to this, the adsorption efficiency for linuron on the regenerated adsorbent changed slightly between three cycles. The Figure II. 1 (c) shows the adsorption-desorption cycles (C1, C2 and C3) of isoproturon pesticide, which decrees from 93.70% to 89.66% at third cycle. Figure II. 1 (c) shows the adsorption-desorption cycles (C1, C2 and C3) of isoproturon pesticide, which decreased from 93.70% to 89.66% at the third cycle. The total decrease in the adsorption efficiency of SCG for carbendazim, linuron and isoproturon were 14.77%, 0.95% and 4.04% after three adsorption-desorption cycles, respectively. Figure 5. 31 shows the changes in pesticide removal when coadsorption is applied. During three cycles, percentage of carbendazim and linuron removal decreased from 96.1% to 88.55% and 94.65% to 84.72%, respectively. Comparing with results obtained from single pesticide adsorption, slightly better percentage removal was achieved for linuron.

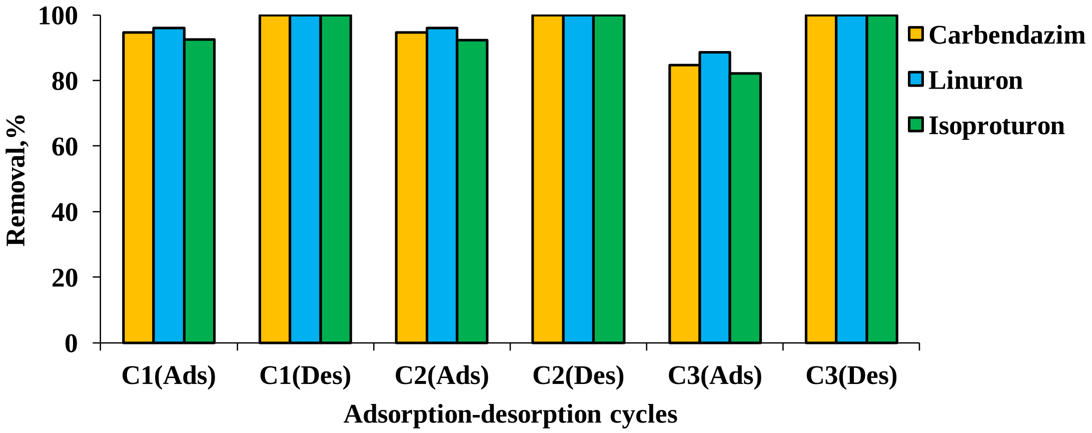


Figure 5. 31. Adsorption/desorption study mixture of carbendazim, linuron and isoproturon per cycle (C1, C2 and C3).

5. 10. 2. Desorption and regeneration studies (DSAC)

From an economic and benefit perspective, the DSAC potential for regeneration is very significant. Studies of desorption help to recover the pesticides and reuse the saturated adsorbent. Using thermal activation to regenerate the DSAC in each cycle may require high energy and adsorbent loss [326]. The results of adsorption-desorption cycles (C1, C2 and C3) of carbendazim, linuron and isoproturon pesticides were depicted in Figure II. 2 (a, b, c). It is apparent from Figure 5. 32. that the adsorption and desorption were 92.73% and 100% for carbendazim, 95.70% and 100% for linuron and 87.85% and 100% for isoproturon, respectively after the first regeneration cycle. After third regeneration cycle adsorption and desorption decreased down to 66.39% and 100% for carbendazim, 79.42% and 100% for linuron and 69.59% and 100% for isoproturon respectively. Such results showed promising DSAC regeneration potential that could be successfully used three times after regeneration to extract and recover pesticides from aqueous waste. Pesticides can be effectively removed from activated carbon such as DSAC using dilute acids. Unlike strong acids (HCl, H_2SO_4), H_3PO_4 has a slightly negative effect on the adsorption potential and structure of the regenerated DSAC and a very high capacity to desorb pesticides as well. Pesticides that bind active sites are released on the DSAC surface during the regeneration process.

DSAC can be graded as a cost-effective and environmentally friendly separation medium for water purification based on these characteristics.

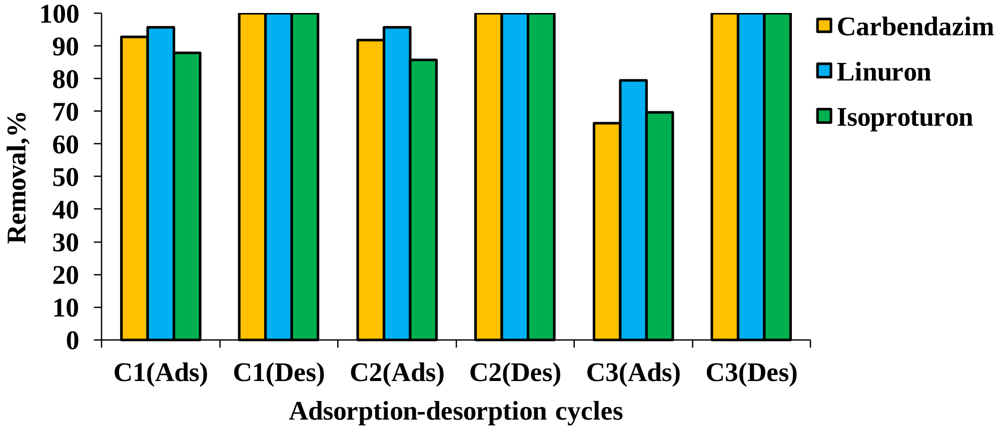


Figure 5. 32. Adsorption/desorption study mixture of carbendazim, linuron and isoproturon per cycle (C1, C2 and C3).

5. 11. Adsorption mechanism of carbendazime, linuron and isoproturon on SCG and DSAC

Adsorption mechanism of pollutants in water treatment could not be described as single mechanism, due to the complex interactions between different pollutants. The selection of the primary mechanism is based on physicochemical properties of adsorbents (SCG and DSAC), and chemical and structural characteristics of the selected pesticides [327].

Many types of degradation have been published for selected pesticides (carbendazime, linuron and isoproturon) based on oxidative decomposition processes [328,329], electrochemical degradation [330,331], solar degradation [332] and bacterial degradation [333].

The adsorption mechanism of selected pesticides on activated carbon prepared from spent coffee gorunds and date stones are proposed according to FTIR analysis results and the established functional groups on the adsorbents surface Figure 33 and 34.

SCG and DSAC surfaces are sutable for specific electron-donor-acceptor (EDA) interactions, based on electronic charge being transferred between molecular entities and the association of molecules leading to $\pi - \pi$ interactions between the aromatic structures of adsorbent and selected pesticides. Also, aromatic structure of selected pesticides initiated $n - \pi$ interactions due to the bonding of -OH, -COOH or polyphosphate species of adsorbents. Aromatic ring of pesticides was electron acceptor, while carbonyl oxygen from functional groups of SCG and DSAC plays the role of electron donor.

Specific hydrogen-donor-acceptor (HDA) interactions, such as dipole-dipole H-bond interaction (between the -OH group on the adsorbents surface and the nitrogen atom of the pesticide) and Yoshida bonds (between the -OH or -COOH group of the adsorbent and the aromatic ring of the pesticide) were proposed based on the presence of polar oxygen and hydroxyl groups in the selected pesticides, but also phosphor containing functional groups (peaks detected at 3000-3500 cm^{-1}, 1160.78 cm^{-1} and 874.04 $cm^{-1}$for the DSAC, as weel as peaks detected at 3433.06 cm^{-1} and 1046.60 cm^{-1} for the SCG).

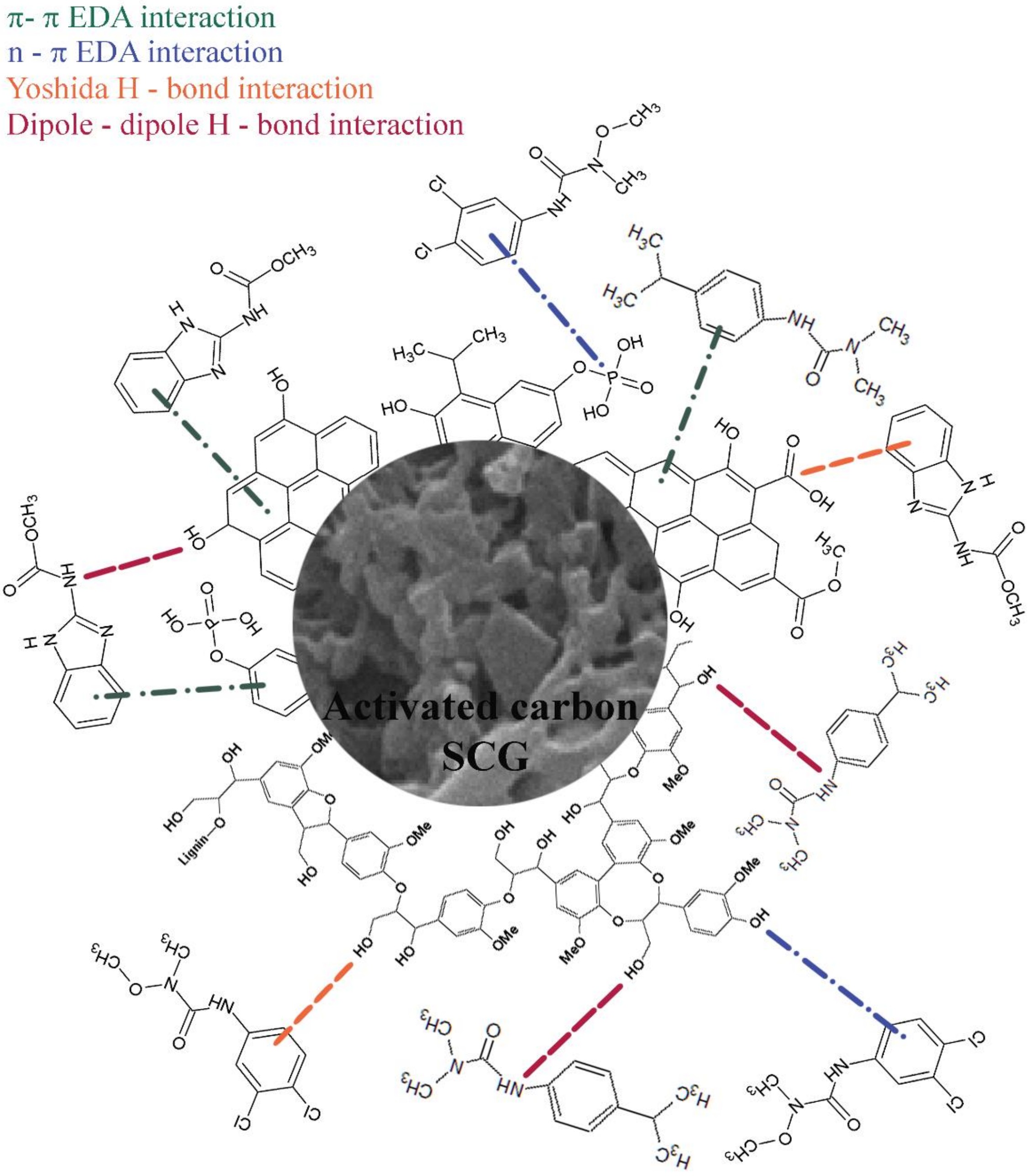


Figure 5. 33. Proposed adsorption mechanism of carbendazime, linurone and isoproturon on SCG.

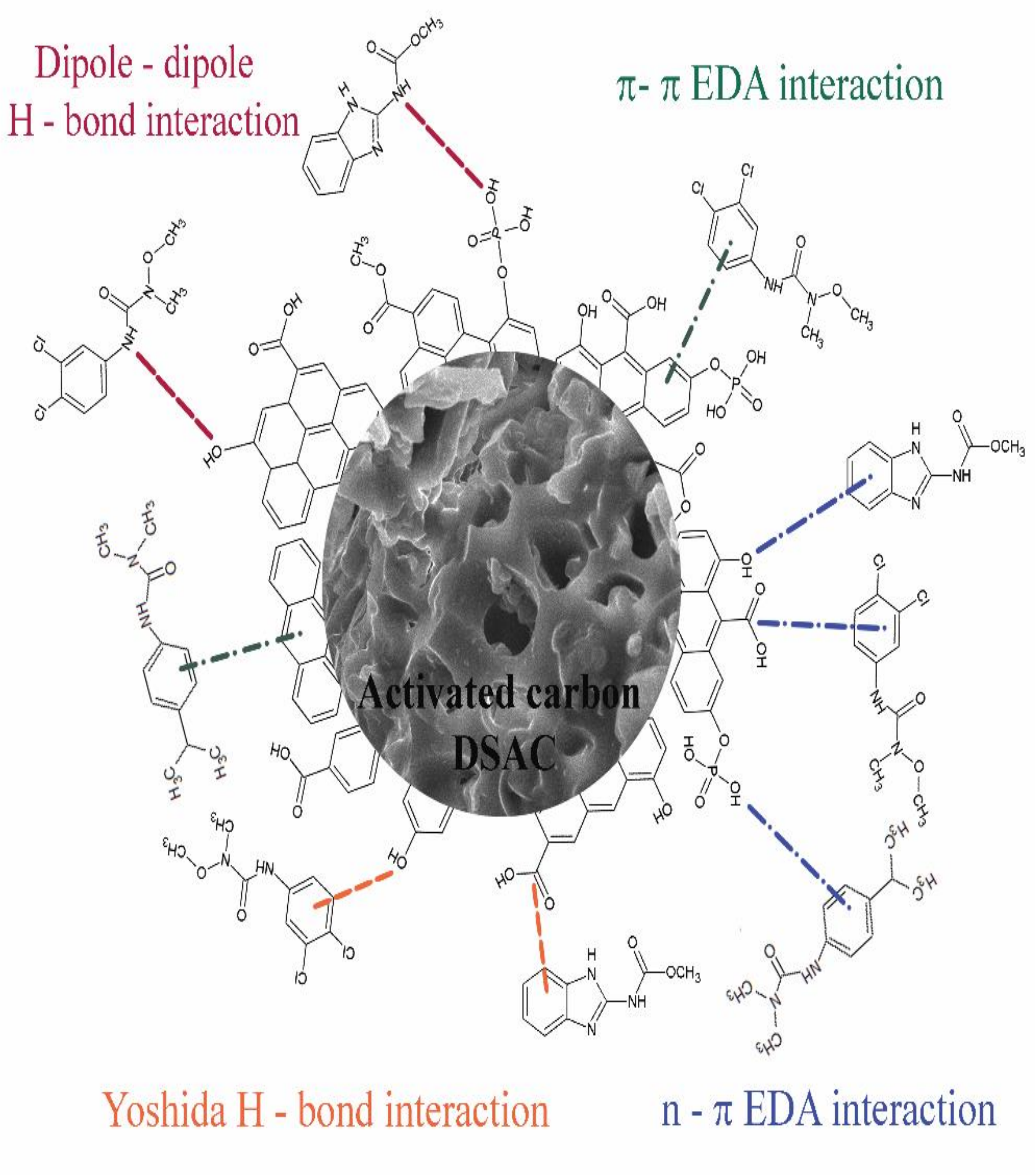


Figure 5. 34. Proposed adsorption mechanism of carbendazime, linurone and isoproturon on DSAC

5. 12. Economic benefit

One of the most important issues in selection of appropriate adsorbent is price of adsorbent. Therefore the economic benefit of investigated adsorbents needs to be considered. SCG and DSAC adsorbents, which are converted chemically by phosphoric acid and by heating into activated carbon, require extra processing cost. Also, cost of grinding of date stones need to be included in the total cost of adsorbent. Cost of collection and transportation of adsorbents could not be assessed and is calculated as overhead cost, 10% of net cost [334]. Considering the expenses for collection and transport of suggested material (spent coffee grounds and date stones), activation agent (phosphoric acid and distilled water) and electrical energy for drying the material, the financial cost of the SCG and DSAC would be approximately 0.5 US$ and 0.55 US$ per kg, respectively (Table 5.19). The cost of commercial activated carbon for separation of pollutants from aqueous media varies between US$ 2.2 – 5 per kg based on the quality of activated carbon. The newly developed AC from coffee waste and date stones are cost-effective alternative to the existing commercial activated carbons, which may be used as ecologically compatible adsorbents. SCG and DSAC can be classified as economical and environmentally friendly separation selected mediums for water purification.

Table 5. 25. *Cost benefit of SCG and DSAC adsorben*

Process	**Price per kg SCG (US$)**	**Price per kg DSAC (US$)**
Grinding	-	0.05
Drying	0.09	0.09
Activation (phosphoric acid, distilled water)	0.36	0.36
Net cost	0.45	0.50
Overhead cost (10 % of net cost)	0.045	0.05
Total cost	0.495	0.55

5. 13. SWOT analysis

The investigation and usage of low-cost adsorbents, obtained by thermochemical conversion of lignocellulosic waste implies better opportunities in management of water treatment system. The performance, competition, risk, and current and future potential of treatment process based on adsorbents produced from coffee waste and date stone can be determined by SWOT (Strength, Weakness, Opportunities and Threats) analysis (Table 5.20).

Table 5. 26. SWOT analysis of usage of SCG and DSAC adsorbents

Strengths
Cheap and/or Inexpensive materials – waste products Affordable – everyday coffee and dates consumption produces a large amount of spent coffee grounds and date stones as waste; Efficacy – high removal rates, simple, effective treatment
Opportunities
Economical – reduced cost of treatment process Environmental friendly **-** the use of waste materials, Modification can improve removal properties of applied materials After modification could be marketable products Food waste and circular economy
Weaknesses
Consumption of chemicals – e.g. phosphoric acid for modification Regeneration
Threats
Power consumption Production of sludge (could be toxic) **-** waste management Lack of knowledge about behavior of applied materials in real industrial systems

The strengths of those alternative adsorbents are in the fact that they are affordable, low cost and effective. The everyday consumption of coffee drinks and dates leads to the generation of spent coffee grounds and date stones as waste. If those types of waste are not well managed, they could cause toxic and unpleasant vapor and environmental pollution. Also, the efficiency of treatment process, with high removal rates supports the strength to usage of low-cost bioadsorbents.

Opportunities on the usage of SCG and DSAC adsorbents are economical, according to the reduced cost of treatment process as environmental friendly, since the waste materials are used as adsorbents. The modification of proposed adsorbents results to improvement of their physico-chemical properties for efficient removal of selected pollutants as well as their change into marketable products.

The weakness is based on the consumption of phosphoric acid for modification and regeneration of sorbents. The regeneration processes of selected adsorbents are effective for three to five times, after which sorbent saturation is achieved and the removal efficiency of pollutants is reduced. Therefore, the threat is generation of sludge which could be toxic and requires proper waste management. Additionally, there is a lack of experience and knowledge about testing materials with real industrial effluents.

Technical applicability/implementation in real systems, simplicity of the operation and low cost effectiveness, as well as environmental protection are the key factors which determine the suitable treatment process.

Based on the SWOT analysis, it could be concluded that the low cost adsorbents based on lignocellulosic waste have promising opportunities in water treatment processes and management. The low cost adsorbents, such as SCG and DSAC can replace the high cost treatment system based on conventional methods and commercial adsorbents such as activated carbons NORIT SA2 or HYDRODARCO C.

The future analysis needs to take into consideration PEST (Political, Economic, Social, Technology) analysis together with SWOT analysis in order to get better information of implementation possibilities of suggested adsorption for successful and efficient treatment in real industrial systems.

5. 14. Comparison of SCG and DSAC with commercial adsorbents

The results from three analyses of commercial adsorbents (Activated carbon (NORIIT SA2), Activated carbon (NORIT HYDRODARCO C) and Zeolite, type: ZSM-5) and low-cost adsorbents made from SCG and DSAC were analysed and compared with competitive advantages.

No significant changes in removal efficiency of pesticides by SCG, DSAC and commercial adsorbents were observed for different pH values. The removal efficiencies for linuron and isoproturon were slightly higher for SCG and DSAC by comparing to commercial adsorbents.

Increase in removal efficiency with increase in adsorbent dosage was noticed especially for adsorption of isoproturon on SCG and DSAC and for adsorption of linuron on SCG and zeolite ZSM-5. For other adsorption processes of pesticides on SCG, DSAC and commercial adsorbents significant change in removal efficiency with change in adsorbent dosage was not observed.

The removal time is essential parameter during the water treatment. The sorption process is fast at the begining of the contact period, while it becomes slower near the equilibrium and the removal efficiencies stop to change significantly with prolonging the contact time. The longest contact time till equilibrium (60 min) was observed for adsorption of pesticides on zeolite ZSM-5. The equilibrium was reached from 10 to 60 min for adsorption on Activated carbon NORIT SA2 and from 5 to 30 min for adsorption on Activated carbon NORIT HYDRODARCO C for linuron, carbendazim and isorpoturon. The shorter contact time till equilibrium was noticed for adsorption of pesticides on SCG.

The removal efficiencies were reduced when the concentrations of carbendazim, linuron and isoproturon were raised. High removal efficiencies (above 89.5 %) for all studied adsorbents were noticed at concentrations of pesticides of 2 mg L^{-1}.

According to the obtained results, simple conclusion could not be drowning since the different adsorbents achieve the highest recoveries at different conditions. The maximum obtained recoveries at optimal conditions were presented at Figure 5.35. It could be concluded that adsorbents prepared from waste materials, spent coffee grounds and date stones, were efficient as well as the commercial adsorbents.

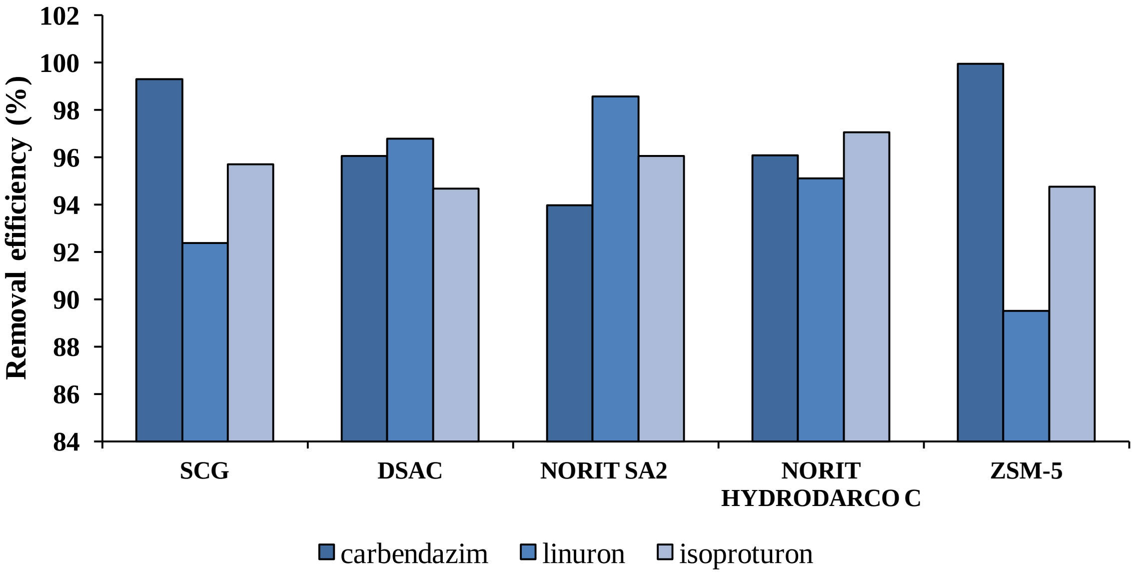


Figure 5. 35. Comparison of removal efficiencies for SCG, DSAC and commercial adsorbents

6. 0. Conclusions

In the current research study, the capacity of low-cost activated carbons; spent coffee grounds (SCG) and date stones (DSAC) was compared with commercial Activated carbon (NORIIT SA2), Activated carbon (NORIT HYDRODARCO C) and Zeolite, type: ZSM-5 to remove carbendazim, linuron and isoproturon pesticides from aqueous solution were explored. From the results, it can be concluded that SCG and DSAC showed quite good capabilities in removing selected pesticides from water. Also, commercial adsorbents were highly efficient. The influences of the main parameters such as contact time, the initial pesticides concentration, adsorbent dose, pH and temperature on the efficiency of the separation process were investigated during the batch operational mode. Adsorption Isotherms, Adsorption Kinetics and Thermodynamic study of the processes has been done, which can adequately describe the adsorption process. Based on comprehensive experiments and analysis of all the results obtained, the following can be concluded:

- ❖ The high surface area of activated carbons can be prepared from the chemical activation of the coffee residue and date stones with H_3PO_4 as activating agent. The activation temperature and increasing the chemical concentration (from 30 % to 50 %) also did influence the carbon yield possibly due to the phosphate linkages formed during the activation step. Sample impregnated with a 30 % phosphoric acid solution and (H_3PO_4/coffee residue and date stones) ratio of 3:1 showed the best results leading to higher adsorption capacities.
- ❖ SEM analysis of SCG and DSAC before and after adsorption of the analyzed selected pesticides shows a changed morphology of the adsorbent surface after the selected pesticides adsorption. SEM micrographs clearly show the developed porous structure of adsorbents
- ❖ FTIR analysis of SCG and DSAC showed the presence of functional groups that are typical of activated carbon and essential for the adsorption of the analyzed pollutants such as pesticides. A visible difference can be observed by comparing the FTIR spectrum before and after adsorption of carbendazim, linuron and isoproturon pesticides on SCG and DSAC. Displacement of the functional groups –OH and –C–H occurs within the range of 3500 –2800 cm^{-1}, suggesting the weakening of these bonds due to the potential electrostatic

attraction of the cations. In the 1200-800 cm^{-1} region, displacement of acidic phosphate and other phosphate functional groups occurs, indicating that in addition to covalent bonds, the interaction of pesticides with the active surface of the adsorbent also takes place with van der Walsz bonds. Specific electro-donor acceptor (EDA) and hydrogen-donor acceptor (HDA) interactions, such as the dipole-dipole H-bond interaction (between the -OH group on the adsorbent surface and the pesticide nitrogen atom) and the Yoshida bond (between -OH or -COOH groups of adsorbents and aromatic pesticide ring) are characteristic mechanisms of pesticide binding to the SCG and DSAC adsorbent surface.

- The SCG and DSAC have a highly developed BET surface area (803.422 and 307.450 m2 g^{-1}), respectively.
- The adsorption kinetics can be best explained by pseudo-second order theoretical model suggesting that the chemical adsorption is the rate-limiting phase, rather than mass transmission.
- The study of the interaction between the selected pesticides and adsorbents was modeled using three isotherms: Langmir's, Freundlich's and Temkin's isotherms that showed satisfactory correlation coefficients. Adsorption of carbendazim, linuron and isoproturon on Activated carbon NORIT SA2 fitted very well to the Freundlich model. Activated carbon NORIT HYDRODARCO C indicated different behavior for selected pesticides: carbendazim and isoproturon pesticides sorptions are well described by Freundlich isotherm, while linuron was fitted the best by the Langmuir equation. Adsorption of carbendazim on Zeolite, type: ZSM-5 was defined the best by the Langmuir law, linuron fitted the Temkin isotherm, and isoproturon was well described by the Freundlich and Temkin models.
- The negative values for $\Delta H°$ indicate the exothermic nature of the adsorption, which explains the decrease of pesticides adsorption efficiency as the temperature increased.
- The financial cost of the SCG and DSAC would be about US$ 0.5 and 0.6 per kg, respectively. The cost of commercial activated carbon for removal of contaminants from aqueous media changes between US$ 2.2 - 5 per kg based on the quality and kind of activated carbon.

- Considering the efficiency and the satisfied criteria in the field of green technologies, it can be concluded that applied low-cost adsorbents, obtained by thermochemical conversion of lignocellulosic waste, can successfully replace commercial activated carbon and be used in the adsorption of pollutants such as pesticides from the landfill and wastewater under tertiary treatment.
- SCG and DSAC can be classified as cost effective and environmentally friendly adsorbents for water treatment.
- Investigatigation of the most effective, the cheapest available materials originated from the waste such as SCG and DSAC, which could be widely and economically used is important for the implementation of the circular economy principles, whereby the waste management practice is focused on the waste generation prevention as well as on reduction of its volume by kepping the value of products for a long period of time.
- The efficiency of the regeneration process of SCG and DSAC, with the high re-application efficiency in the removal of pollutants, supports the importance of their application.
- Modification of the proposed adsorbents results in improvement of their physicochemical properties for efficient removal of selected pollutants as well as their ability to be applied as marketed products.

7. 0. References

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8. 0. Appendices

8. 1. Appendix I

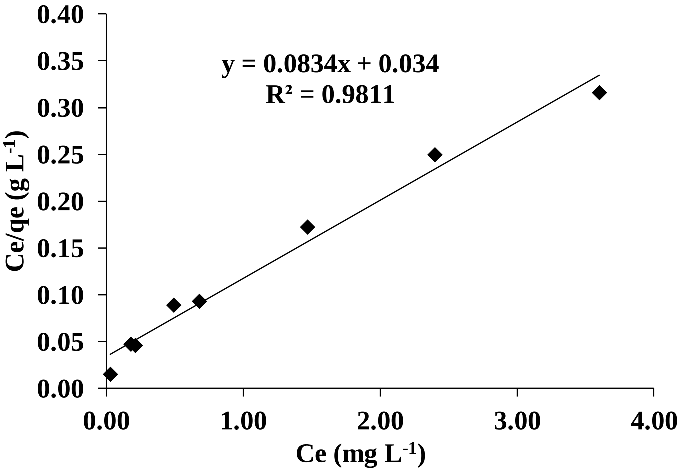


Figure I. 1 a. Adsorption isotherm of Carbendazim on (SCG)

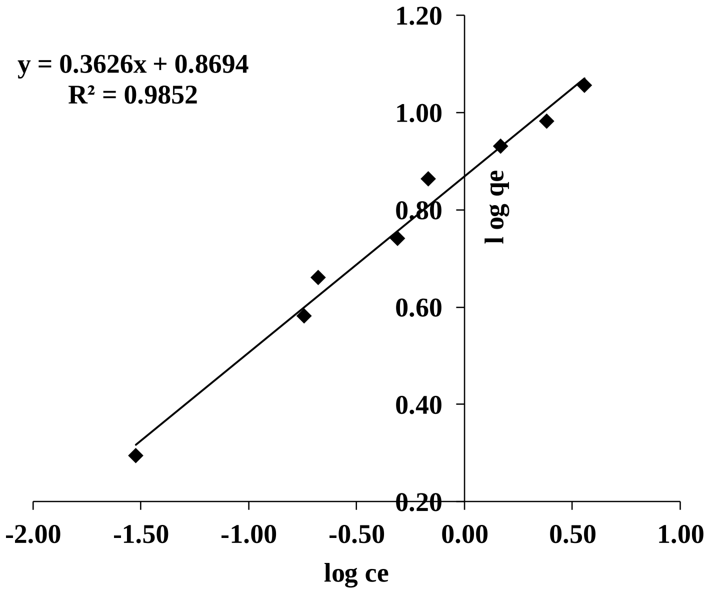


Figure I. 1 b. Linear plot of Freundlich isotherm of carbendazim sorption on (SCG)

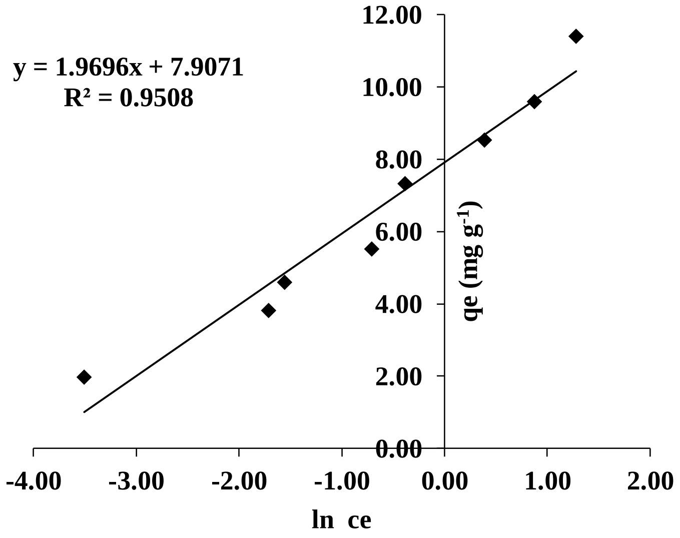


Figure I. 1 c. Temkin adsorption isotherm of carbendazim sorption on (SCG)

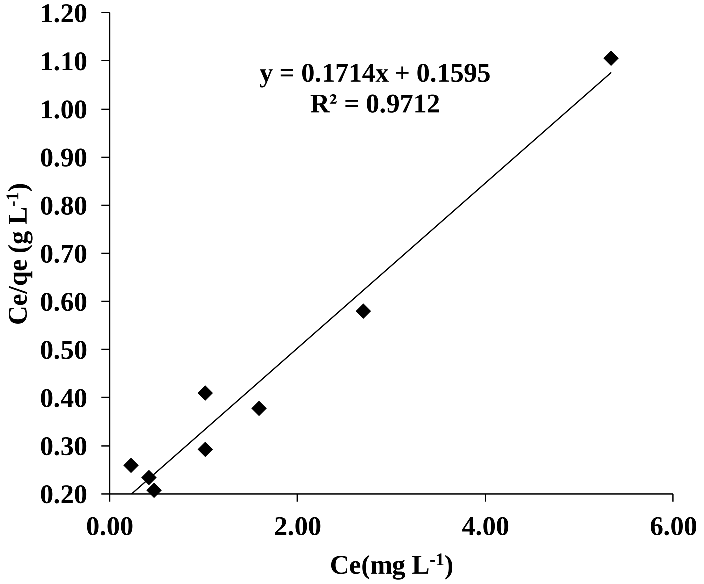
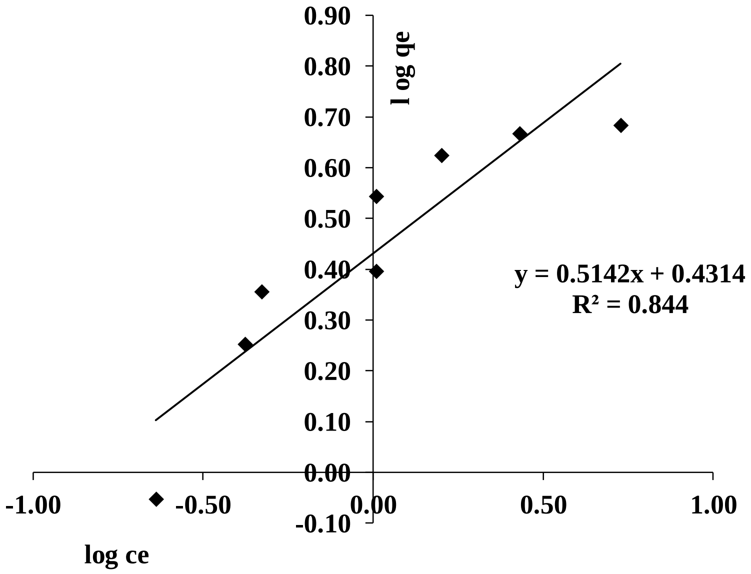


Figure I. 2 a. Adsorption isotherm of Linuron on (SCG)



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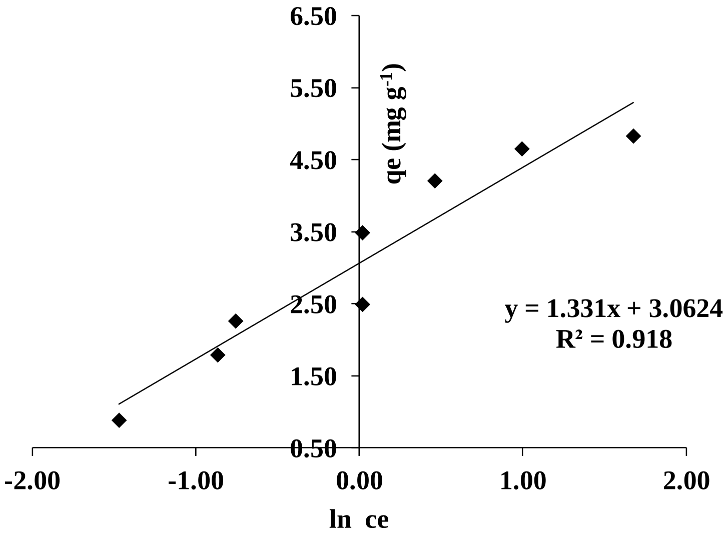


Figure I. 2 c. Temkin adsorption isotherm of Linuron sorption on (SCG)

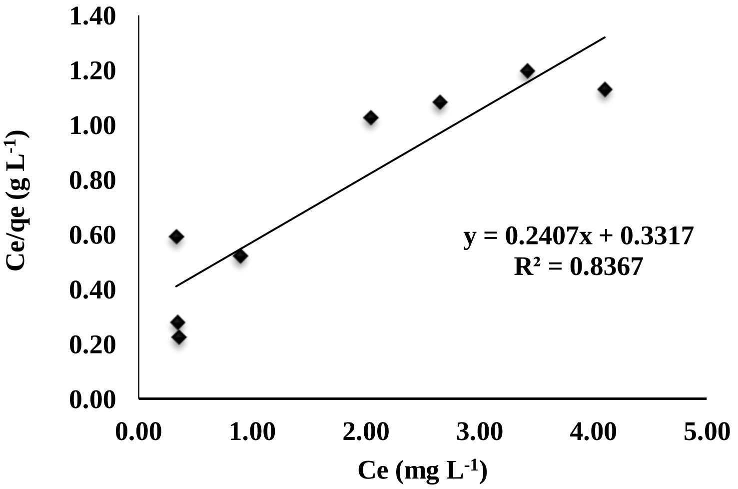


Figure I. 3 a. Adsorption isotherm of isoproturon on (SCG)

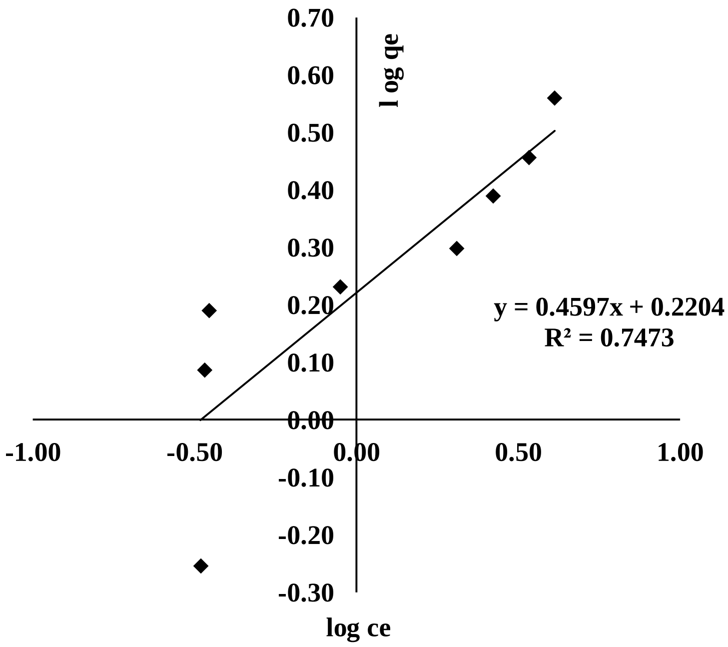


Figure I. 3 b. Linear plot of Freundlich isotherm of isoproturon sorption on (SCG)

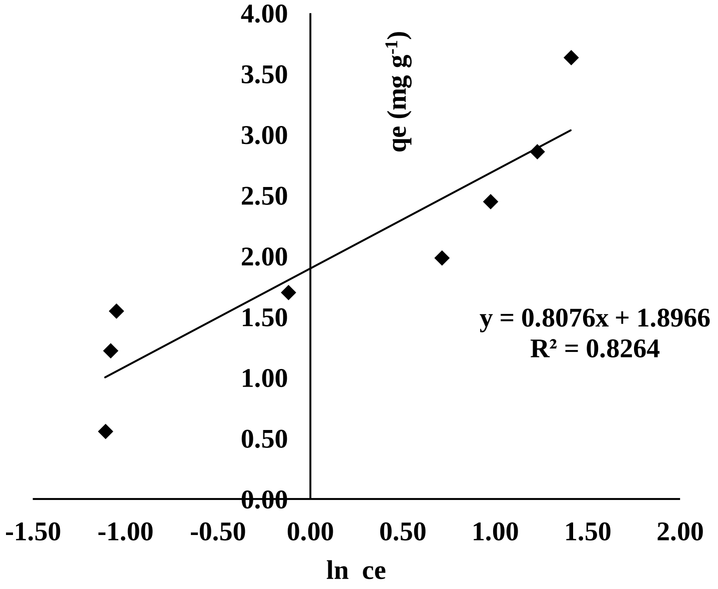


Figure I. 3 c. Temkin adsorption isotherm of isoproturon sorption on (SCG)

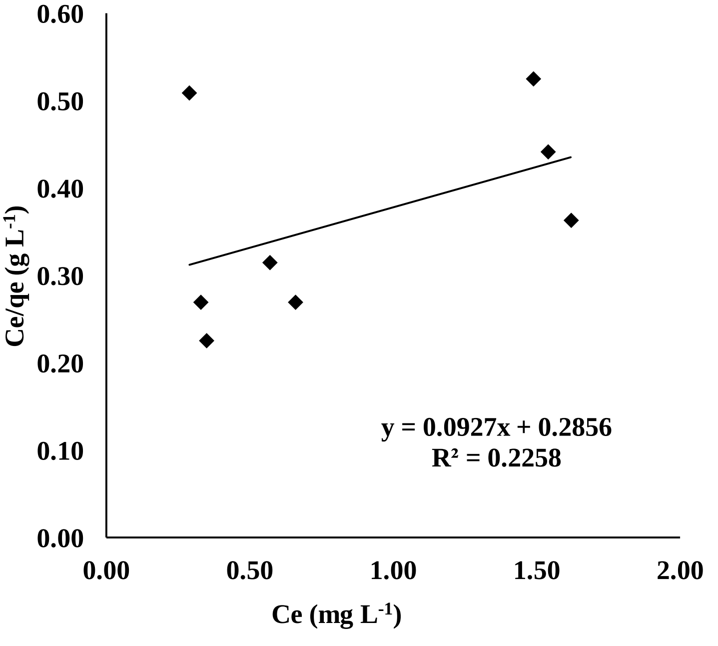


Figure I. 4 a. Adsorption isotherm of carbendazimon on DSAC

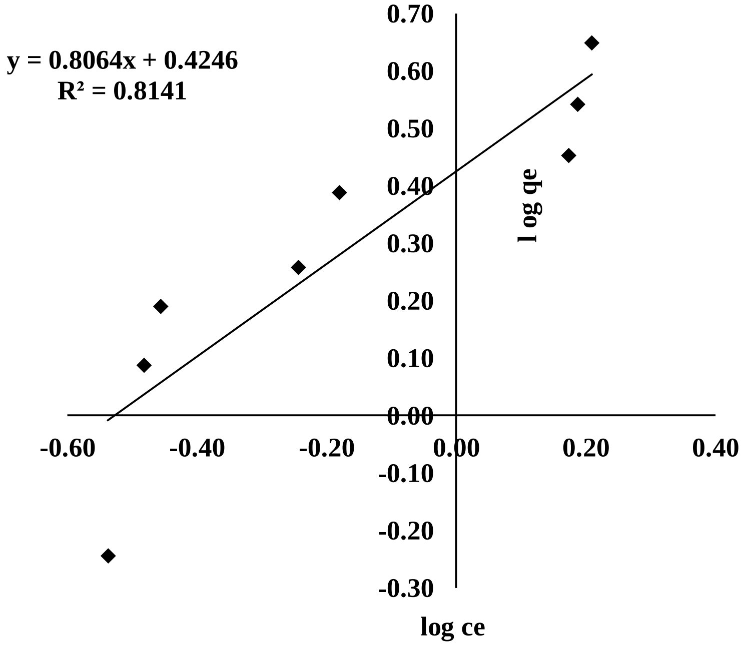


Figure I. 4 b. Linear plot of Freundlich isotherm of carbendazim sorption on DSAC

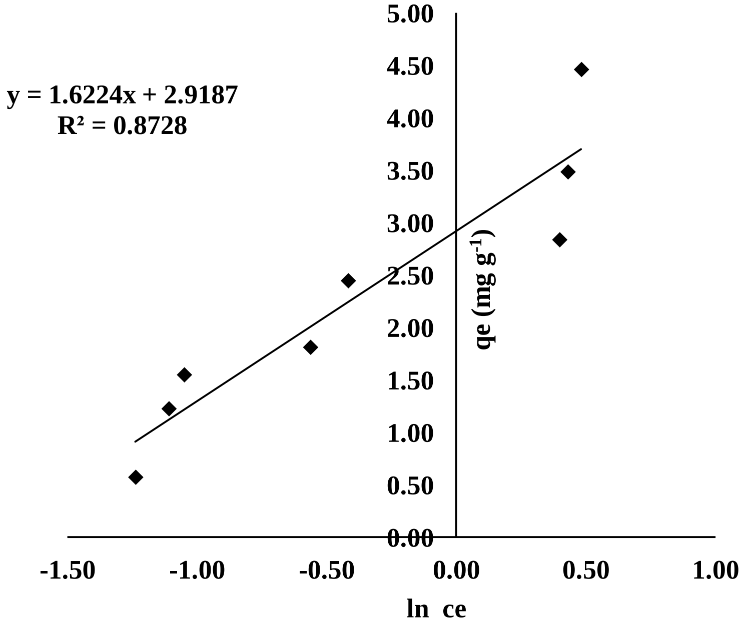


Figure I. 4 c. Temkin adsorption isotherm of carbendazim sorption on DSAC

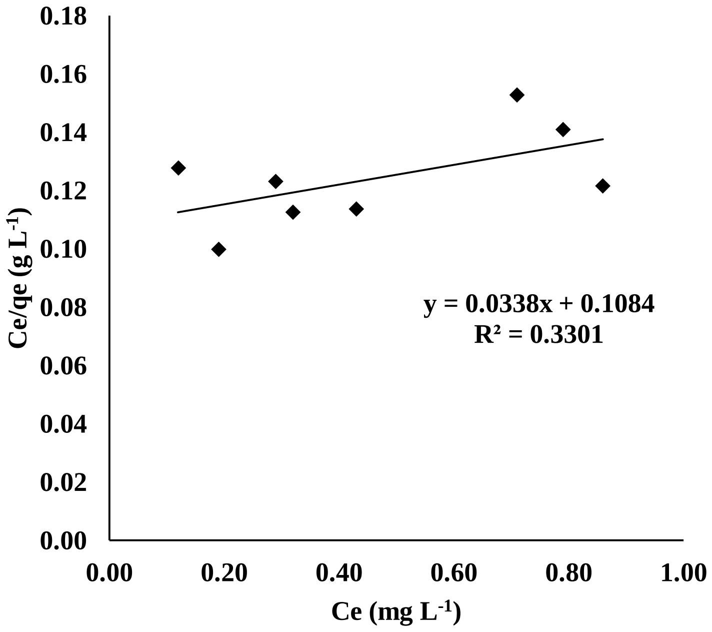


Figure I. 5 a. Adsorption isotherm of linuron on DSAC

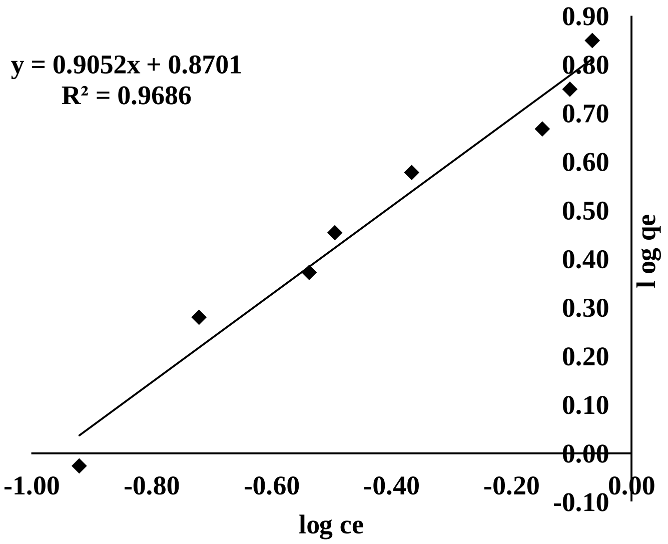


Figure I. 5 b. Linear plot of Freundlich isotherm of linuron sorption on DSAC

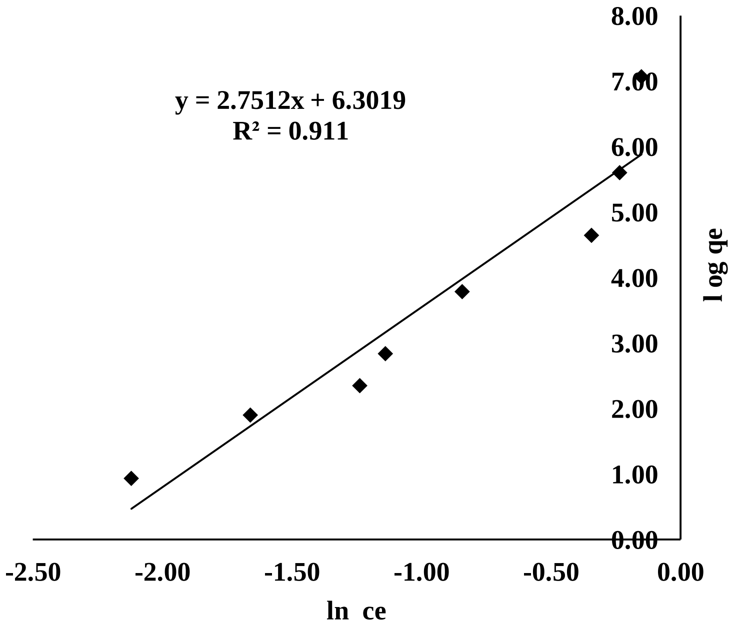


Figure I. 5 c. Temkin adsorption isotherm of linuron sorption on DSAC

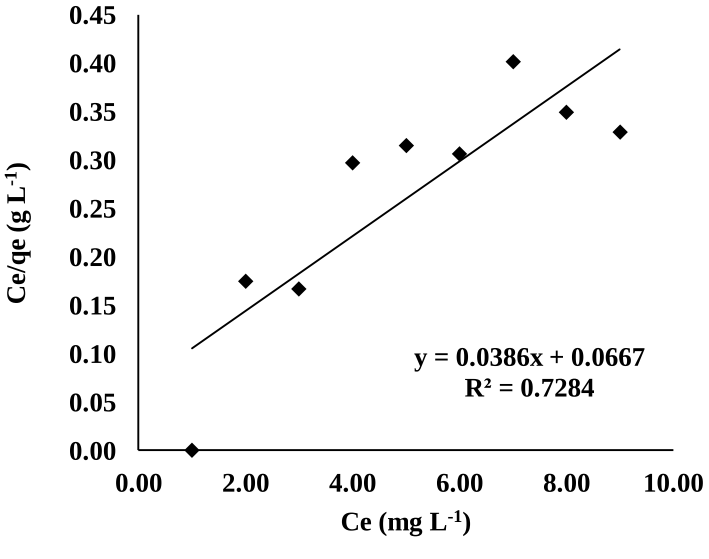


Figure I. 6 a. Adsorption isotherm of isoproturon on DSAC

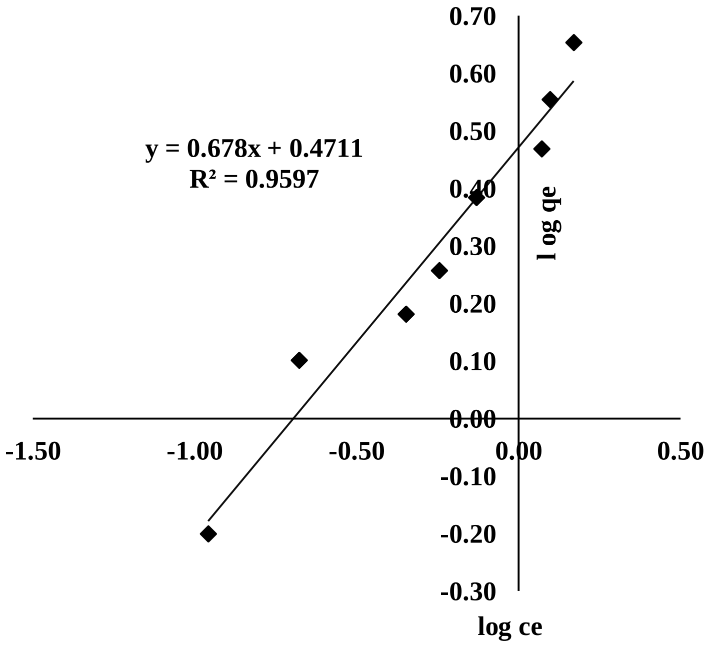


Figure I. 6 b. Linear plot of Freundlich isotherm of isoproturon sorption on DSAC

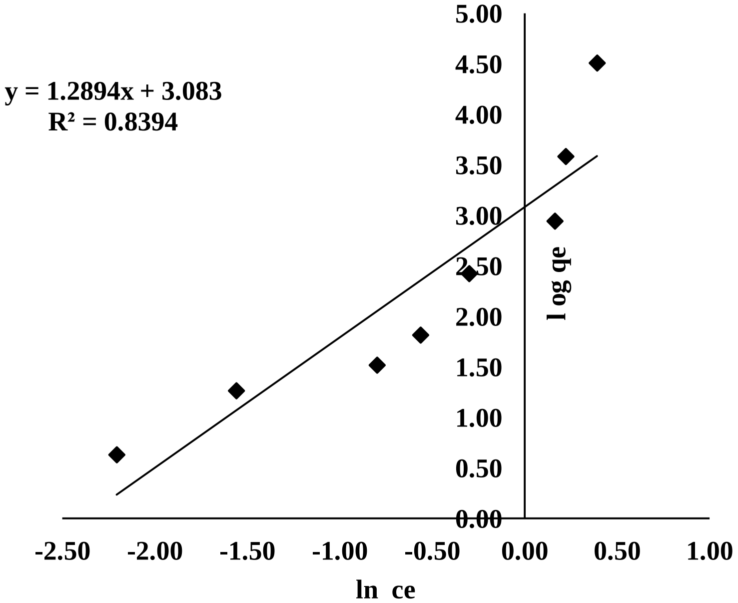


Figure I. 6 c. Temkin adsorption isotherm of isoproturon sorption on DSAC

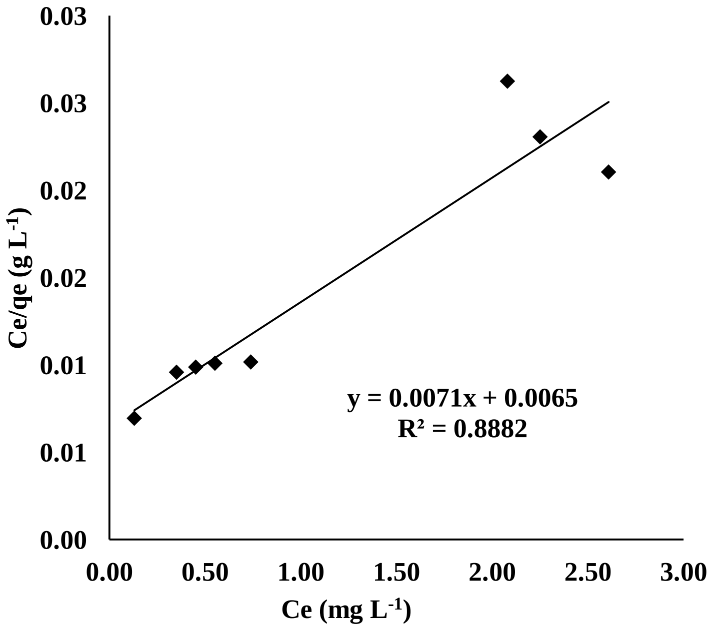


Figure I. 7 a. Adsorption isotherm of carbendazim on Activated carbon NORIT SA2

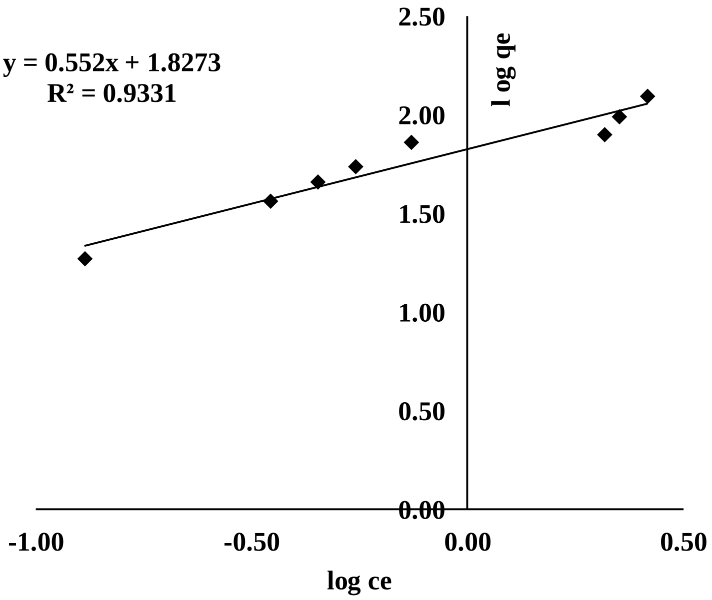


Figure I. 7 b. Linear plot of Freundlich isotherm of carbendazim sorption on Activated carbon NORIT SA2

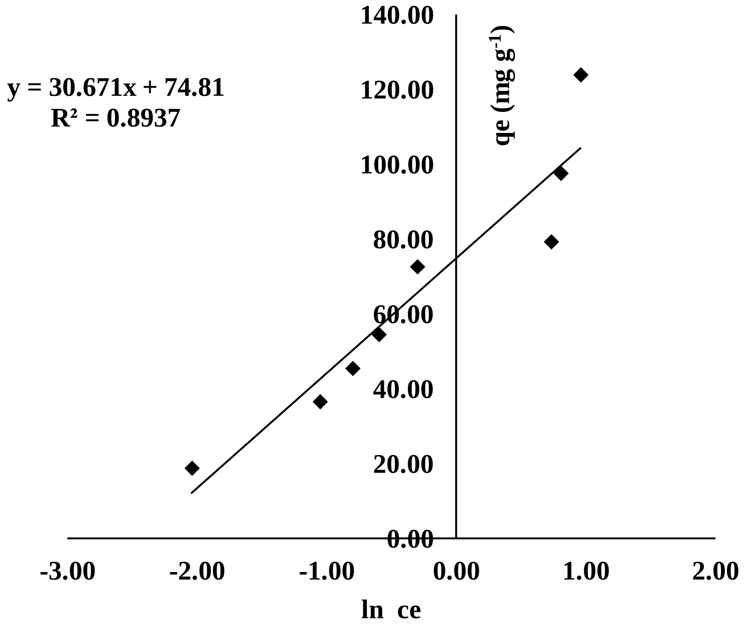


Figure I. 7 c. Temkin adsorption isotherm of carbendazim sorption on Activated carbon NORIT SA2

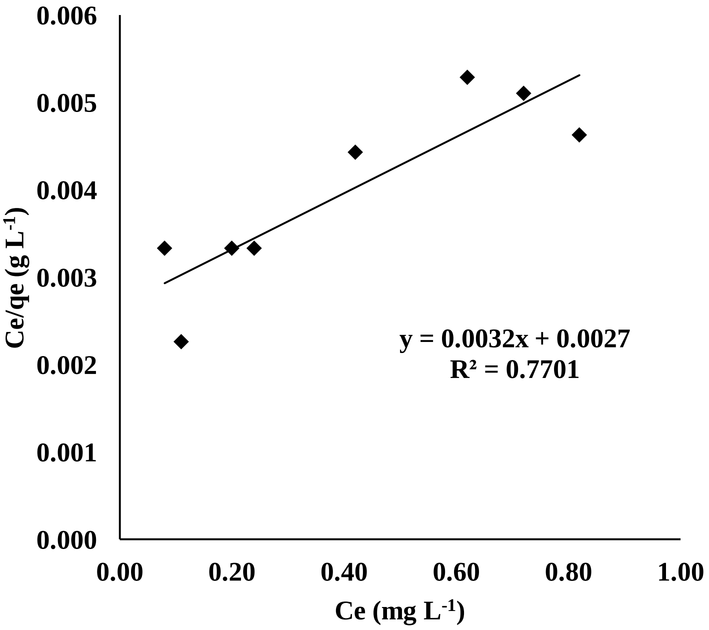


Figure I. 8 a. Adsorption isotherm of linuron on Activated carbon NORIT SA2

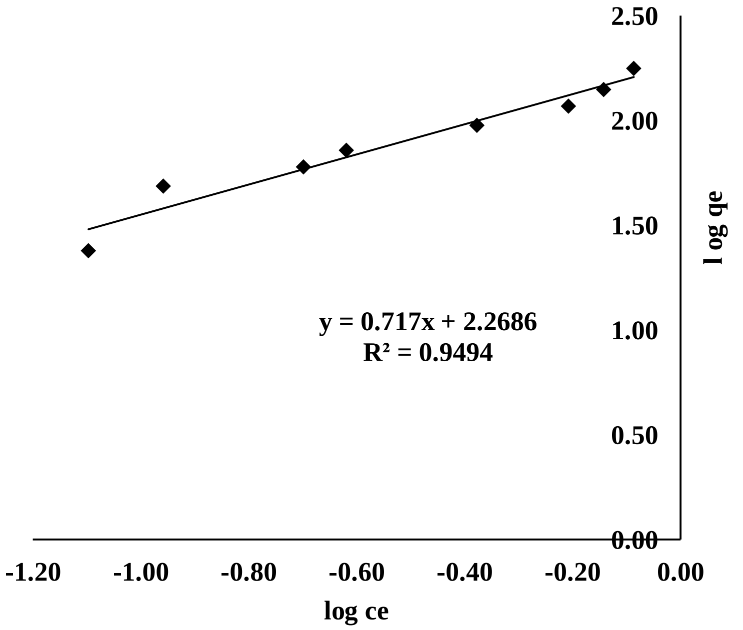


Figure I. 8 b. Linear plot of Freundlich isotherm of linuron sorption on Activated carbon NORIT SA2

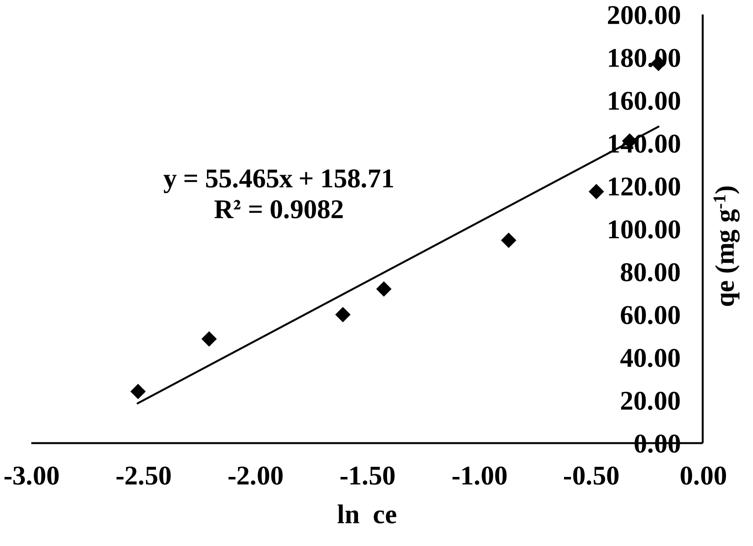


Figure I. 8 c. Temkin adsorption isotherm of linuron sorption on Activated carbon NORIT SA2

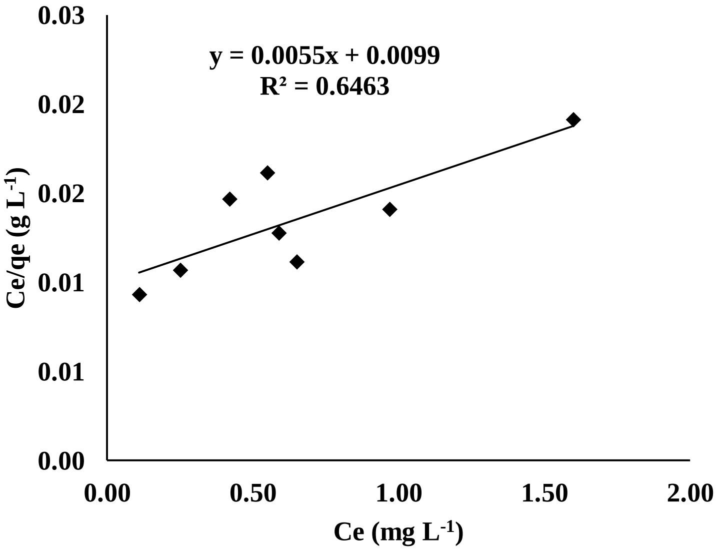


Figure I. 9 a. Adsorption isotherm of isoproturon on Activated carbon NORIT SA2

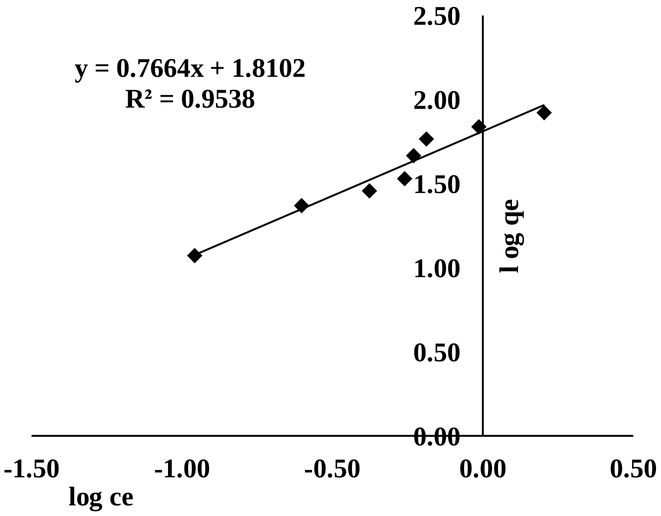


Figure I. 9 b. Linear plot of Freundlich isotherm of isoproturon sorption on Activated carbon NORIT SA2

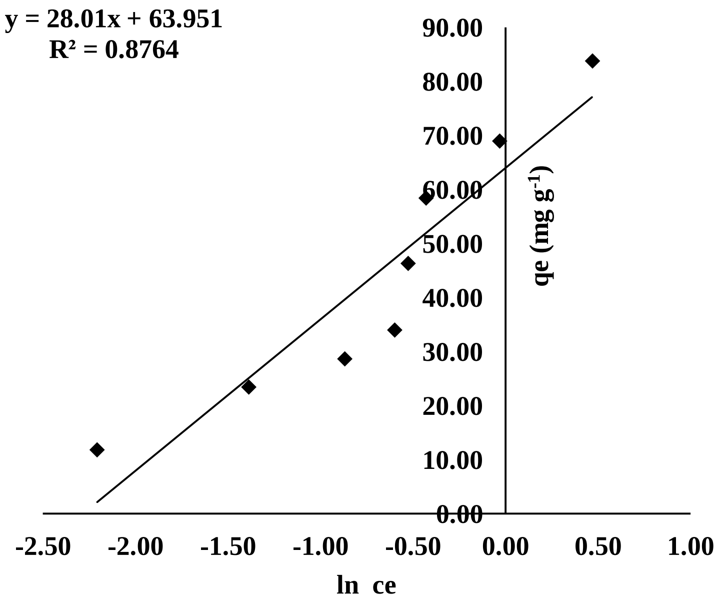


Figure I. 9 c. Temkin adsorption isotherm of isoproturon sorption on Activated carbon NORIT SA2

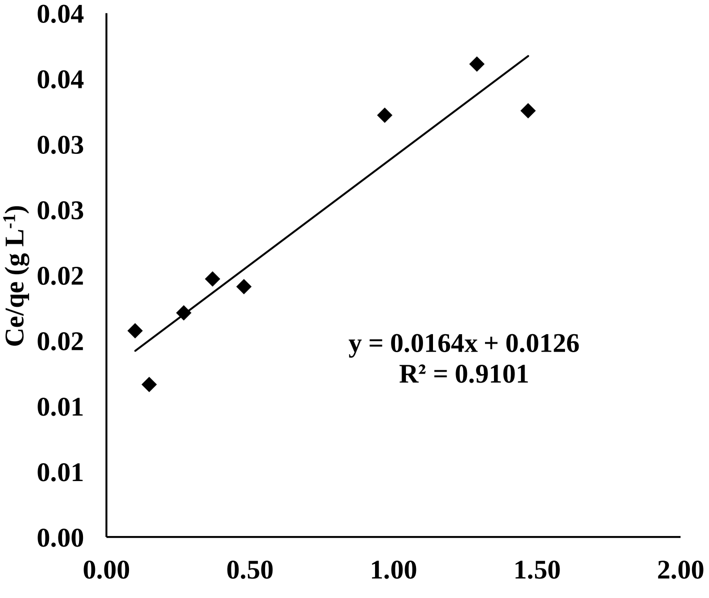
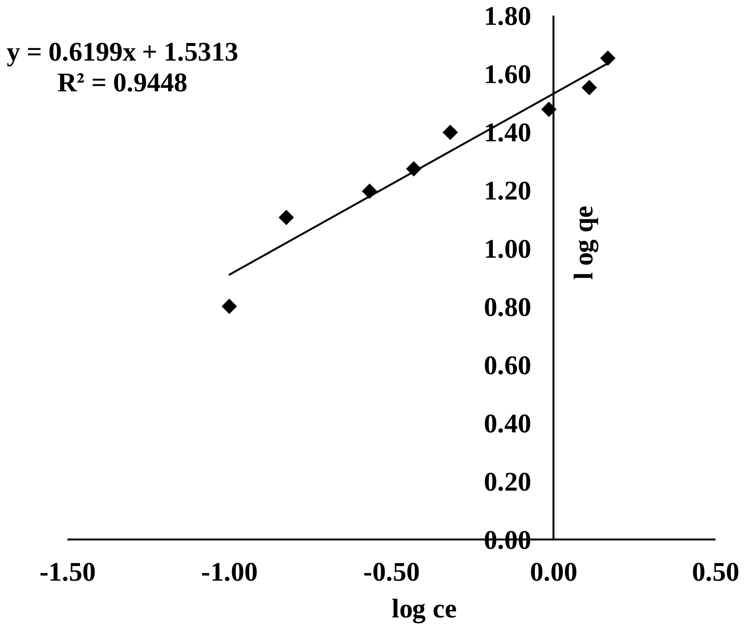


Figure I. 10 a. Adsorption isotherm of carbendazimon (Activated carbon (NORIT HYDRODARCO C))



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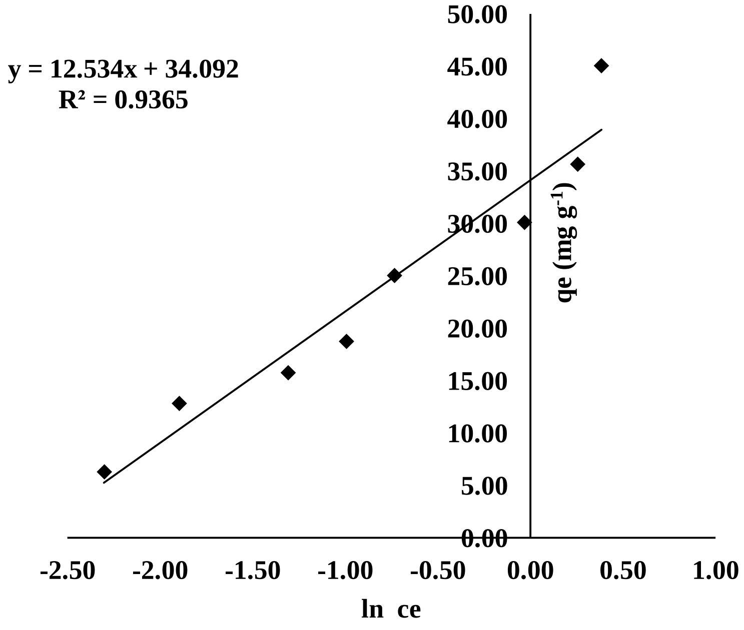

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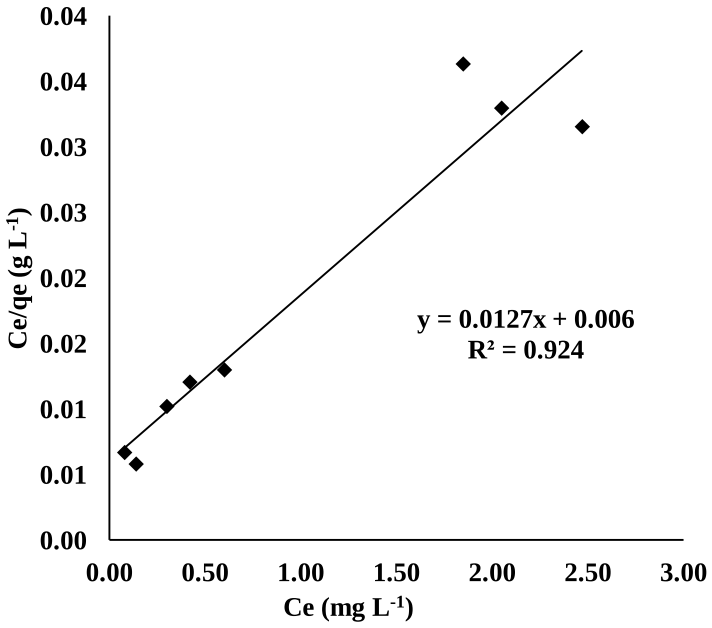
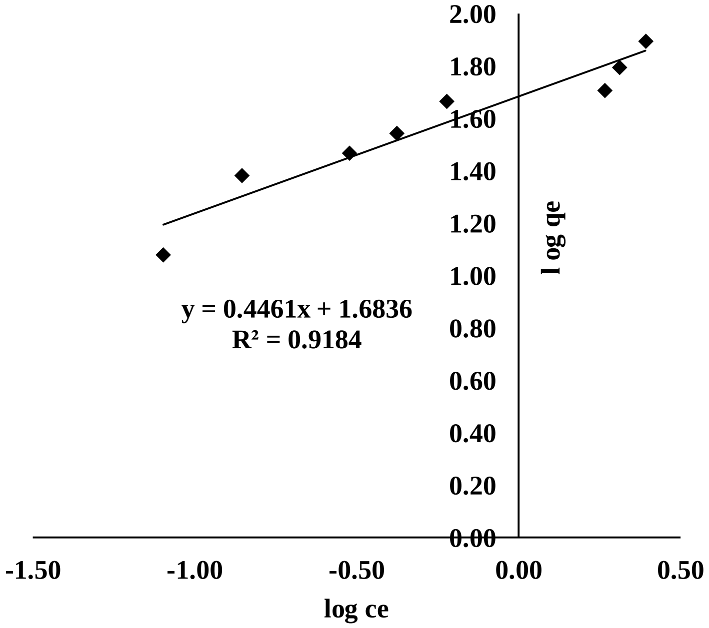


Figure I. 11 a. Adsorption isotherm of linuron (Activated carbon (NORIT HYDRODARCO C))



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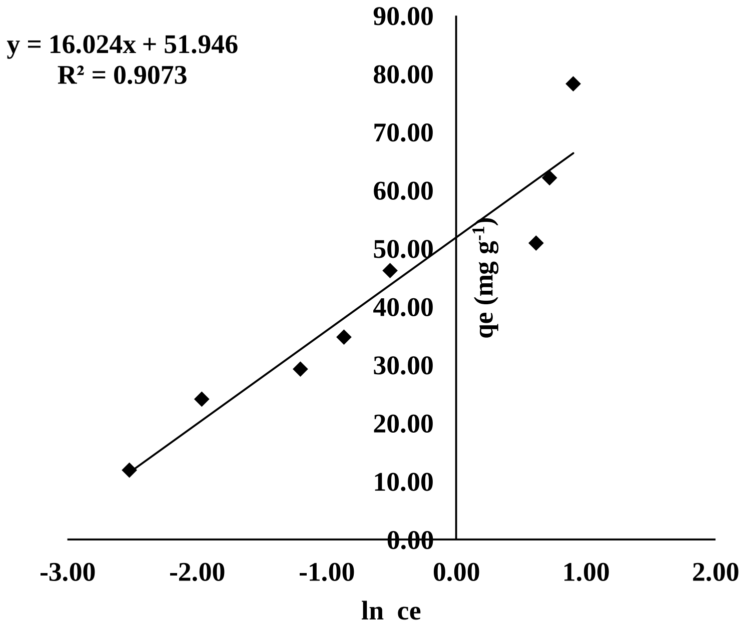

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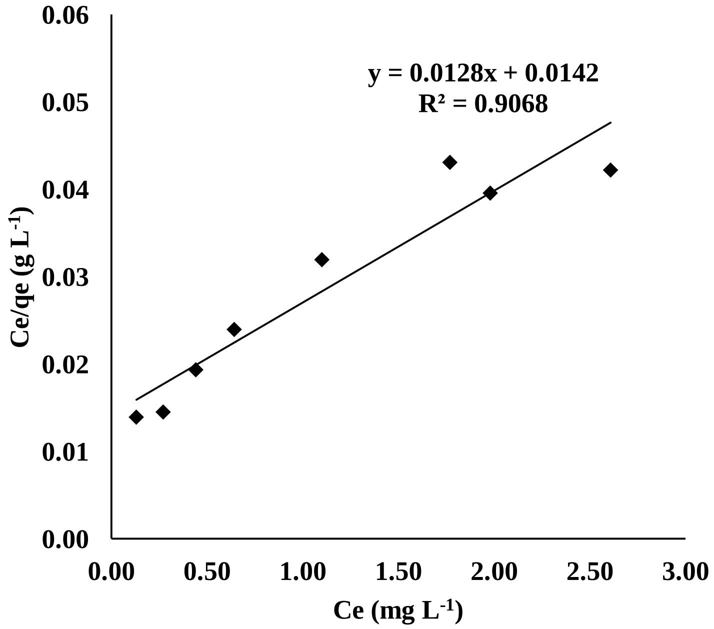

Figure I. 12 a. Adsorption isotherm of isoproturon (Activated carbon (NORIT HYDRODARCO C))

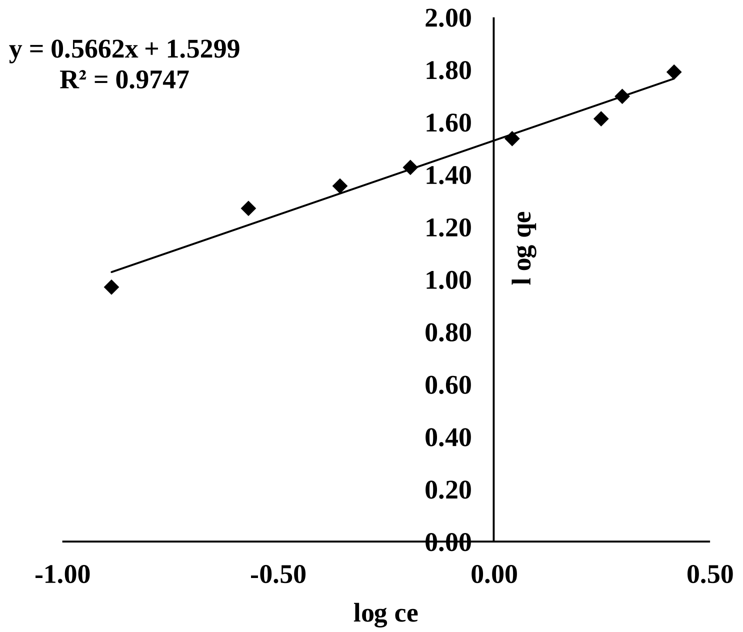

Figure I. 12 b. Linear plot of Freundlich isotherm of isoproturon sorption on (Activated carbon (NORIT HYDRODARCO C))

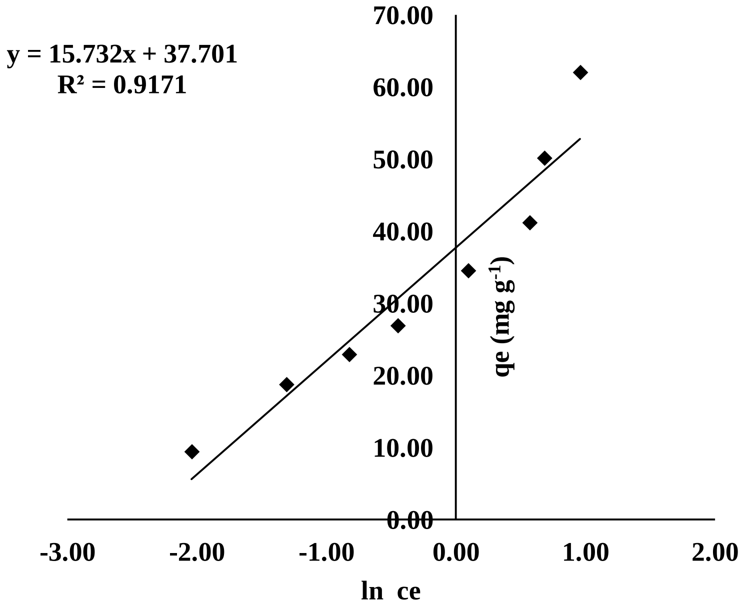

Figure I. 12 c. Temkin adsorption isotherm of isoproturon sorption on (Activated carbon (NORIT HYDRODARCO C))

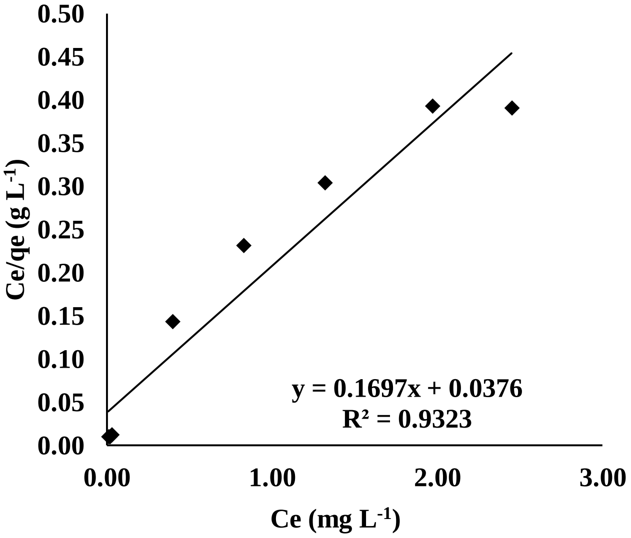

Figure I. 13 a. Adsorption isotherm of carbendazimon (Zeolite, type: ZSM-5)

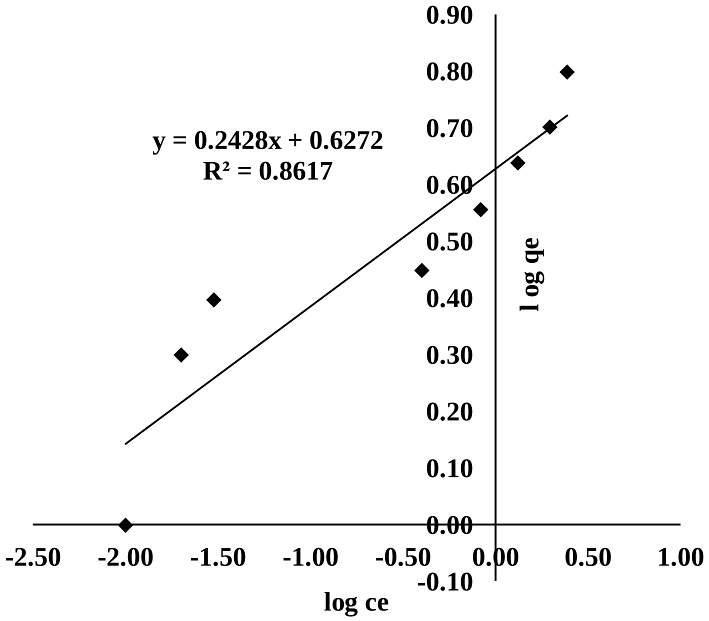

Figure I. 13 b. Linear plot of Freundlich isotherm of carbendazim sorption on (Zeolite, type: ZSM-5).

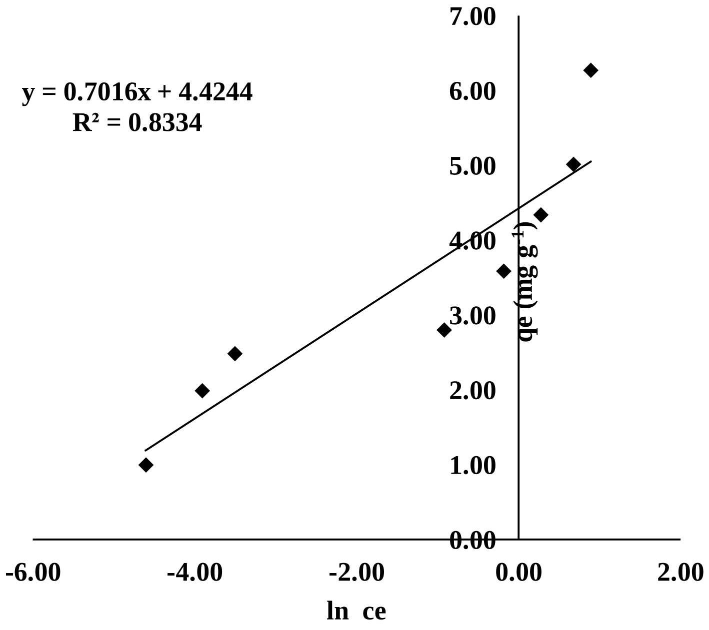

Figure I. 13 c. Temkin adsorption isotherm of carbendazim sorption on (Zeolite, type: ZSM-5)

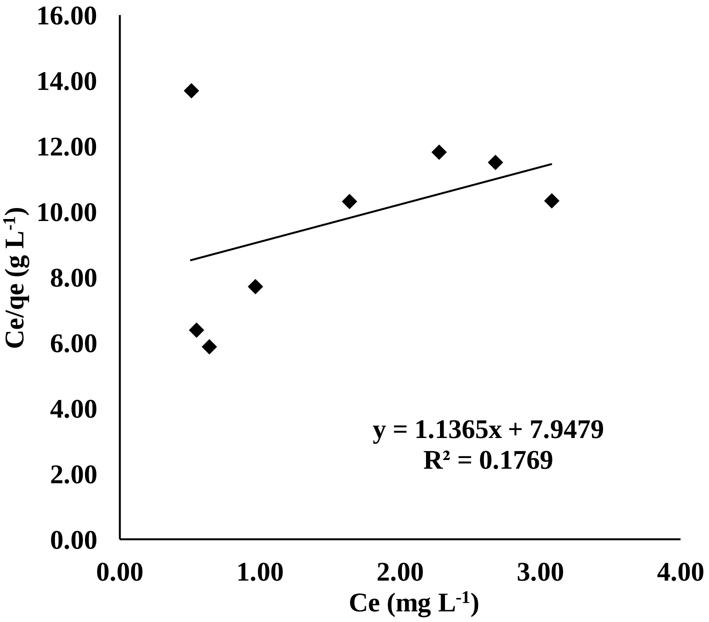

Figure I. 14 a. Adsorption isotherm of linuron (Zeolite, type: ZSM-5)

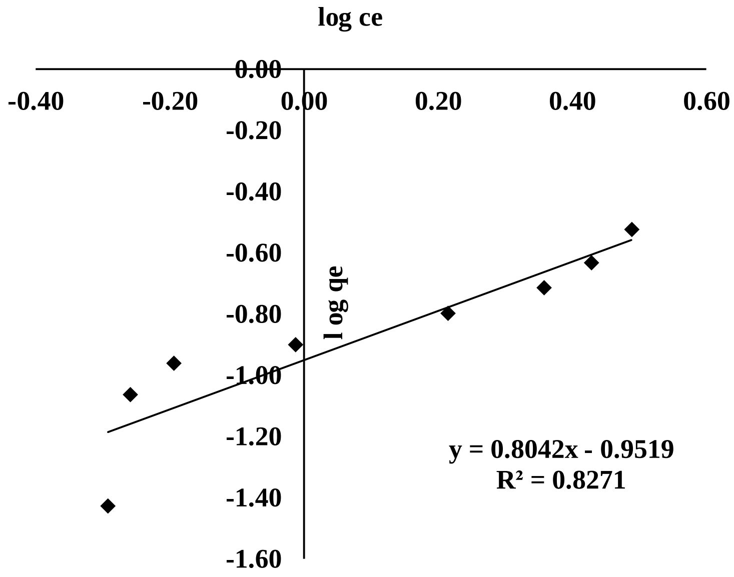

Figure I. 14 b. Linear plot of Freundlich isotherm of linuron sorption on (Zeolite, type: ZSM-5).

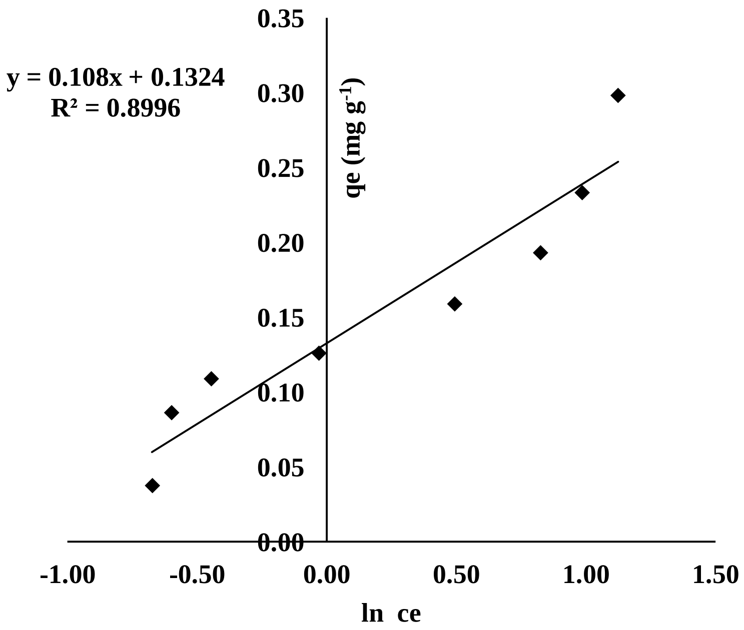

Figure I. 14 c. Temkin adsorption isotherm of linuron sorption on (Zeolite, type: ZSM-5)

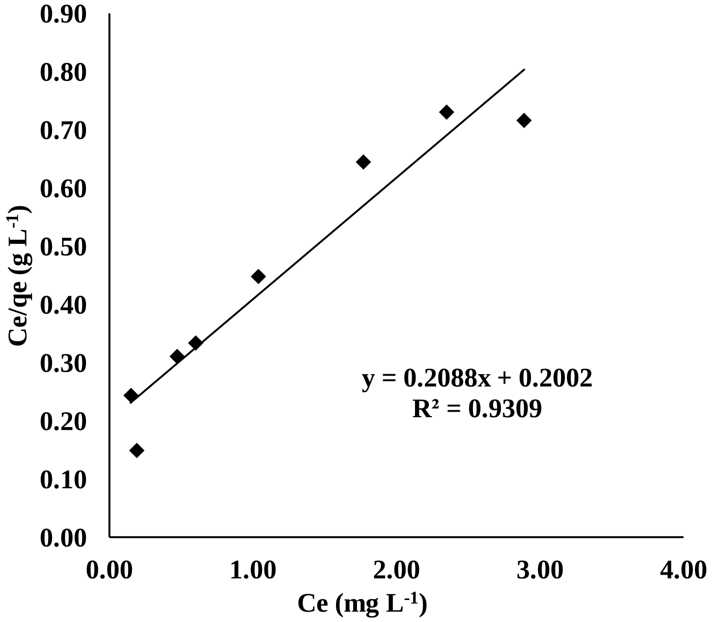

Figure I. 15 a. Adsorption isotherm of isoproturon (Zeolite, type: ZSM-5)

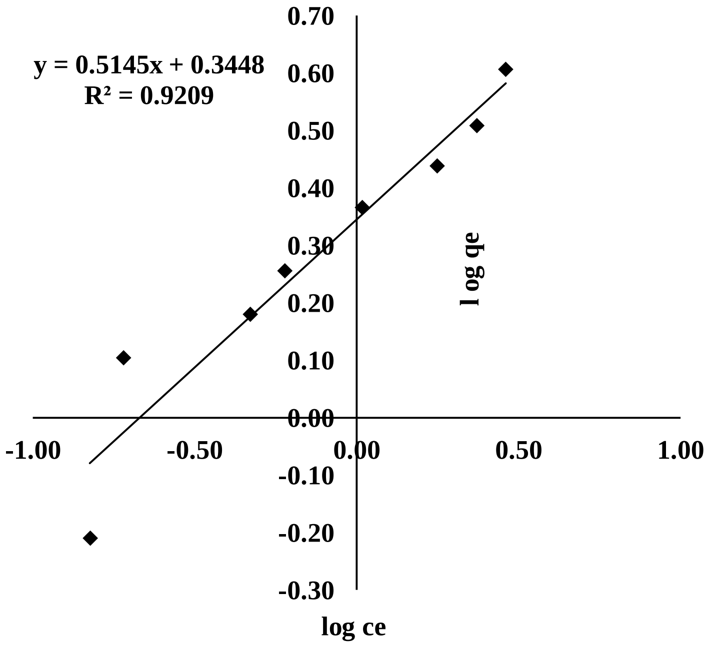

Figure I. 15 b. Linear plot of Freundlich isotherm of isoproturon sorption on (Zeolite, type: ZSM-5)

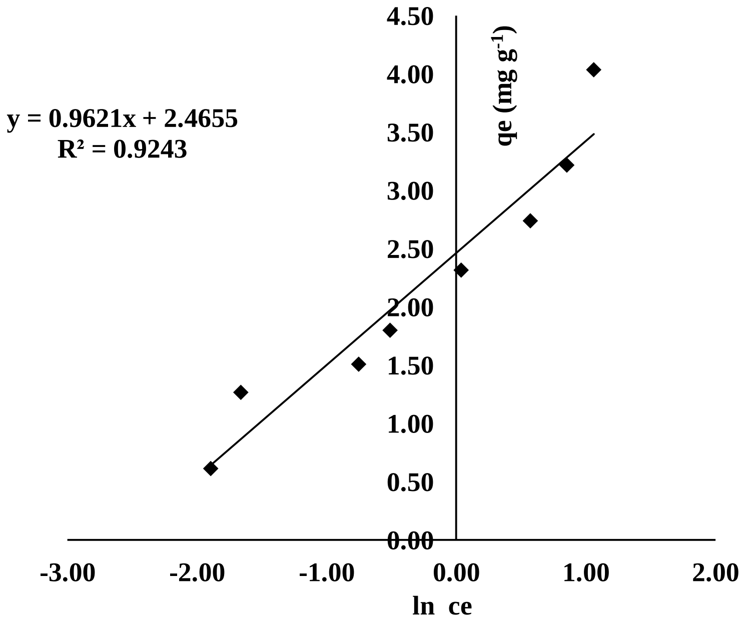

Figure I. 15 c. Temkin adsorption isotherm of isoproturon sorption on (Zeolite, type: ZSM-5)

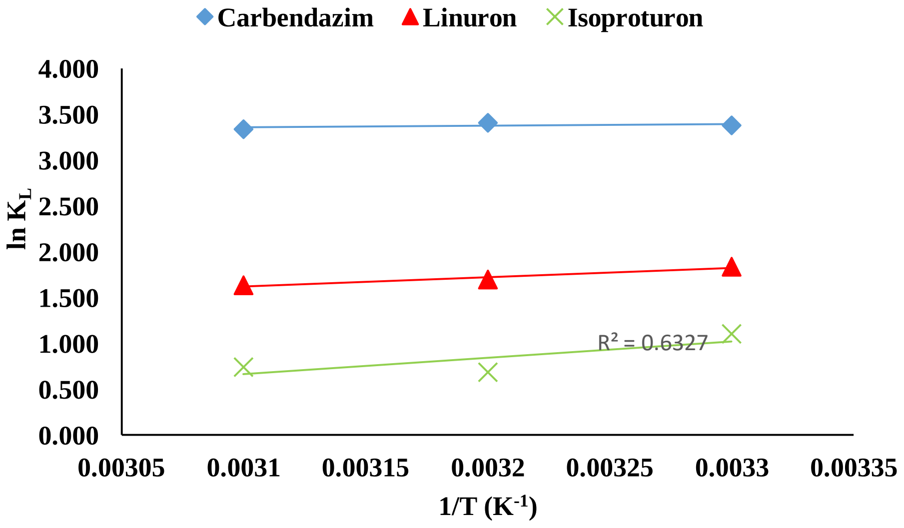

Figure I. 16 a. Van't Hoff plots lnK$_L$ versus 1/T for carbendazim, linuron and isoproturon onto SCG

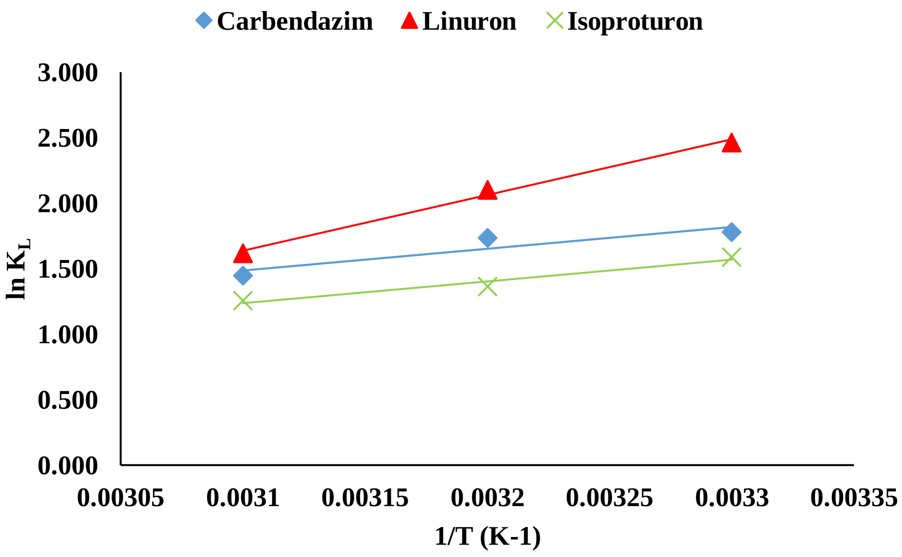

Figure I. 16 b. Van't Hoff plots lnK_L versus 1/T for carbendazim, linuron and isoproturon onto DSAC

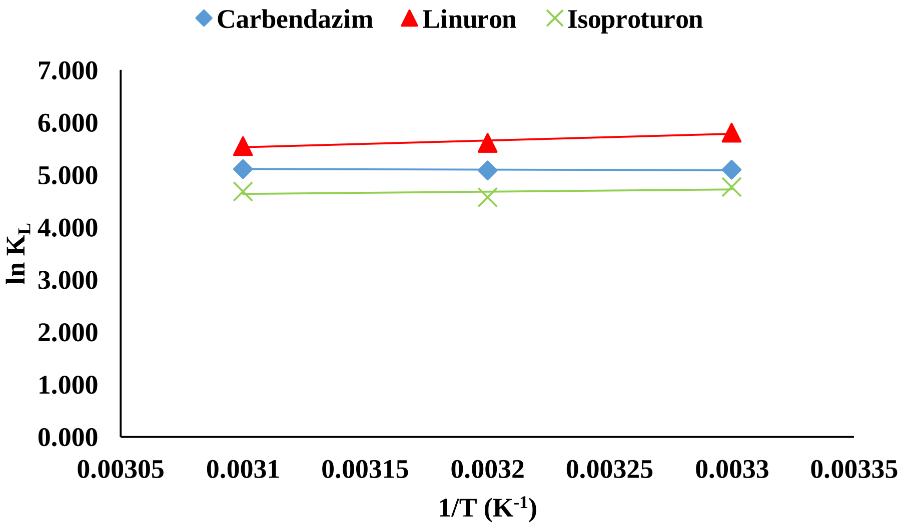

Figure I. 16 c. Van't Hoff plots lnK_L versus 1/T for carbendazim, linuron and isoproturon onto Activated carbon (NORIT SA2).

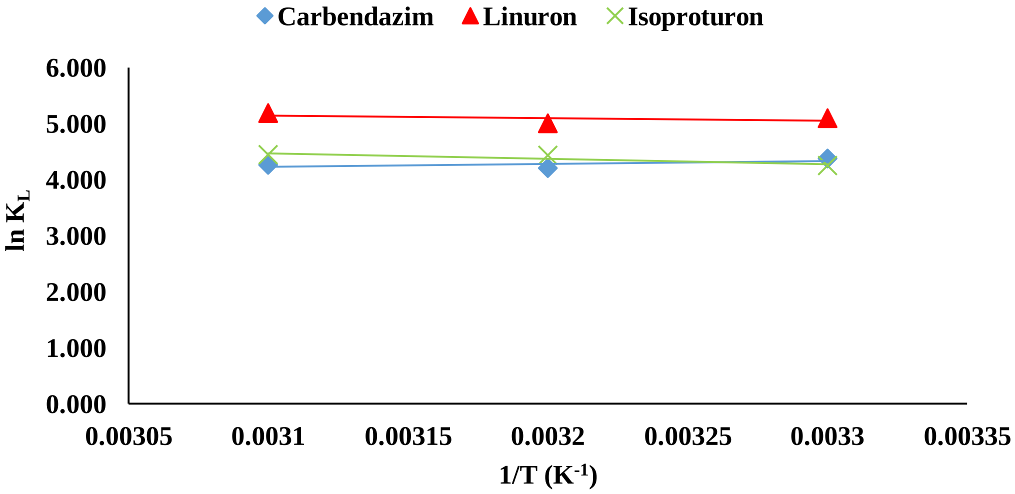

Figure I. 16 d. Van't Hoff plots lnK$_L$ versus 1/T for carbendazim, linuron and isoproturon onto Activated carbon (NORIT HYDRODARCO C).

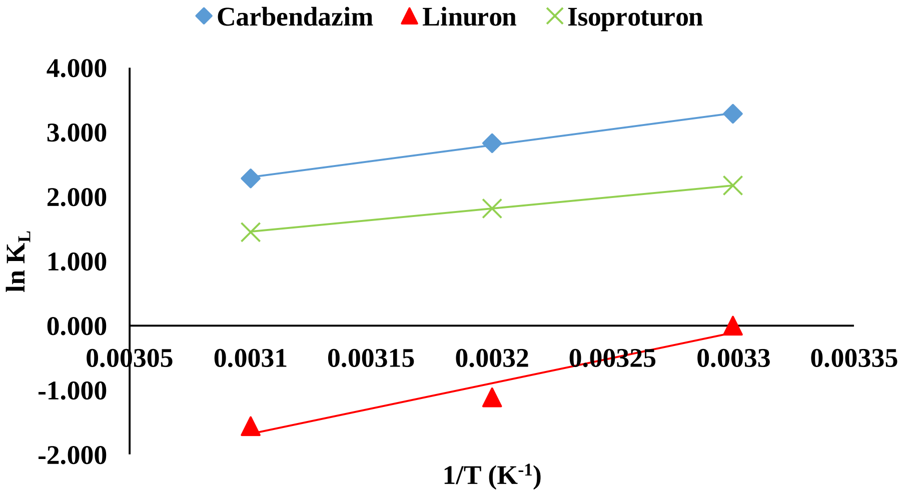

Figure I. 16 e. Van't Hoff plots lnK$_L$ versus 1/T for carbendazim, linuron and isoproturon onto Zeolite, type: ZSM-5.

8. 2. Appendix II

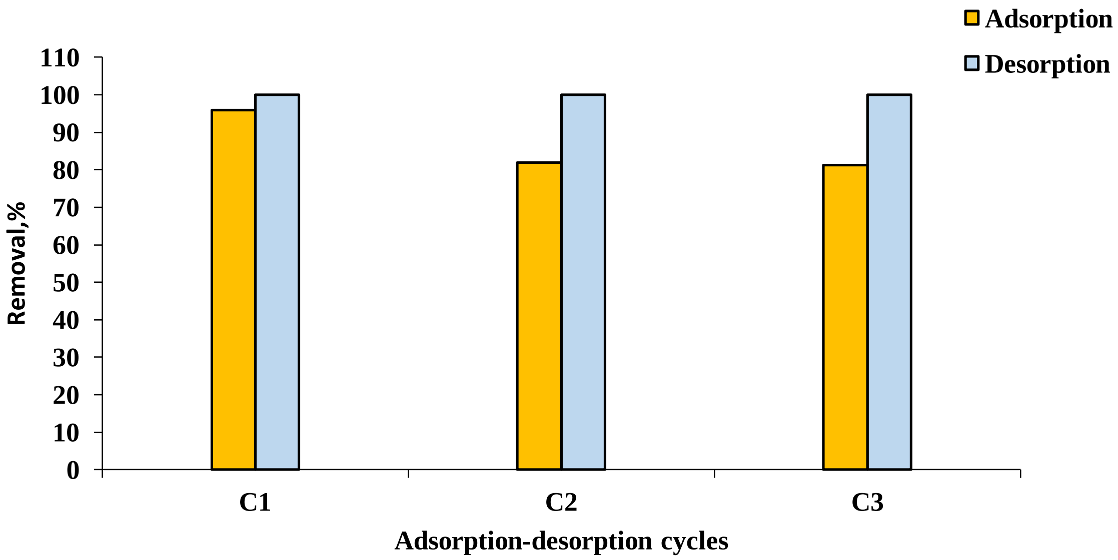

Figure II. 1 a. Adsorption/desorption study of carbendazim per cycle (C1, C2 and C3).

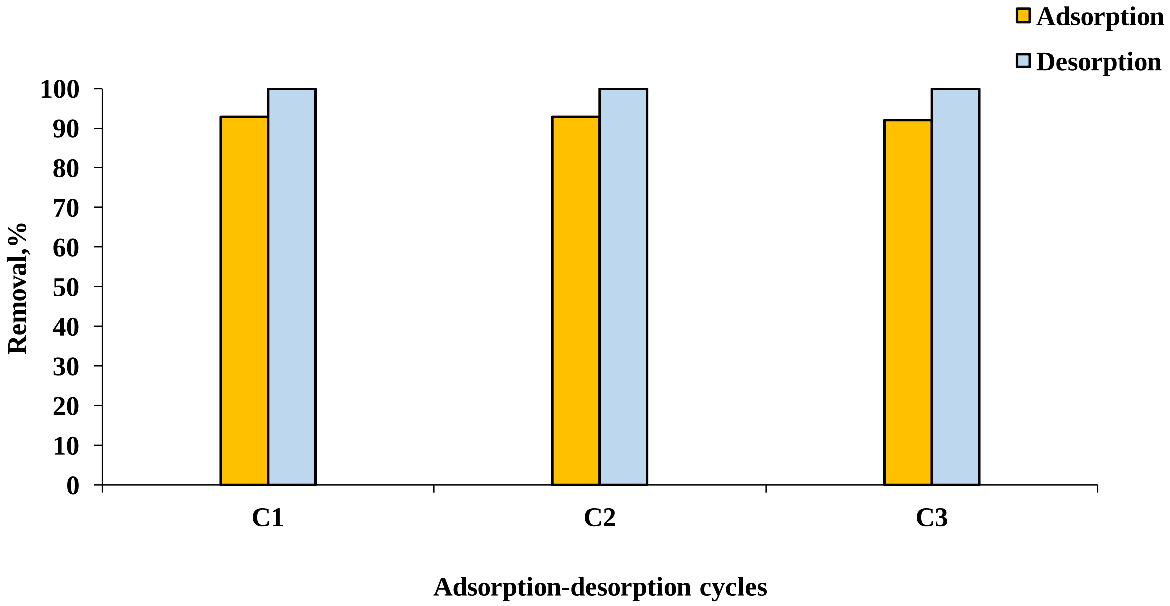

Figure II. 1 b. Adsorption/desorption study of linuron per cycle (C1, C2 and C3).

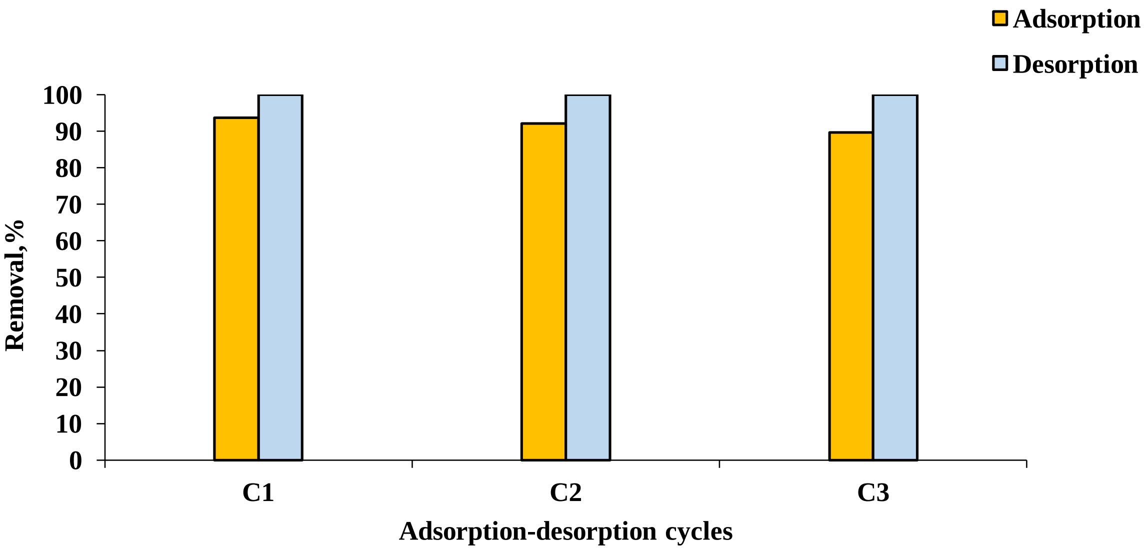

Figure II. 1 c. Adsorption/desorption study of isoproturon per cycle (C1, C2 and C3).

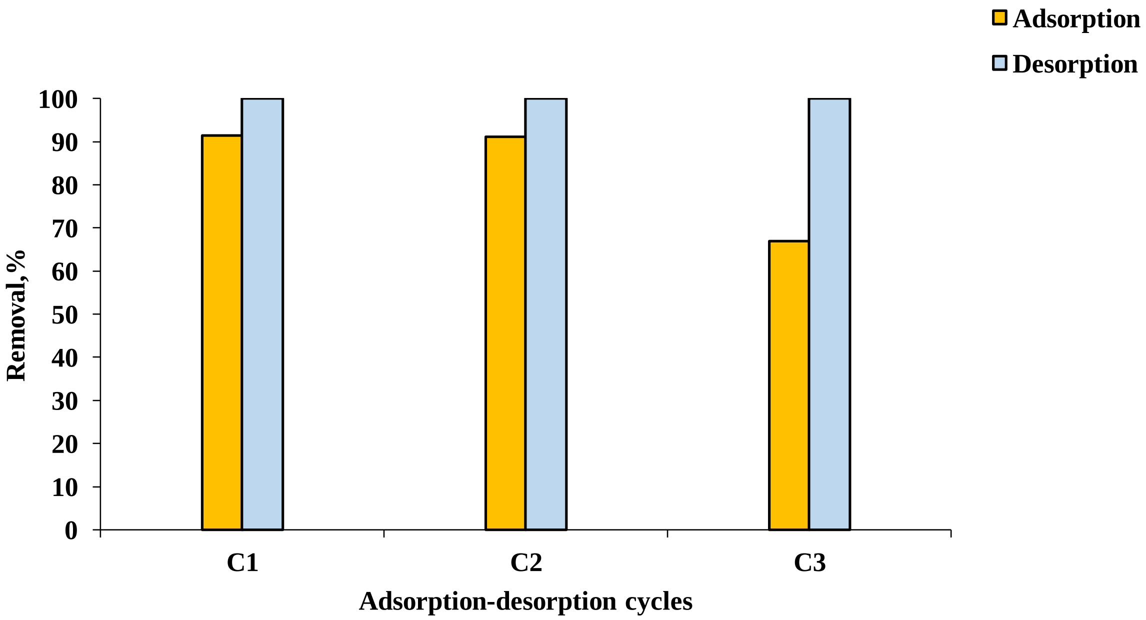

Figure II. 2 a. Adsorption/desorption study of carbendazim per cycle (C1, C2 and C3)

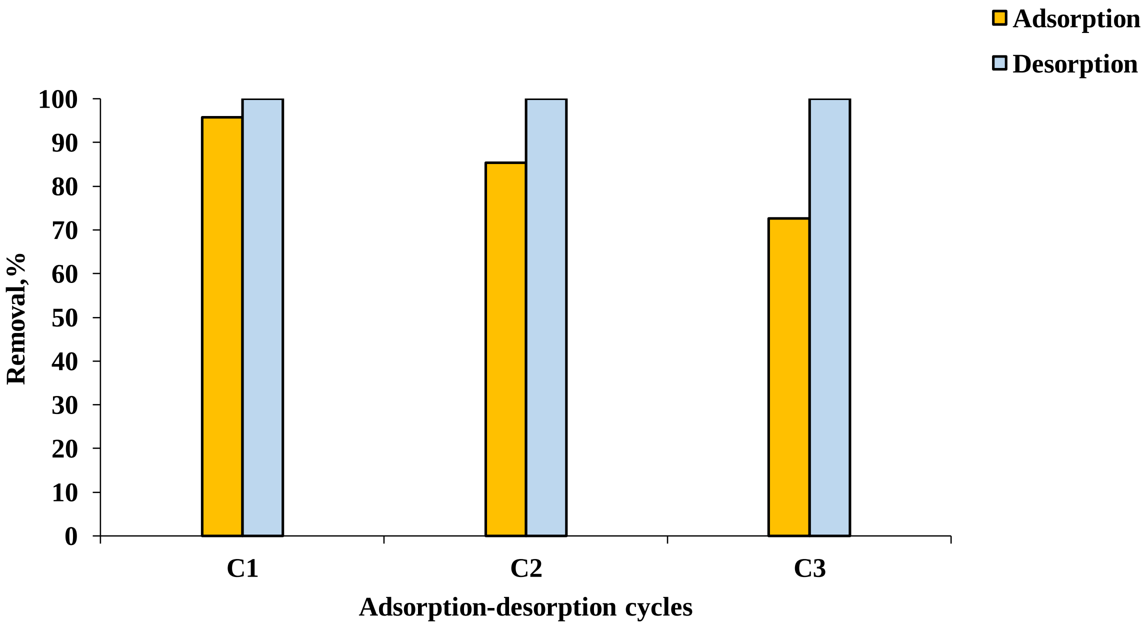

Figure II. 2 b. Adsorption/desorption study of linuron per cycle (C1, C2 and C3).

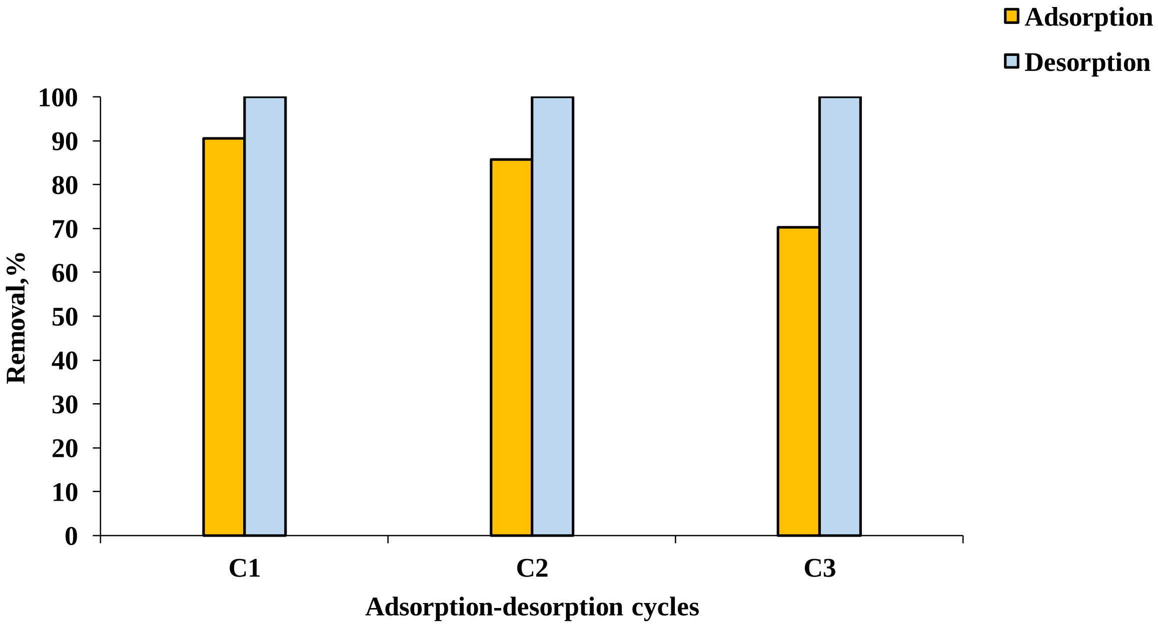

Figure II. 2 c. Adsorption/desorption study of isoproturon per cycle (C1, C2 and C3).