UDK: 504.5:661.162.2
628.161.3:661.183.2

Ali HGEIG, Mladenka NOVAKOVIĆ, Maja SREMAČKI,
Maja PETROVIĆ, Ivana MIHAJLOVIĆ

UKLANJANJE LINURONA IZ VODE KORIŠĆENJEM AKTIVNOG UGLJA (NORIT SA2)

REMOVAL OF LINURON FROM WATER USING ACTIVATED CARBON (NORIT SA2)

IZVOD

Linuron je sorbovan iz vode korišćenjem komercijalnog aktivnog uglja, NORIT SA2. Posmatrani su adsorpcioni parametri: pH vrednost, doza adsorbenta, vreme kontakta (CT) i inicijalna koncentracija linurona u vodi. Pored primarnih adsorpcionih parametara posmatrana je i temperatura adsorpcije na aktivnom uglju NORIT SA2. Resultati su modelovani Langmirovim, Frojdlihovim i Temkinovim izotermama. Adsorpciona kinetika je ispitana korišćenjem kinetičkih modela pseudo-prvog reda, pseudo-drugog reda i intrapartikularnog difuzionog modela. Dobijeni podaci odgovaraju najbolje modelu pseudo-drugog reda. Sprovedena studija ukazuje na to da je NORIT SA2 efikasan adsorbent za uklanjanje herbicida linurona iz vodenih rastvora.

Ključne reči: Aktivni ugalj, NORIT SA2, pesticid, adsorpcija

ABSTRACT

Linuron was removed from water using commercial activated carbon, NORIT SA2. The following adsorption process parameters were observed: pH, adsorbent dosage, contact time (CT) and initial concentration of linuron. In addition, the influence of temperature for adsorption on NORIT SA2 was studied. Results were modeled by Langmuir, Freundlich and Temkin isotherms. Adsorption kinetics were investigated using commonly used kinetic models such as the pseudo-first order model, the pseudo-second order model, and the intraparticle diffusion model. The pseudo-second order model fit the data the best. This study shows that NORIT SA2 is an effective adsorbent for removing linuron from water solutions.

Key words: Activated carbon, NORIT SA2, pesticide, adsorption

UVODNA RAZMATRANJA

Herbicidi mogu direktno ili indirektno putem procesa difuzije da dovedu do visokog stepena zagađenja podzemnih i površinskih voda. Linuron (3-(3, 4-dihlorofenil)-1-metoksi-1-metilurea) je herbicid koji se koristi za kontrolu trava i korova, pospešujući rast ekonomski značajnih biljaka. Linuron ima nizak stepen otrovnosti i ima visoku primenu za zaštitu pšenice, šećerne repe, krompira, kukuruza i pamuka. Linuron se brzo degradira pri ulasku u životinjske i ljudske organizme, a godišnja doza od 125 mg/kg ne dovodi do detektibilnih promena, kancerogenih ili mutagenih efekata, iako se može detektovati u krvi, masti, jetri, bubrezima i slezini [1].

INTRODUCTION

Herbicides pollute ground and surface water either directly or indirectly through diffusion. Linuron (3-(3, 4-dichlorophenyl)-1-methoxy-1-methylurea) is an herbicide that is used to control grass and weeds while also promoting the growth of economically valuable plants. Linuron has a lower poisoning degree and is used for protection of vide variety of crops such as wheat, sugar cane, potato, corn, and cotton. Linuron degrades quickly after entering the animal or human body, and a two-year dose of 125 mg/kg of linuron does not produce detectable alteration, carcinogenic, or mutagenic effects, despite being detected in blood, fat, liver, kidney, and spleen [1].

Ali Hgeig, Mladenka NovakoviĆ, Maja Sremački, Maja Petrović, Ivana MihajloviĆ, Univerzitet u Novom Sadu, Fakultet tehničkih nauka, Departman za inženjerstvo zaštite životne sredine i zaštitu na radu, Trg Dositeja Obradovića 6, 21000 Novi Sad, Srbija

Aktivni ugalj NORIT SA2 je korišćen kao adsorbent u istraživanju uklanjanja linurona iz vodenih rastvora. Linuron je izabran za ostraživanje jer predstavlja opasnost po vodeni ekosistem i takođe pripada grupi emergentnih supstanci.

U serijski postavljenim eksperimentima, efekti ključnih radnih adsorpcionih parametara su istraženi, početna pH vrednost vode, doza NORIT SA2, CT, temperatura i početna koncentracija polutanta (linurona). Resultati su modelovani Langmirovim, Frojdlihovim i Temkinovim izotermama. Kinetika adsorpcije linurona je takođe istražena tokom sprovedenih eksperimenata. Rezultati kinetike adsorpcije su ispitani korišćenjem kinetičkih modela pseudo-prvog reda, pseudo-drugog reda i intrapartikularnog difuzionog modela.

MATERIJALI I METODE

Materijali i hemikalije

NORIT SA2 je korišćen bez modifikacija. Hemikalije korišćene u eksperimentalnoj studiji su: analitički standard linurona, acetonitril, metanol (Sigma-Aldrich Co. (St. Louis, USA)), HCl (J.T. Baker (USA)) i NH_4OH (Centrohem (Srbija)). Radni rastvor (200 ppm) je pripremljen rastvaranjem 5 mg standarda linurona u 25 mL metanola.

Tačka nultog naelektrisanja

Tačka nultog naelektrisanja (pH_{pzc}) je pH vrednost na kojoj je površinski napon aktivnog uglja jednak nuli [2]. pH "drift" tehnika je primenjena za izračunavanje pH_{pzc} za NORIT SA2.

Instrumenti

HPLC-DAD (Agilent 1260), mehanička mešalica (Heidolph Unimax 1010), pH metar (model PHD 21), analitička i tehnička vaga (KERN) i sušnica (Memmert) su korišćeni za ispitivanje separacije linurona iz vodenih rastvora.

Analiza HPLC-DAD

Razdvajanje je izvedeno na koloni sa reverznom fazom Eclipse XDB-C18 (3 x 150 mm, veličina partikule 3,5 µm). Radni uslovi su: protok 0,4 mL/min, temperatura kolone 30 °C i injekciona zapremina uzorka 10 µL. Kao mobilna faza korišćena je mešavina vode (A) i acetonitrila (B). Binarni gradijent eluacije započet je na 25 % B (1 min), potom je linearno povećavan do 50 % B (5 min), i 25% B (7 min). Kao maksimalna talasna dužina korišćena je 215 nm.

Adsorpcioni eksperiment

Adsorpcija linurona na NORIT SA2 je izvedena kao serija eksperimenata. Prilikom izvođenja svih eksperimenata, NORIT SA2 je dodat u 50 mL rastvora linurona. Erlenmajeri sa rastvorom su potom mešani na 140 rpm. Uticaj početne pH vrednosti vode, doze adsorbenta i temperature na procenat

Activated carbon NORIT SA2 was used as an adsorbent in this study to remove linuron from aqueous solution. Linuron was chosen because it poses a threat to the aquatic environment and also belongs to the group of emerging substances.

In batch mode, the effects of key operating parameters on the adsorption process were studied, including initial pH of water, NORIT SA2 dosage, CT, temperature, and initial concentration of pollutant (linuron). Results were modeled by Langmuir, Freundlich and Temkin isotherms. Adsorption kinetics of linuron was also studied. The results of adsorption kinetics were investigated using kinetic models such as the pseudo-first order model, the pseudo-second order model, and the intraparticle diffusion model.

MATERIALS AND METHODS

Materials and chemicals

NORIT SA2 was used without modification. Chemicals used in the experimental study were: analytical standard of linuron, acetonitrile, methanol (Sigma-Aldrich Co. (St. Louis, USA)), HCl (J.T. Baker (USA)) and NH_4OH (Centrohem (Serbia)). The Stock solution (200 ppm) was prepared dissolving 5 mg of linuron standard in 25 mL of methanol.

Point of zero charge

Point of zero charge (pH_{pzc}) is pH value on which surface charge of activated carbon is zero [2]. The pH "drift" technique was performed to calculate the pH_{pzc} of NORIT SA2.

Instruments

HPLC-DAD (Agilent 1260), mechanical stirrer (Heidolph Unimax 1010), pH meter (model PHD 21), analytical and technical scales (KERN) and oven (Memmert) were used in order to investigate separation of linuron from aqueous solutions.

Analyses via HPLC-DAD

Separation was performed on a reversed phase column Eclipse XDB-C18 (3 x 150 mm, particle size 3.5 µm). The conditions were: flow of 0.4 mL/min, temperature of the column was 30 °C and injection volume of 10 µL. The mobile phase used is water (A) and acetonitrile (B) mixture. The binary gradient elution started at 25 % B (1 min), linearly increased to 50 % B (5 min), and 25% B (7 min). The maximum wavelength of 215 nm was used.

Adsorption Experiments

The adsorption of linuron on NORIT SA2 was examined in batch mode. For all experiments, NORIT SA2 was added to 50 mL of linuron solution. The flask was stirred at 140 rpm. The influences of initial pH, adsorbent dose and temperatures on removal percentage of linuron was analyzed by modifying initial concentration of linuron (5 mg/L) at various adsorpcije linurona su analizirani varijacijom početne koncentracije linurona (5 mg/L) na različitim početnim pH vrednostima (3 - 10), dozama adsorbenta NORIT SA2 (0,04 – 0,24 g/L) i temperaturama (25 - 45 °C). pH vrednosti su varirane pomoću 0,1M rastvora HCl ili NH_4OH. Za kinetičke eksperimente, izvedene su studije sa rastvorom linurona od 50 mL početne koncentracije 5 mg/L na pH 6 i različitim CT (5 - 120 min). Adsopcioni izotermalni parametri su postignuti variranjem početnih koncentracija adsorbata (2 - 15mg/L) na pH 7. Utvrđeni su parametri ravnotežnog kapaciteta adsorpcije, q_e i procenat uklonjenog adsorbata.

Adsorpcione izoterme

Langmirov, Frojndlihov i Temkinov [3] model su fundamentalni modeli za optimizaciju mehanizma adsorpcije, izražavanje karakteristika površine adsorbenta i projektovanje uspešnog adsorpcionog sistema, jer sumiraju korelacije između polutanta i adsorbenta [4].

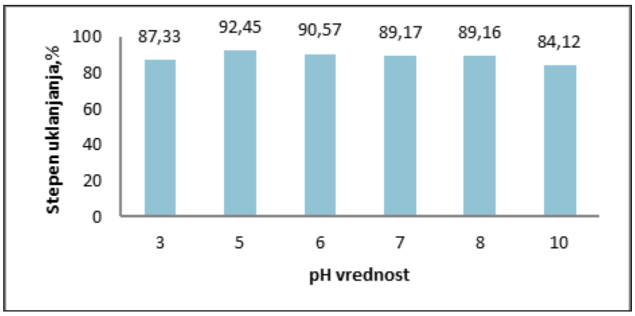
Kinetika adsorpcije

Kinetički modeli mogu da se primene na analize upravljačkog mehanizma adsorpcionog procesa i potencijalnih inhibicionih procesa kao što su transferi i hemijske reakcije [5]. U cilju istraživanja adsorpcije linurona na NORIT SA2 i interpretacije dobijenih eksperimentalnih podataka, 3 kinetička modela su korišćena – pseudo-prvog reda, pseudo-drugog reda i interpartikularni kinetički model.

REZULTATI I DISKUSIJA

Uticaj pH vrednosti na efikasnost procesa adsorpcije

Na slici 1 prikazani su efekti pH vrednosti na proces adsorpcije linurona na NORIT SA2. Procenat uklanjanja linurona je visoko zavisan od pH vrednosti, pri čemu je dokazano da pH = 7 daje najviši procenat uklanjanja. Zavisnost adsopcionog potencijala od pH vrednosti može se objasniti jonizacijom linurona i protonizacijom funkcionalnih grupa NORIT SA2. Dobijeni su podaci da pH_{pzc} za NORIT SA2 iznosi 7,65 (Slika 2). Kada je pH vrednost niža od utvrđene pH_{pzc}, adsorbent ima pozitivno opterećenje površine i može da funkcioniše kao anjonski izmenjivač, ali ako je pH vrednost viša od pH_{pzc}, površinsko opterećenje adsorbenta je negativno, što je optimalno za katjone.



Slika 1 Efekat pH vrednosti na adsorpciju linurona na NORIT SA2

initial pH values (3 - 10), NORIT SA2 dose (0.04 - 0.24 g/L) and temperature (25 - 45 °C). The pH values were modified by 0.1M solution of HCl or NH_4OH. For the kinetic experiments, studies were performed with 50 mL of linuron solution with initial concentration of 5 mg/L at pH 6 and various CT (5 - 120 min). Adsorption isotherm parameters were acquired by varying the initial adsorbate concentrations (2 - 15mg/L) at pH 7. The equilibrium adsorption capacity, q_e and percentage of adsorbate removal were determined.

Adsorption isotherms

Langmuir, Freundlich and Temkin [3] models are fundamental for optimization of the adsorption mechanism path-ways, expression of the surface properties and capacities of adsorbents, and productive design of the adsorption systems, since they summarize how pollutants correlate with the adsorbent [4].

Adsorption kinetics

Kinetic models may be applied to analyze the managing mechanism of adsorption process and the potential rate-limiting actions such as transfer and chemical reaction [5]. In order to study the adsorption of linuron on the NORIT SA2 and to interpret the obtained experimental data, 3 kinetic models, the pseudo-first order, pseudo-second order and intraparticle kinetic model have been used.

RESULTS AND DISCUSSION

Effect of pH value on the efficiency of adsorption process

Figure 1 shows the effect of pH on the adsorption of linuron on the NORIT SA2. The removal percentage of linuron is dependent on pH, with pH = 7 yielding the highest removal efficiency. The pH dependence of adsorption capability could be explained by linuron ionization and NORIT SA2 functional group protonation. The pH_{pzc} of the NORIT SA2 was determined to be 7.65 (Figure 2). When the pH is lower than pH_{pzc}, the adsorbent has a positive surface load and can function as an anion exchanger; however, when the pH is higher than pH_{pzc}, the adsorbent surface load is negative, which is beneficial to cations.

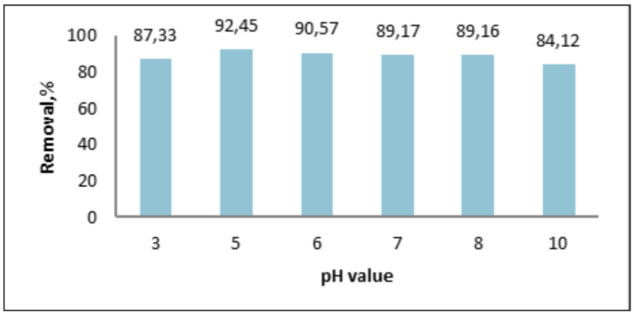
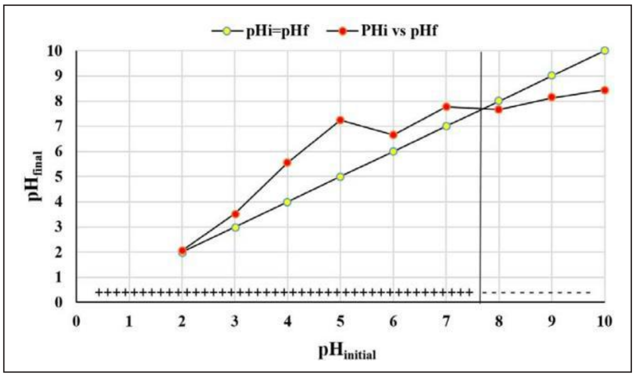


Figure 1 Effect of pH on adsorption of linuron on NORIT SA2



Slika 2 pH$_{pzc}$ za NORIT SA2

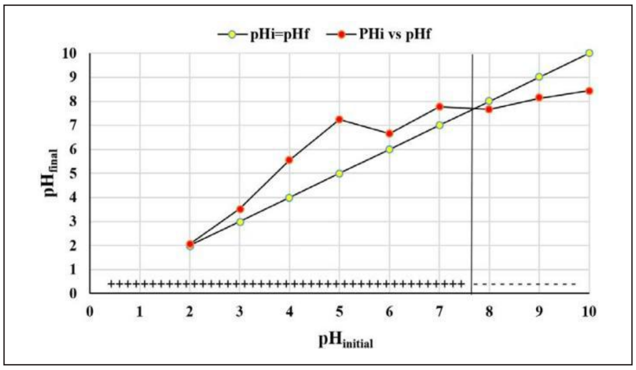
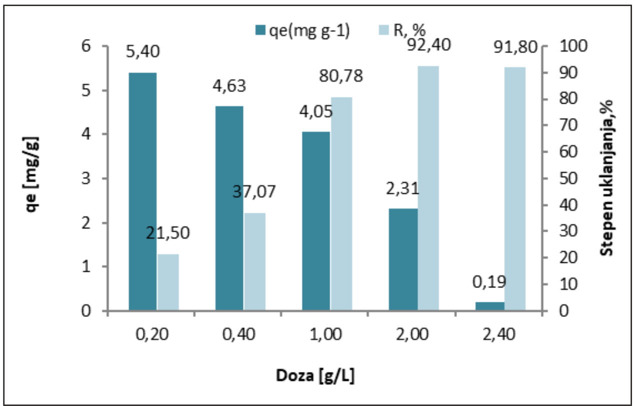


Figure 2 pH$_{pzc}$ of NORIT SA2

Uticaj doze NORIT SA2 na efikasnost procesa adsorpcije

Na slici 3 prikazana je efikasnost uklanjanja linurona korišćenjem NORIT SA2. Statističkom analizom je utvrđeno da je optimalna doza NORIT SA2 0,08 g/L na pH 7 i za CT 30 minuta. Efikasnost adsorpcije linurona se smanjila sa 118,50 na 20,04 mg/g, pri povećanju količine adsorbenta sa 0,04 na 0,08 g/L. Količina aktivnih sorptivnih mesta na površini aktivnog uglja u odnosu na koncentraciju adsorbenta utiče na niski stepen adsorpcije.



Slika 3 Uticaj doze NORIT SA2 na proces adsorpcije

Uticaj CT na efikasnost procesa adsorpcije

Eksperimentalni uslovi za ispitivanje uticaja CT na efikasnost procesa adsorpcije su: linuron 5 mg/L, NORIT SA2 0,08 g/L, pH 7 na sobnoj temperaturi (25 ± 2 °C). Veće kontaktno vreme omogućava veću efikasnost uklanjanja linurona, razdvajajući proces adsorpcije u dve izrazite faze. U prvoj fazi (faza brze adsorpcije), u prvih 20 minuta adsorpcija linurona se odvija veoma brzo (> 90 % početne koncentracije). U drugoj fazi (ravnotežna faza), ravnoteža se postiže za ≥30 minuta.

Uticaj početne koncentracije na efikasnost procesa adsorpcije

Adsorpcija linurona je evaluirana prema variranim početnim koncentracijama u vodi, od 2 do 15 mg/L (Slika 4), pri čemu se kapacitet adsorpcije povećao

Effect of NORIT SA2 dosage on the efficiency of adsorption process

Figure 3 shows the efficiencies of linuron removal by NORIT SA2. The statistical analysis revealed that the optimum NORIT SA2 dosage is 0.08 g/L at pH 7 and CT of 30 minutes. The adsorption efficiency of linuron decreased from 118.50 to 20.04 mg/g, as the adsorbent dose increased from 0.04 to 0.08 g/L. The amount of active sorption sites on the activated carbon surface in relation to the concentration of adsorbents influences the low adsorption percentage.

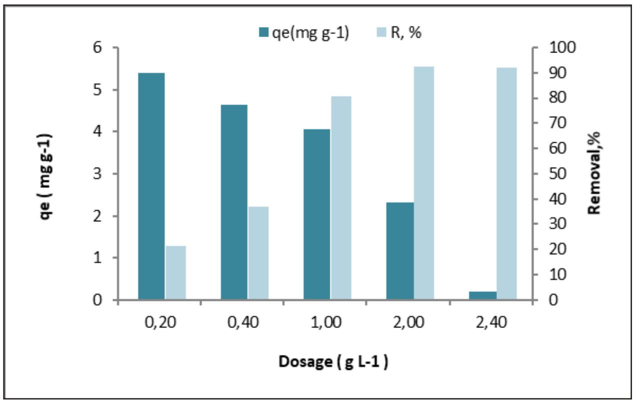


Figure 3 Influence of NORIT SA2 dosage on adsorption process

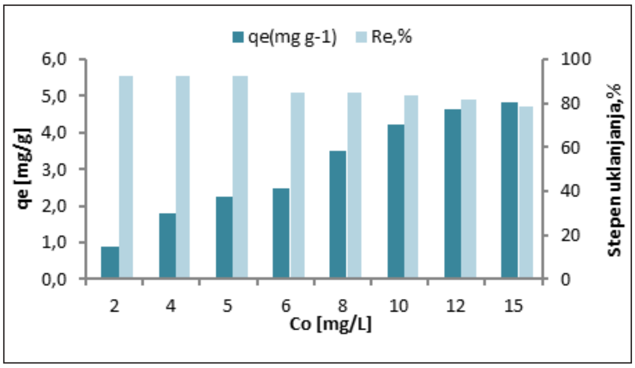
Effect of CT on the efficiency of adsorption process

Experimental conditions for investigation of effect of CT on removal of linuron were: linuron 5 mg/L, NORIT SA2 0.08 g/L, pH 7 and room temperature (25 ± 2 °C). The higher CT improved the uptake of linuron, separating the adsorption process into 2 distinct phases. In the first phase (rapid adsorption phase), linuron adsorption occurred at a high rate (>90 % of original concentration) in the first 20 minutes. In the second phase (equilibrium phase), the equilibrium has been achieved in ≥30 minutes.

Effect of initial concentration on the efficiency of adsorption process

Linuron adsorption was evaluated at various initial concentrations in water, from 2 to 15 mg/L (Figure 4), and the capacity of adsorption increased from sa 24,00 mg/g do 177,25 mg/g, respektivno. Prema dobijenim podacima, adsorpcija linurona je značajno zavisi od početne koncentracije linurona u vodenom rastvoru.

24.00 mg/g to 177.25 mg/g, respectively. According to the obtained data adsorption of linuron is strongly reliant on the initial concentration of linuron in water solution.



Slika 4. Uticaj početne koncentracije linurona na procces adsorpcije

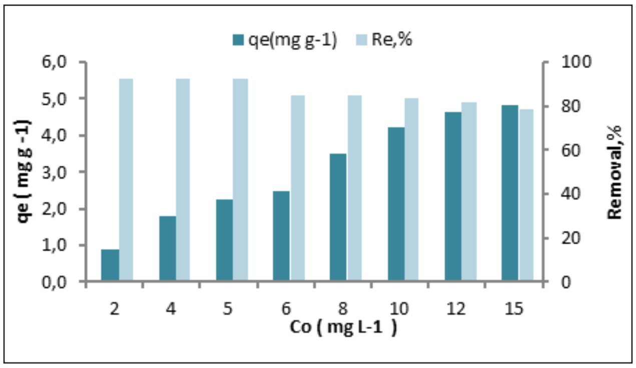
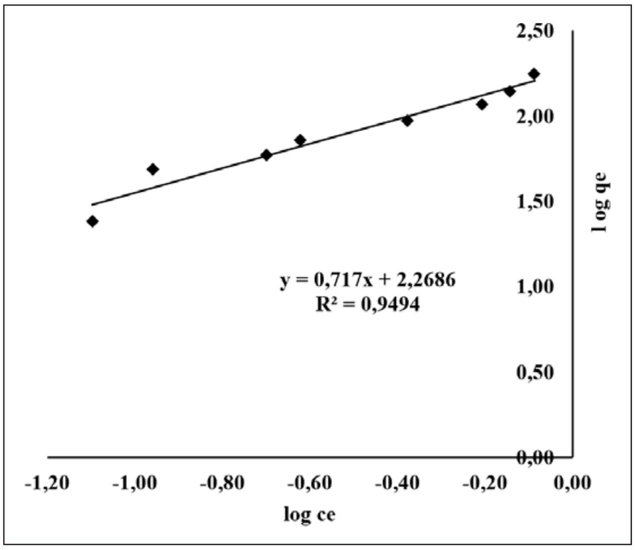


Figure 4. Influence of the initial linuron concentration on the adsorption process



Slika 5. Frojndlihova izoterma sorpcije linurona na NORIT SA2

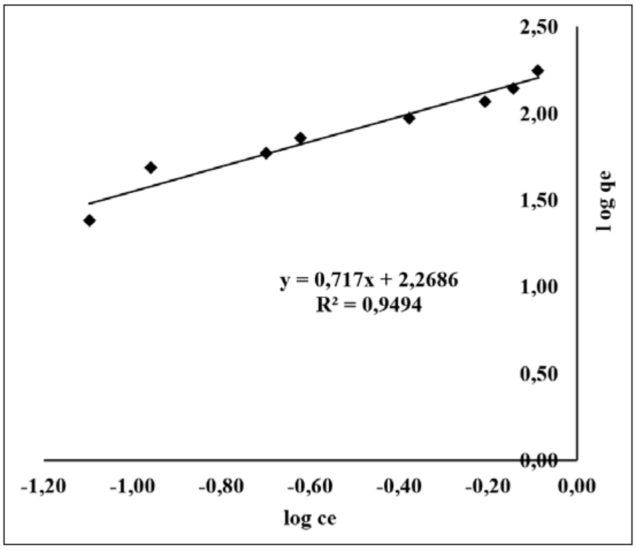


Figure 5. Freundlich isotherm of linuron sorption on NORIT SA2

Modelovanje adsorpcionih izotermi

Frojndlihov model (Figure 5) daje najbolji opis procesa adsorpcije, sa najvišom vrednošću q_f za linuorn (185.6 mg/g).

Kinetika adsorpcije

Istraživanje brzine adsorpcije je izvedeno u cilju stvaranja brzog i efikasnog modela. Adsorpcija linurona je najbolje prikazana pomoću modela pseudo-drugog reda prema posmatranim uslovima. U tom modelu vrednost korelacije je r = 0,999. Kada konstanta k_2 ima visoku vrednost, faktor vremenskog podešavanja, odnosno vreme koje je potrebno sistemu da postigne ravnotežu je kratko [6].

Termodinamički pristup analizi procesa adsorpcije

Temperatura utiče na mehanizam adsorpcije i difuziju molekula u pore adsorbenta [7]. Termodinamički parametri adsorpcije linurona na NORIT SA2 prikazani

Modeling of adsorption isotherms

The Freundlich model (Figure 5) provides the best description of the technique of adsorption, with the highest qf value for linuron (185.6 mg/g).

Adsorption Kinetics

Adsorption rate investigations were carried out in order to create a rapid and efficient model. Linuron adsorption is best defined by pseudo-second order at the studied conditions. The pseudo-second order correlation was defined by r = 0.999. When the k_2 constant is high, the time-adjusting factor, i.e. the time it takes for the system to reach equilibrium, is short [6].

Thermodynamic approach to analyses of adsorption process

The temperature affects the adsorption mechanism and the diffusion of molecules in the pores of su u Tabeli 1. Vrednosti ΔH°<0 definišu adsorpcioni proces kao egzotermni proces, što objašnjava smanjenje efikasnosti adsorpcije pri povišenim temperaturama. Dobijene vrednosti ΔH° niže od 20 kJ/mol potvrđuju da je dominantan proces adsorpcije linurona fizisorpcija. Vrednosti ΔS°>0, sugerišu nepostojanost čvrsto-tečnog interfejsa tokom adsorpcije linurona. Vrednosti ΔG°<0, prikazuju proces adsorpcije linurona kao spontan proces.

the adsorbent materials [7]. The thermodynamic parameters for adsorption of linuron on NORIT SA2 are presented in Table 1. The ΔH°<0 indicate the exothermic adsorption, which explains the decrease of adsorption efficiency as the temperature increases. The lower values of ΔH° (<20 kJ/mol) confirm that the physisorption is the dominant process in adsorption of linuron. The ΔS°>0, indicate increasing impermanence of the solid/liquid interface during linuron adsorption. The ΔG°<0, indicate that the process of linuron adsorption is spontaneous.

Tabela 1. Termodinamički parametri adsorpcije linurona na NORIT SA2
Table 1. Thermodynamic parameters for adsorption of linuron on NORIT SA2

Herbicid / Herbicide	Temperatura [K] / Temperature [K]	ΔH°[kJ/mol]	ΔS°[J/mol·K]	ΔG°[kJ/mol]
Linuron	298	-10.891	12.16	-14.515
	308			-14.636
	318			-14.758

ZAKLJUČNA RAZMATRANJA

Dobijeni podaci i rezultati istraživanja prikazuju da se aktivni ugalj NORIT SA2 može efikasno koristiti kao medijum za uklanjanje linurona iz vodenih uzoraka. Serijski eksperimenti pokazali su da na proces adsorpcije značajno utiču parametri pH vrednost, CT, početna koncentracija linurona i doza NORIT SA2. Optimalni kapacitet adsorpcije aktivnog uglja, NORIT SA2, za uklanjanje linurona je dobijen u prvih 10 do 20 minuta pri pH vrednosti 7. Efikasnost uklanjanja linurona gradijentno je opadala kako se početna koncentracija adsorbenta povećala iznad 5 mg/L. U istraženom opsegu parametara, Frojndlihov model bolje odgovara ravnotežnoj adsorpciji u odnosu na Langmirov i Temkinov model. Kinetička studija adsorpcije linurona prikazuje da model pseudo-drugog reda najbolje korelira sa dobijenim sorpcionim podacima, što prikazuje hemisorpciju kao faktor koji ograničava brzinu adsorpcije.

CONCLUSIONS

The data and results obtained in this study show that activated carbon, NORIT SA2, can be used effectively as a sorbent for linuron removal from water samples. Batch experiments revealed that adsorption is significantly affected by pH, CT, initial concentration of linuron and NORIT SA2 dosage. The optimum adsorption capacity of activated carbon, NORIT SA2, for linuron removal was obtained in 10 and 20 minutes at pH 7. Linuron removal efficacy decreases gradually as the initial adsorbate concentration rises above 5 mg/L. In the investigated parameter range, the Freundlich model fits the equilibrium adsorption data better than the Langmuir and Temkin models. The kinetic study of linuron adsorption shows that the pseudo-second order model correlates better with the sorption data, indicating that chemisorption may be the rate-limiting stage.

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