

KINETIC AND THERMODYNAMIC STUDY OF ELIMINATION OF AN ACID HERBICID BY DIATOMITE

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Abstract

The objective of this work ,is to study the adsorption power of an algerian aluminosilicate materials diatomite and acid –modified diatomite to remove an organic pollutant ,an herbicid ,Quinmerac (Qm),the materials ,were characterised by X-ray diffraction analysis ,X-ray fluorescence ,transmission electron spectroscopy ,scanning electron microscopy and physical adsorption of gases .The experiments were carried out at ambient temperature in bath mode at different pH, results showed that, the amount of Quinmerac adsorbed increased at higher pH attaining a maximum pH at PH2,5.The Langmuir model presented the best correlation of experimental data for Quinmerac adsorption .It was found that the acid –modified diatomite Demonstrates relatively better efficient activity in removal of Quinmerac than raw diatomite, modified diatomite is effective in the elimination of herbicides and could be interesting alternative materials for removing specific pollutant from environment.

Key words: Adsorption –isotherms- Quinmerac –diatomite –modified diatomite

Introduction

Water contamination is nearly always the results of human activity ,industries or agriculture intentionally or accidently ,that well runs the risk of its usefulness to humans and other organisms in nature .so

the control and security of surface and ground water from pollution is a growing concern in many area ¹,in recent years much attention has been paid to environmental problems ,especially the presence of contaminants such as (herbicides ,pesticides, and polycyclic aromatic carbons) derived from agriculture and industrial activities in water² Herbicides are the frequently used to remove certain types of plants and kill weeds quickly in yards and gardens .some of them have active ingredients and persist in soils for long periods of times and may contaminate surface and ground water .Substituted quinolinecarboxyle acids are relatively new class of highly selective auxin herbicides which Quinmerac (7-chloro-3-methylquinoline-8-carboxylic acid-cas no90717-03-6,C₁₁H₈ClNO₂) has been in comercial use in the past years or so ³(grossman and sheltrup) .Quinmerac is active substance that can effectively control important weeds such as (galium aparine) and (quakgrass) in gardens .Quinmerac has found in ground water ,surface water ,and drinking water(franzen et al)⁴ ,Quinmerac is well soluble in water and hardly degradable⁵ in addition to that Quinmerac can be transfered through chaine food posing problems to human health and the entier ecological environment ,for soils that are contaminated by organic pollutants ,there are available technologies for remediation ,in situ remediation and ex situ remediation⁶.

Adsorption is a process that can be applied either in situ with permeable reactive barriers or ex situ, is relatively simple compared to the others and can achieve quite satisfactory removal efficiencies⁷. to remove pollutants from water different adsorbent can be efficiency including activated carbon⁸ zeolites⁹ kaolinit¹⁰ and bentonite¹¹. Natural or modified diatomite (chemically or thermally) has already been used for the adsorption of different contaminants from waste water¹². In this study, raw and chemically modified diatomite have been tested for their adsorption potential for removal of Quinmerac from aqueous solution. Diatomite is fine grained, low density, biogenic sediment, which consists essentially of amorphous silica derived from opals centric frustules of diatoms. It consists of low wide variety and high surface area¹³. It is also known as diatomaceous earth or Kieselguhr. Diatomite is composed of skeletons of diatoms, single celled of algae which accumulated in huge beds in various parts of the world. There are over 10000 species of diatoms, some of which lived in fresh water and other in salt water¹⁴. It is used in many industrial areas as filtering –utility materials, filling material, insulation material, adsorbent abrasive material and surface cleaning material, catalyst carrier, light construction material and silica source in chemical material manufacturing, because of its physical and chemical characteristics^{15 16}

Materials and methods

Reagent

Raw diatomite was obtained from the site deposit located in the west ward of Algeria. All reagents used in this experiment were of analytical grade. Quinmerac of 98,2% purity was obtained from Sigma – Aldrich chemicals. and all other reactants were also purchased from Sigma-Aldrich

chemicals. It was employed the ultra pure water for preparation of solutions. The chemical structure of Quinmerac used is shown in Fig 1

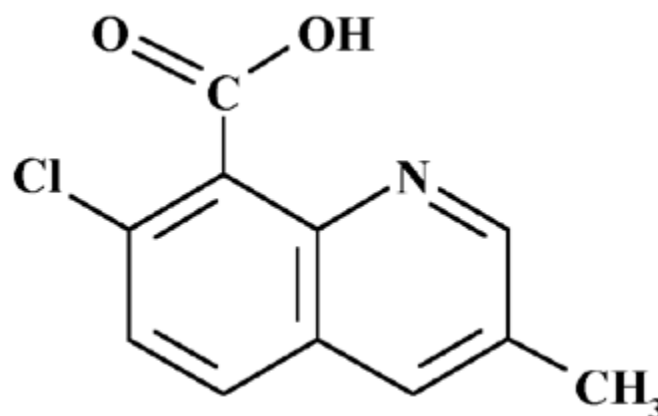


Fig.1 chemical structure of Quinmerac [Peer Review of the pesticide risk assessment of the active substance quinm rac]

clay adsorbents

20g of raw clay was washed with distilled water to remove impurities. After that sample was dried at 105°C for 5 hours and crushed after that using a porcelain ceramic balls and stored for later use. It is denoted as (Rc). Another 20g of raw diatomite was activated in acid sulfuric by refluxing 20g of clay in 200ml 0,25M H₂SO₄ for 6 h. It was then washed several times by distilled water until it will be free of SO₄²⁻ and reach pH of 7.8 and was also dried at 105°C for 5h finally the sample was crushed, the resulting acid-modified diatomite and it is denoted as (Mc). The chemical composition of the both samples is included in (table 1)

Table 1 composition in weight percent of (Rc) and (Mc)

Oxides	SiO ₂	Al ₂ O ₃	
Fe ₂ O ₃	TiO ₂	MgO	K ₂ O
SrO ₃	ZrO ₂		
Rc	92.664	3.992	1.952

0.35	0.889	1.040	0.022
Mc		93.517	3.299
1.383		/	/
0.882	0.007		

Characterisation of the clay adsorbent

Gas adsorption at 77K

The porous texture of all samples was determined by physical adsorption of gases N₂ at 77K and CO₂ at 273K) using an automatic adsorption system (autosorb-6 Quantachrome corporation) under vacuum for 4h. Surface area (SBET) was calculated using a relative pressure range from 0.05 to 0.20¹⁷, the both total pore volume were obtained by converting the amount N₂ gas adsorbed (cm³/g) at relative pressure of 0.97, V_{DR} (N₂) is the volume of micropores obtained by nitrogen adsorption (below 2nm in diameter) and V_{DR} (CO₂) the narrowest micropore volume obtained by (CO₂) adsorption (below 0.7 nm in diameter) and V_{mes} the volume of mesopores were worked for the both samples of diatomite^{18 19}. The surface and pores characteristics of these two samples used as adsorbents in the present work

TEM analysis

The transmission electron microscopy (TEM) observations, the samples were dispersed in water and supported on TEM grids the images were collected using the JEOL (JEM2010) Microscope working at an operation voltage of 200KV.

XRD diffraction

The X-ray diffraction of the both powder samples, Rc and Mc allows us to obtain and know the crystalline phase of adsorbent solids.

SEM analysis

For Microscope electronic spectroscopy (SEM), the images were collected using the Mini Sem 3200M working at an operation of 5 to 30 Kv

Herbicide adsorption study

0,5g of each sample (Rc and Mc) is added to 100ml beaker containing 50ml of Quinmerac of varied initial concentrations ranging from (0,5 to 100ppm). experiments were carried out in shaker bath mode at 25°C for 24h (adsorption equilibrium time) after equilibrium the mixture was centrifuged at 2500rpm for 10 min, the supernatant was analysed by UV-visible Spectroscopy using the unicam UV2-100 double beam scanning, the quantity of the removed Quinmerac was calculated from the difference between the initial concentration (C₀) and equilibrium concentration (C_e). the quantity of herbicide adsorbed per unit amount of adsorbent Q_e was obtained from equation:

$$Q_e = \frac{(C_0 - C_e) \cdot v}{m_{ads}}$$

with m=0,5g and V=50ml

where Q_e is the adsorption capacity at equilibrium (mg/g) C₀ and C_e are respectively the initial and equilibrium concentrations (mg/L), V is the volume of solution and m is the mass of adsorbents²⁰

kinetic models

to interpret the kinetic batch experiments data two kinetic models were used the pseudo-first-order^{21 22} and the pseudo-second-order kinetic model^{23 24 25}

pseudo-first-order equation

the pseudo-first-order kinetic equation is presented as:

$$\frac{dQ_t}{dt} = K_1 \cdot (Q_e - Q_t) \quad 26$$

where K₁ is the pseudo-first-order rate constant (min⁻¹) and Q_e, Q_t are the amount of adsorbent at equilibrium and at time t (mg/g) by integration the linear form of the equation becomes: (Q_e - Q_t) = ln Q_e - K₁t

pseudo-second-order equation

the pseudo-second-order kinetic equation is expressed as :

$$\frac{dQt}{dt} = K_2 \cdot (Q_e - Q_t)^2$$

where K_2 is the pseudo-second-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), by integration we obtain the linear form as :

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$$

the plot of $\frac{t}{Q_t}$ gives the linear equation resulting the values of Q_e and K_2 to be computed²⁷

Results and discussion

Fig2 shows the nitrogen adsorption isotherms of (Rc) and (Mc). The curve indicates clearly the difference between the two adsorbents, on the basis of the (BDDT) classification, the curves of adsorption-desorption isotherms contrast to the typical type II, improving that the diatomite and its modified solid are mesoporous powders with pore diameters larger than micropores²⁸. After being treated with H_2SO_4 , the surface area of the diatomite increased up from $26.47 \text{ m}^2/\text{g}$ to $39.906 \text{ m}^2/\text{g}$ (table 2), and its porosity was improved significantly, confirmed by **Fig3** that shows the pore size distribution curves desorption based on pore areas of the Barrett-Joyner-Halenda (BJH). It is observed that the distribution of pore diameters of (Rc) and (Mc) has been heterogeneous, for diameter ranges below about 100 \AA , which made our supports useful for their possible applications in adsorption of contaminants with large molecular size from liquid phase²⁹

Table 2 main physical properties of (Mc) and (Rc) used as adsorbents

Sam ples	$S_{\text{(BET)}}$ m^2/g	$V_{\text{DR}}(\text{N}_2)$ cm^3/g	$V_{\text{DR}}(\text{CO}_2)$ cm^3/g	$V_{\text{mes}}(\text{C})$ m^3/g
Rc	26.47 1	0.01 1	0.009	0.101
Mc	39.90 6	0.01 4	0.009	0.103

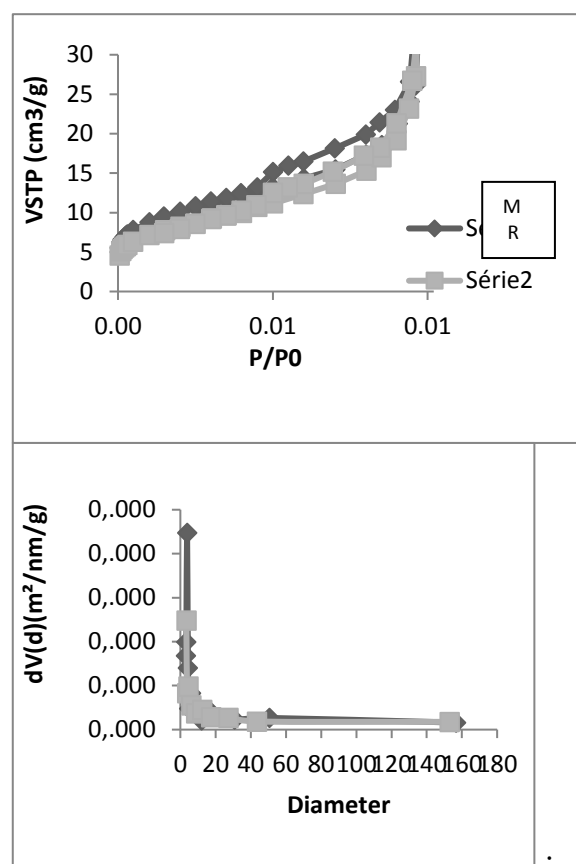


Fig2 N_2 adsorption-desorption (273K)
Fig3 pore size distribution of (Mc) and (Rc)

The SEM image of raw diatomite in **Fig4** showed that the circle form of diatomite with small pores on the surface due to the impurity which made the pores even blocked, after acid-modification with sulfuric acid 0.25M the diatomite still showed the multi-pore structure larger, opened and cleaned pores from impurities. However, in order to verify the removal of

this impurities element analyses of (Rc) and (Mc) were performed by EDS as is shown in Fig5, similar study has been reported by Zhang, et al³⁰

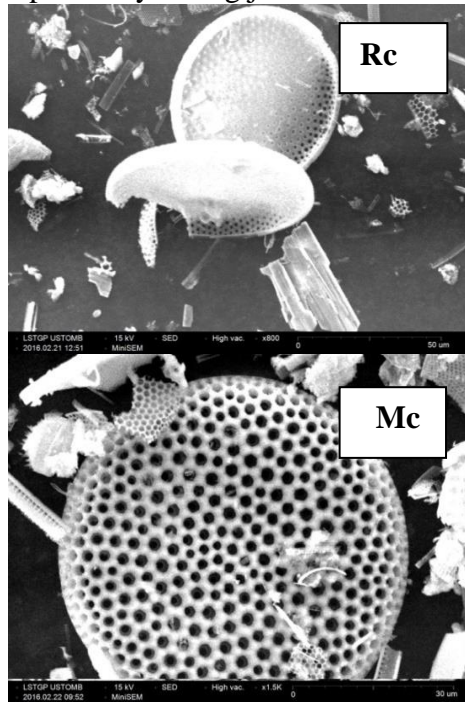


Fig. 4 SEM image of diatomite and acid modified- diatomite

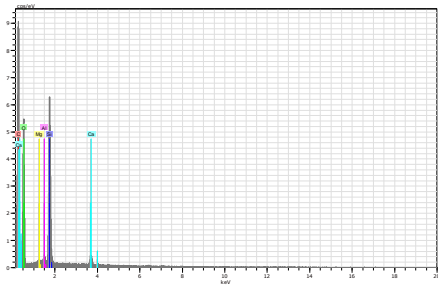


Fig.5 EDS spectra of raw and acid modified diatomite

Table 3 Element composition from EDS of raw diatomite and acid –modified diatomite

	Bulk composition (wt%)						
	C	O	Al	Si	Mg	Ca	K
RC	-- -	84.59	0.74	12.63	0.22	1,78	0,17
MC	-- -	83.84	0.56	15.60	---	---	

For the MET analysis in **Fig6** was done in order to confirm the observation obtained from SEM, and shows the morphology on the surface of the prepare samples more precisely³¹, however, clear differences can be observed in the morphology of (Mc) and (Rc).

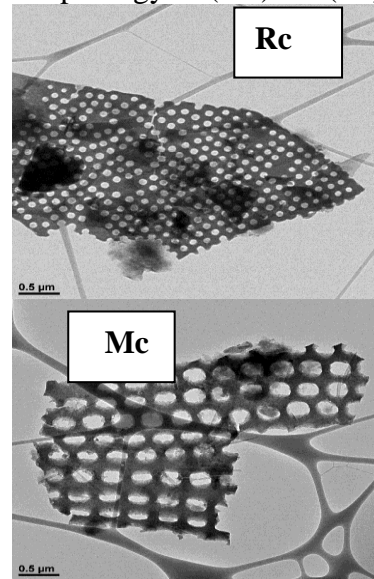


Fig.6 TEM image of diatomite and acid modified diatomite

X-ray analysis resulting **Fig7** demonstrate that diatomite is principally constituted of amorphous phase of silica in peak of 26.328 Å° and some quartz in 4.27 Å°, whereas the 3.03 and 2.90 Å° are respectively for calcite and cristoballite and ankerite²⁹.

Fig 8 shows the differences between (Rc) and (Mc) as it is shown, peaks of silica has increased through acid treatment, however, the crystallite size of the three crystalline phases (cristobalite, quartz and ankerite) was decreased, that it improves the removal of impurities after acid – modification with H₂SO₄ 0.25M.

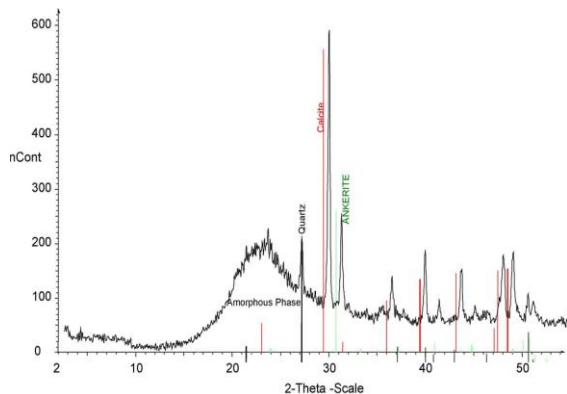


Fig7 XRD patterns of raw diatomite [Hadjadj-Aoul et al.2005]²⁹

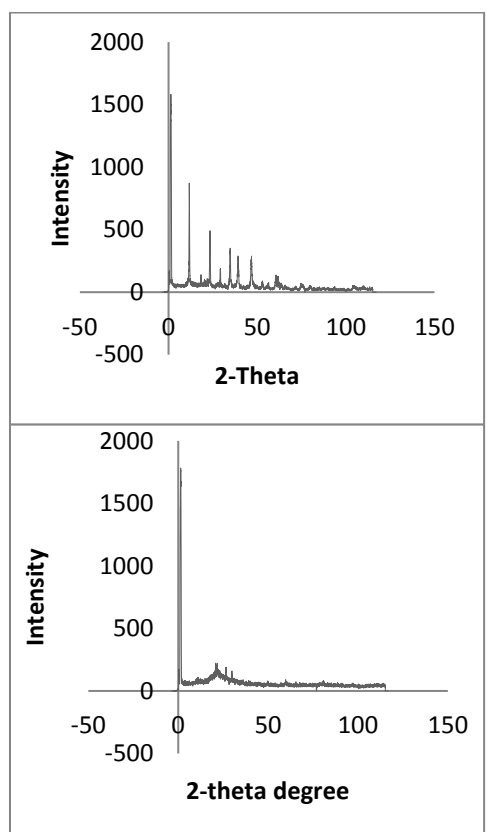


Fig 8 XRD patterns of raw and acid-modified diatomite

Adsorption study

Effect of pH

The solution pH is one of the important factors controlling the effectively degradation of organic contaminants³²; in this work the pH study was conducted to determine the optimum pH at which

maximum herbicide removal could be achieved, with raw and modified diatomite using different pHs ranging from 1,1 to 9 ,the results are shown in **Fig9**. As like observed ,at the first ,the uptake of Quinmerac increased slowly with increasing in pH,reaching a maximum of pH =2.5 and decreased again at higher pH .It was conclude that the Quinmerac adsorption is highly dependent on the pH of solution .If pH >3.0),is negatively charged due to the variable charge from pH dependent surface hydroxylsites .the point of zero charge pH(pzc) is 5.2 for (Rc) and (5.9),So the diatomite charge surface will be positively charged in acidic media (pH<pH(pzc)),and negatively charged in alkaline media pH>pH(pzc)) ,with PKa values of Quinmerac are 2.9 and5.2 in the anionic form³³.In pH 2.5the degradation rate attains maximum .In the other hand, the degradation rate increases when Quinmerac change in to the Zwitter-ionic form and then to anion ,this, creates more important interaction with the surface of our supports (Mc)and (Rc)that contain essentially of silica(SiO₂) .Generally ,the adsorptive characteristics of the adsorbents below and above the Ph of maximum adsorption can apparently change as a function of –the surface charge of adsorbent-the degree of ionization of the adsorptive molecule and extent of dissociation of functional groups on the active sites of the adsorbents (naudit)³⁴

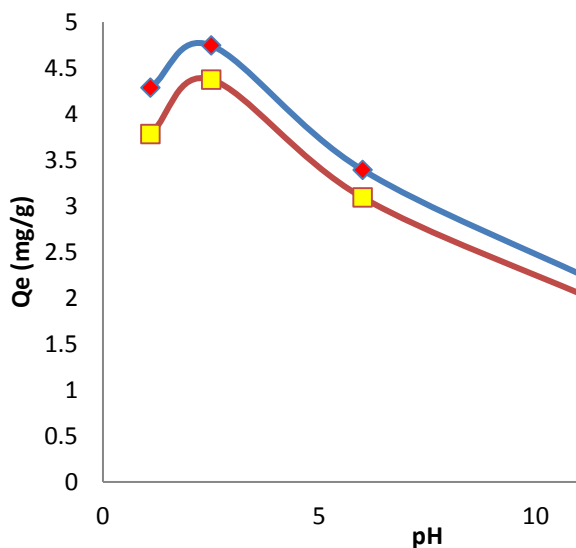


Fig9 Effect of the solution pH on the degradation of Quinmerac using 0.5g of Rc and Mc (concentration of Quinmerac solutions 5 to 100 ppm, $T^{\circ}=25^{\circ}\text{C}$, time agitation 24h)

Adsorption isotherms

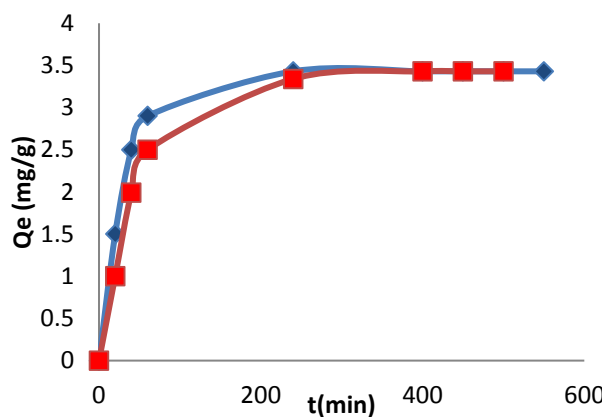


Fig 8 Adsorption isotherm on Rc and Mc at $T^{\circ}=25^{\circ}\text{C}$, $C=100\text{ mg/L}$ Quinmerac and $\text{pH}=2$

Isoterm studies were carried out in 100 ml flasks where a fixed mass of diatomite and acid-modified diatomite of 0.5 g was introduced in 50 ml of herbicide solution with different concentrations ranging from (0.5 to 100 ppm) at different pHs ranging from (1.1 to 9) during 24 h at 25°C in bath mode shaker. The most widely used

isotherms for modeling adsorption are: Langmuir isotherm^{35, 36, 37}, and Freundlich isotherm³⁸. In the present study the experimental data were applied, on Langmuir and Freundlich models using linear regressions, to describe results. The parameters belonging to the isotherm models for (Rc) and (Mc) were given in (table 3). It is observed that values of Langmuir coefficients K_L , n and R^2 in raw diatomite and acid-modified diatomite were higher than those of Freundlich isotherm, in contrast the Langmuir isotherm is more suitable to express experimental data for removal of Quinmerac than Freundlich isotherm for the both samples of diatomite as it is shown in **Figures 10** and **11**.

The linear forms of well-known Langmuir and Freundlich isotherm equations used for adsorption of monolayer levels, on a homogeneous surface with no interaction between adsorbed molecules were chosen respectively as follows³⁹:

$$\frac{C_{eq}}{Q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_{eq}}{q_m}$$

$$\ln q = \ln k_f + 1/n \ln C_e$$

Where K_f and n are coefficient of adsorption capacity and adsorption strength respectively in the Freundlich model. A linear plot of ($\ln Q_e$ vs $\ln C_e$) gives K_f and n as is shown in **Fig 10**. And from Langmuir model we obtain K_L from linear plot of ($1/Q_e$ vs $1/C_e$). The experimental data fit both models, well ($0.90 > R^2 > 0.94$) for Langmuir and ($0.84 > R^2 > 0.93$) for Freundlich model. Also for the Langmuir adsorption capacity increases in the order $\text{Mc} > \text{Rc}$, (table 4) includes the different values of Langmuir and Freundlich constants:

Table 4 Parameters extracted from application of mentioned adsorption models

forces by sharing or exchange of electrons between adsorbent and adsorbate⁴⁰

Adsorbants		Langmuir			Freundlich			
		Q _m (mg/g)	K _L (l/mg)	R ²	1/n	n	K _F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	R ²
RD	1H	2,62	0,48	0.995	0.704	1.42	0,45	0.912
	4H	3,52	0,73	0.996	0.684	1.47	0,95	0.929
	24H	3,49	1,01	0.998	0.632	1.58	1,2	0.940

kinetics

to investigate the mechanism of Quinmerac adsorption on diatomite and acid-modified diatomite ,the pseudo-first-order and pseudo-second-order equations were used together as are included in (table5).

The pseudo-first order is one of the popular and empirical models for adsorption kinetics, from the data it can be seen that the second-order model fits better .The uptake of Quinmerac was the most

Tableau 5 parameters of first and second-order kinetic models

Conclusion

It was shown in the present investigation that the treatment of diatomite with sulfuric acid improved its performance as adsorbent for Quinmerac.this improvement in acid-modified

Adsorbant	Quinmerac (ppm)	Pseudo-first –order model				Pseudo-second-order model		
		Q _e _{exp} (Mg.g ⁻¹)	K ₁ (Min ⁻¹)	Q _e _{cal} (Mg.g ⁻¹)	R ²	K ₂ (Min ⁻¹)	Q _e _{cal} (Mg.g ⁻¹)	R ²
RD	100	3.43	0.09	3.32	0.933	0.0024	4.30	0.998
MD	100	4,3	0.008	9.24	0.935	0.001	5,3	0.999

rapid in case of Mc and the slowest for Rc .The second order model is based on the assumption that the rate-limiting step may be a chemical adsorption involving valence

diatomite was contributed to increasing in surface area from 26.461m²/g to 39.906m²/g and the well-developed porous structure that it was confirmed by SEM analyses. From XRD patterns ,it can be seen that diatomite is an expensive source of amorphous silica with quartz and cristoballite phase that it improve its

mechanical strength.According to the figures of removal isotherm of Quinmerac on the diatomite samples may be classified as H-type of the giles classification ,this suggests that the algerian diatomite has a

good attraction with herbicide Quinmerac, Langmuir parameters present higher values than those of Freundlich isotherm. From kinetic study it was found that pseudo-second order is the best to present the experimental data for removing Quinmerac from aqueous solution. Finally, we can conclude that diatomite and its modified form can be used as support adsorbent to remove pollutants from wastewater and resolve some environmental problems.

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