

Removal of Ametryn from Wastewater Using Modified Kaolinite

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ملخص البحث

المبيدات الحشرية تعتبر من المواد البيئية الخطرة لأنها من المواد الضارة علي البيئة و الصحة العامة. لذلك تهدف الدراسة الي إز الة مركب الأميترين من مياة الصرف الصحي بواسطة الكاولينا المعدلة و تم قياس مركب الأميترين بواسطة جهاز الكروماتوجرافي السائل المزود بمقياس الكتلة. و استخدمت الكاولينا المعالجة بالحمض و القاعدة كطريقة جديدة لأز الة الأميترين. و أثناء الدراسة تم دراسة حركية الادمصاص و الديناميكا الحرارية لأدمصاص الأميترين. و كانت النتائج كالتالي و هي أن قدرة أمتز از مركب الأميترين علي سطح الكاولينا المعالجة بواسطة مض الهيدروكلوريك و حمض الكبرتيك كانت جيدة ووصلت قدرة الأمتز از الي 8.60 مجم / جم و 8.00 مجم / جم بالترتيب و كانت اعلي من الكاولينا المعالجة بواسطة هيدروكسيد البوتاسيم التي لم تزيد عن 0.01 مجم / جم. و حركية الأدمصاص اثبتت ان ادمصاص الأميترين علي سطح الكاولينا المعالجة بواسطة حركية الأدمصاص التبيد من الكاولينا المعالجة بواسطة هيدروكسيد البوتاسيم التي لم تزيد عن 0.01 مجم / جم. و الحركية الأدمصاص الثبت ان ادمصاص الأميترين علي سطح الكاولينا المعالجة بموذج المعادلة الحركية الأدمصاص البيت ان المعالجة بواسطة الميترين علي سطح الكاولينا المعالجة بالمعاد المعاد المعاد المعاد الم

ABSTRACT

Pesticides residues are considered dangerous environmental pollutants because it has a potential harmful impact on environment and human health. This work aims to treat Ametryn by modified Kaolin. The identification and quantification of Ametryn were explored using LC/MS/MS spectrometer. The acidic and alkaline modified Kaolinite is proposed as a new solution for the adsorption of the Ametryn. The adsorption kinetics and thermodynamics are investigated. The obtained results reveal high adsorption capacity of Ametryn over Kaolinite treated by HCl (K-HCl) and Kaolinite treated by H₂SO₄ (K-H₂SO₄) which has reached 0.68 mg g⁻¹ and 0.84 mg g⁻¹ for K-HCl and K-H₂SO₄, respectively. Meanwhile, Kaolinite treated by KOH (K-KOH) showed low adsorption capacity <0.10 mg g⁻¹ after 75 min. Pseudo-second order model is well fitted with the experimental data with a correlation coefficient (0.999) for (K-HCl)and K-H₂SO₄). Moreover, the thermodynamics Calculation show that the adsorption of Ametryn over o acidic modified Kaolin is exothermic and physical in nature.

Keywords

Kaolinite; Ametryn; wastewater; Thermodynamic; Reaction kinetic

Introduction

Ametryn is a water soluble (185 mg L^{-1}), sulfur-containing triazine, and its chemical structure is [2-(ethylamino)-4-isopropylamino-6-methyl-thio-s-triazine] is a second generation herbicide and used to control broadleaf weeds and annual grasses in sugarcane, bananas, maize and pineapple fields. Besides, it is also used to control general weed in potato crops. Additionally, this herbicide is also applied as a vine desiccant on dry beans and potatoes. In this way, it is distributed globally in various water bodies. But it is toxic to human beings creating nausea, vomiting, diarrhea, muscle weakness, salivation and cancer. Besides, it creates irritation to the skin, eyes

and respiratory tract. It is also toxic to terrestrial and aquatic animals (Ali et al., 2016). (Farré et al., 2002) reported toxic nature of Ametryn and its four degradation products. Briefly, Ametryn and its biodegradation products are threats to the animals, human beings and ecosystem. Despite of useful application of Ametryn, it is being contaminated water resources and soils. It has been reported in the ground water at many places in the world (Sanagi et al., 2015). (Pfeuffer and Rand, 2004; Harman-Fetcho et al., 2005) concluded that Ametryn is the most commonly detected herbicides in Florida irrigation and drainage canals, also Ametryn were detected in the following places in Brazil: (i) in the surface waters of the Ipojuca River in the State of Pernambuco - Brazil, at concentrations ranging from 0.01 to 0.06 μ g L⁻¹ (Ferreira et al. 2016); (ii) in groundwater samples in Assis city, located in the State of São Paulo, with a concentration of $1.56 \pm 0.04 \ \mu g \ L^{-1}$ (Scheel and Tarley 2017); (iii) in the Northeastern Pantanal Basin (located in southern Mato, Grosso, Brazil) in stream water samples (0.002– 0.009 μ g L⁻¹), river water samples (0.003–0.082 μ g L⁻¹) and river sediment samples (0.5–1.1 µg Kg⁻¹) (Laabs et al. 2002) ; making water unfit for drinking, re-creation and other purposes. Therefore, the scientists, academicians, Governments and non-governmental organizations (NGOs) are very much worried about water contamination due to Ametryn. Hence, removal of ametryn from water is of the most importance (Ali et al., 2016). One of the most popular removal techniques is adsorption by low cost material, non-toxicity and effective, such as clay, chitosan (Mckay & Blair, 1989), sawdust (Chakraborty et al., 2005), rice husk (Malik, 2003) and bagasse (Juang et al., 2002) (Mall et al., 2006). Kaolin clay from natural aluminosilicates clay is evaluated as an appropriate adsorbent due to its high surface area (Demirbaş et al., 2015). Kaolinite clay was used by (Clausen et al., 2001) in removing atrazine and isoproturon from wastewater, (Chen et al., 2009) used montmorillonite, kaolinite and goethite in adsorption and biodegradation of carbaryl., and (Paloti et al., 2006) used Kaolinite in removing Aniline. So that this Work aims to remove Ametryn from wastewater using Kaolinite as a low coast technique.

Materials and Methods

2.1 Materials

Kaolin was purchased from El Nasr mining company (Egypt). Ametryn was obtained from (Accustandard). Potassium phosphate dibasic and potassium phosphate monobasic were purchased from panreac. Methanol 99.9% was obtained from Sigma. Sodium hydroxide and Hydrochloric acid was given from (Fisher).

2.2 Methods

2.2.1 Preparation of kaolinite

Powdered kaolin was calcined at a temperature of 600 °C for 2.0 h to form metakaolinite in an electric muffle to loosen the structural water. Then metakaolinite was leached by using 6.0 M HCl, 6.0 M H₂SO₄ and 6.0 M KOH to prepare kaolinite-HCl (K-HCl), kaolinite-H₂SO₄ (K-H₂SO₄) and Kaolinite-KOH (K-KOH) by attaining a solid/liquid ratio of 1.0: 20 by weight. (K-HCl), (K-H₂SO₄) and (K-KOH). The reaction flask was fitted with a reflux condenser and the mixture was stirred with the magnetic stirrer for 6.0 h. The temperature of the mixture was set at 70 °C, and then leached acid/alkali kaolin was cooled then filtered and washed by milli Q water and methanol (**Sarkar and Das 2015**).

2.2.2 Preparation of Ametryn

Working standard solution 10 mg L^{-1} was prepared by direct dilution of 1000µg/ml Ametryn stock solution using methanol. Series of standards solutions were prepared in deionized water for instrument calibration and batch experiments.

2.2.3 Instrumentation

pH meter model (Hach, Sension1) equipped with reference electrode used to adjust the solutions pH, Rotor shaker 15 position model (THERMO, SHKE2000) equipped with batch experiments, (LC/MS/MS) ultra-performance timer used to liquid chromatography (Acquity UPLC) equipped with mass selective detector (Xevo -TQS) used to quantification of Ametryn in the aqueous phase. Each sample before analysis was centrifuged at 6000 rpm for 15 min to remove fine kaolinite particles, then 10 µl aliquot was injected (direct injection) into a reverse phase UPLC column C8 (1.7µm*2.1*50mm). Separation of the analytes was achieved using gradient eluent conditions with a mixture of (A) water and (B) methanol HPLC grade. Eluent gradient started by 90% (A) in the first 2.5 min, 10% (A) from 2.5 to 7.75 min, 100% (B) from 7.75 to 8.50 min and then backed to 90% (A) from 8.5 to 10 min. The flow rate was 0.450 ml min⁻¹, after elution from the UPLC column, the analytes were detected by MS/MS detector using Electron-Spray-ionization (ESI) in positive mode with the following conditions, 228.1(m/z) parent ion was fragmented into 68.1(m/z) and 186.1(m/z) daughters ion by 32 con volt, 36 and 18 collision energy, respectively, 450 °C dessolvation temperature, 800 Lhr⁻¹ dessolvation, 150 L hr⁻¹ Cone and 7.0 bar Nebulize (r). Each batch controlled by calibration curve, Lab Control Sample (LCS) and reagent water blanks. Calibration curve consists of seven points from 0.005 to 1 μ g L⁻¹ to cover water samples concentration and lab control sample (LCS) concentration was 0.2 µg L⁻¹ to check LC/MS/MS instrument performance. Reagent water blanks to control cross contamination during sample preparation blank concentration should be less than limit of quantification (LOQ) (0.05 μ g L⁻¹).

2.2.4 Adsorption batch experiments

The batch experiments were carried out to study the optimum conditions for removal processes such as solution pH, kaolinite dose (K-HCl, K-H₂SO₄ and K-KOH), initial concentration of Ametryn, contact time, ionic strength and reaction temperature. Batch experiments were carried out at room temperature (22 °C) by adding a known amount of (K-HCl, K-H₂SO₄ or K-KOH) to 50 ml of Ametryn solution into number of 100 ml conical flasks sealed with aluminum foil on a rotary shaker at 250 rpm for 15 min. The effect of pH was conducted to (K-HCl, K-H₂SO₄ and K-KOH) by adding 0.1 g of (K-HCl, K-H₂SO₄ or K-KOH) to 50 ml of 2.0 µg L⁻¹ Ametryn solution at different pH values (3.0 to 9.0) which adjusted by phosphate buffer solution and 0.1 M HCl or 0.1 M NaOH. The effect of adsorbent dosage was conducted by adding desired amounts of (K-HCl, K-H₂SO₄ or K-KOH) (0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0 g) to 50 ml of 2 µg L⁻¹Ametryn solutions at the optimum pH values (pH 3.0 for K-HCl, K-H₂SO₄ and K-KOH). To investigate the effect of Ametryn concentration, experiments were carried out by adding 0.3 g of K-HCl & K- H₂SO₄ and K-KOH to 50ml of Ametryn solutions at concentrations (0.005, 0.01, 0.02, 0.05, 0.1, 0.8, 2.0, 4.0, 8.0, 16 and 20 mg L^{-1}) at optimal pH values. Equilibrium time was conducted by adding 0.3 g of K-HCl and K-H₂SO₄ to 10 and 8 mg L⁻¹ for K-HCl, K-H2SO4, respectively at different time intervals of (5, 15, 30, 45, 60, 90, 120, 150 and 210 min). To investigate the effect of

thermodynamics the experiments were carried out at optimal pH, optimal concentration and optimal adsorbent dose at equilibrium time. To investigate the effect of ionic strength, experiment carried out at different concentrations of $CaCl_2$ (0.01, 0.05, 0.1, 0.3, and 0.5 M) at optimum conditions that mentioned previously.



3. Result and discussion 3.1 Effect of pH

Figure 1: Effect of pH on the Ametryn removal %. Initial ametryn concentration $2\mu g L^{-1}$, clay dosage 0.1 g/50ml and contact time 15min.

The effect of pH on the adsorption of Ametryn onto modified kaolinite was studied by varying the pH of the solution from pH 3.0 to 9.0. The results are shown in Fig. 1. It was observed that the maximum percentage removal of Ametryn was observed at pH 3.0. As the pH of the solution was increased from 3.0 to 9.0, the percentage removal of Ametryn decreased from 80.1 to 13.2% and from 88.2 to 22.9 % in case of K-HCl and K-H₂SO₄ respectively. While in case of K-KOH there is no significant change in percentage of removal with increasing the pH value from 3.0 to 9.0. The maximum adsorption at pH 3.0 is due the external hydrogen bonds formed between amine groups of Ametryn and the hydrogen bonding sites on the kaolinite. Also the effect of solution pH could be explained in term of the dissociation constant, (pKa) of Ametryn and (pH_{zpc}) of modified kaolinite, which indicates the electrical neutrality of the adsorbent surface. The pH_{zpc} of modified kaolinite has been identified to be 7.18, 6 and 6.03 for K-KOH, K-H₂SO₄ and K-HCl. Therefore, the surface of kaolinite has a net positive charge (protonated) at $pH < pH_{zpc}$, and a net negative charge at the $pH > pH_{zpc}$. The dissociation constant, (pKa) of Ametryn is 4.1. At the pH values higher than 4.1, these ametryn molecules would be dissociated, and presented as Ametryn anions in the aqueous solution (Shattar et al., 2017). The degree of dissociation increased by increasing the solution pH, to generate electrostatic repulsive force between the ionized Ametryn molecules, with the negatively surface of kaolinite. In the acid medium, the protonation of Ametryn would increase the fraction of positive charge. These undissociated protonated Ametryn would hold tightly on the negatively charged kaolinite to enhance the percentage of removal. Similar observation has been reported by (Shattar et al., 2017) on the adsorption of Ametryn onto the montmorillonite soil and (Ahmad et al., 2001) on the adsorption of Ametryn onto colloids soil.

3.2 Effect of adsorbent dose



Figure 2: Effect of adsorbent dose on the ametryn removal %. Initial Ametryn concentration $2\mu g/l$, pH 3 and contact time 25min.

Adsorbent amount was varied from 0.01 to 1 g/50ml. As the adsorbent amount has increased, the percentage removal of Ametryn has increased with maximum removal was 94.1 and 97.4% for K-HCl and K-H₂SO₄, respectively at 0.3 g/50ml as shown in **Fig.2**. This attributed to availability of the active sites or surface area at higher adsorbent doses (**Çalışkan and Göktürk, 2010**). This result confirmed by (**Lemić et al., 2006**) indicated that the increase of adsorption efficiency of Atrazine, Lindane and Diazinone from water with increasing concentration of organo-zeolites. (**Ali et al., 2016**) concluded that as the amount of iron nanoparticle was increased, the adsorption capacity of Ametryn increased with maximum adsorption capacity (11µg g⁻¹) at 2.5g L⁻¹. Moreover, in the case of K-KOH, at the same adsorbent amounts, there is no significant removal observed with increasing the adsorbent amounts.



3.3Effect of Ametryn concentration

Figure 3: Effect of initial concentration on removal % of ametryn at kaolinite dosage 0.3g/50ml and 25 min contact time for K-HCl and K-H₂SO₄.

It is evident from **Fig.3** that adsorption of Ametryn has been decreased from 98% to 10% and 98% to 25% by increasing the Ametryn concentration from 0.0005mg/l to 25mg/l and 0.0005mg/l to 10mg/l in case of K-HCl and K-H₂SO₄ respectively. This can be explained that modified kaolinite have a limited number of active sites, which become saturated at a certain concentration (10mg/l). Noticeably, the result showed that by increasing the initial concentration of Ametryn the adsorption capacity increased until reach the maximum adsorption capacity 0.68 mg g⁻¹ and 0.84 mg g⁻¹ for K-HCl and K-H₂SO₄, respectively at initial concentration (C₀) 10 mg g⁻¹. This is owed that higher concentration of Ametryn enhances the transfer of its molecules from solution to kaolinite surface that facilitate the interaction between Ametryn and kaolinite (**Ali et al., 2016**). This result confirmed by (**Ali et al., 2016**) reported that maximum adsorption capacity for Ametryn onto iron nanoparticle was 0.011mg/g at C₀ 30 µg L⁻¹ and (**Wang and Lemley, 2006**) reported that maximum adsorption capacity for Ametryn onto kaolinite 0.430mg g⁻¹.



3.4Effect of contact time

Figure 4: Effect of agitation time on removal% of ametryn at kaolinite dosage 0.3g/50ml and 25 min contact time and ametryn concentrations 10 and 8mg L^{-1} for K-HCl, K-H2SO4 respectively.

The adsorption of Ametryn onto K-HCl and K-H₂SO₄ as a function of time is shown in **Fig. 4**. Generally, the adsorption was rapid at the initial stage of contact time, and then it became slower and reached to the equilibrium after 60min. This phenomenon was due to the fact that a large number of vacant surface sites were available for the adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases of Ametryn (**Shattar et al., 2017**). A similar behavior was reported by (**Wang and Lemley, 2006**) in the adsorption of Ametryn onto the kaolinite clay.

3.5 Adsorbtion Kinetics



Figure 5 (a,b): Kinetic plots of pseudo second order for the adsorption of Ametryn over K-HCl and K-H2SO4

For realizing more data about the adsorption mechanism, different kinetic models are applied; pseudo-first- or pseudo-second-order reaction Eq (1, 2) Pseudo first order:

$$ln(q_e - q_t) = ln q_e - k_1 t$$
Pseudo – second – order:

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

Where (t) is the adsorption time, q_e and q_t , (mg g⁻¹) are the adsorbed amount of TH at equilibrium and time t and k_1 , and k_2 are the rate constants of pseudo-first order and pseudo-second order, respectively.

The experimental data showed good agreement with the pseudo-second order kinetic model, with the correlation coefficient higher than 0.999 for K-HCl and K-H₂SO₄ Moreover, the suitability of the pseudo-second order kinetic model to fit the data was ascertained by the calculated equilibrium adsorption capacity (q_e calc.) that extracted from second order is 0.55and 0.49 mg g⁻¹ that is close to experimentally determined (q_e exp.) 0.48 and 0.47 mg g⁻¹ for K-HCl and K-H₂SO₄ respectively as tabulated in **Table 1**.

Adsorbent	Parameters	Pseudo – first – order	Pseudo – second – order	
K-HCl	R ²	0.96	0.999	
	Q e calc.	3.4	0.55	
	Q e exp	0.48	0.48	
K-H2SO4	R ²	0.93	0.999	
	q e calc.	2.8	0.49	
	Q e exp	0.47		

Table 1: Kinetics parameters of Ametryn adsorption by modified kaolinite

3.6Effect of ionic strength



Figure 6: Effect of ionic strength on removal% of Ametryn at kaolinite dosage 0.3g/50ml, 60 min contact time and ametryn concentrations 10 and 8mg L⁻¹ for K-HCl and K-H₂SO₄ respectively.

Re+sults depicted in **Fig. 6** show that the adsorption of Ametryn on modified kaolinite decrease with increasing CaCl₂ concentration, this due to (i) the addition of CaCl₂ to the solution may cause several competing effects such as an increasing competition for adsorption sites by the electrolyte cations caused by increasing CaCl₂ concentration. Also Ca⁺² is strongly hydrated cation that lead to expand the Clay such as Ca-smectite expand to 15 A° or more in the presence of water, and it is comparatively more difficult to replace the strongly held waters associated with exchangeable Ca⁺² on clay surfaces with nitro aromatic compounds (**Li et al., 2006**). (ii) Decrease in the activity of the charged ions caused by increasing electrolyte concentration. This result confirmed by (**Clausen et al., 2001**) concluded that adsorption of mecoprop, 2,4D and bentazon on calcite decrease with increasing the CaCl₂ concentration.

3.7Effect of thermodynamics

The adsorption of Ametryn by modified kaolinite was carried out at different temperatures. Free energy of adsorption (ΔG°) was calculated from the following Eq. (3):

$\Delta \mathbf{G} = -\mathbf{RT} \ln \mathbf{K}$

(3)

where K is the equilibrium constant and T is the solution temperature, R is gas constant (8.314 J K⁻¹ mol⁻¹). The enthalpy (Δ H^o) and entropy (Δ S^o) were calculated using the Van't Hoff Eq. (4).



$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R} \left(\frac{1}{T}\right)$$
(4)

Figure 7: Plots ΔG° versus T for removal of ametryn by K-HCl and K-H₂SO₄

In order to understand the effect of temperature on the adsorption of ametryn, adsorption experiments were conducted at temperature range from 303 to 328K in case of K-HCl and K-H₂SO₄ and results are shown in **Fig. 7**. Further, a comparison of adsorption shows that adsorption decrease with increasing temperature, indicating that the process is apparently exothermic. The effect of temperature can be explained on the basis of solubility. With increase in temperature the solubility of Ametryn increased and this would cause Ametryn to be more soluble and, therefore, exhibit lower tendency to

go to the adsorbent surface and get adsorbed (**Gupta et al., 2006**). In order to know the nature of adsorption, the values of these parameters are summarized in **Table 2**. The small negative value of ΔH° in case of K-HCl and K-H₂SO₄ indicates exothermic nature and that the adsorption is physical in nature involving weak forces of attraction. Further, the negative ΔG° values indicate spontaneous process in K-H₂SO₄, while in case of K-HCl, ΔG° is positive indicates the nonspontaneous process. Negative ΔS° values indicate that there is decrease in state of disorderness in the molecules during process, which in turn is due to the binding of molecules with adsorbent surface.

K-HCl					
T	Ka	$\Delta \mathbf{G}^{\circ}$	Slope (∆S°) KJ/k mol	intercept(∆H°) KJ /mol	
303	0.77	0.67	-0.04	-10.69	
313	0.66	1.09			
318	0.60	1.37			
328	0.56	1.60			
K-H ₂ SO ₄					
303	1.57	-1.14	-0.03	-11.58	
323	1.14	-0.34			
328	1.13	-0.33			

Table 2: Thermodynamic parameters for Ametryn adsorption on K-HCl and K-H2SO4 under different temperatures

4. Conclusion

The study has considered low cost technique to remove Ametryn using adsorption based on modified kaolin. The Adsorption results of Ametryn demonstrated that the high removal was found at pH 3 for K-HCl, K-H₂SO₄ and K-KOH. Ametryn adsorption has been fulfilled using pseudo-second-order kinetic model rather than pseudo-first-order. The $q_{e(cal)}$ has been presented and compared with the $q_{e(exp)}$. It has been observed excellent agreement between calculation and experimental data which clarify the effectiveness of the utilized model. Thermodynamic calculation has revealed that the adsorption of Ametryn over K-HCl and K-H₂SO₄ is exothermic and physical in nature. To conclude, the modified kaolin could be considered as an excellent candidate to be used as coagulant aid and sorbent for the removal of TH in drinking water treatment plant and wastewater.

5. References

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