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Application of diatomite as a biosorbent material for the removal of chlortoluron and isoproturon from water

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Abstract

Diatomite, one of the cheapest and abundantly available adsorbents was employed for the removal of two phenylurea herbicides, chlortoluron and isoproturon, from aqueous solutions. Physical characteristics of diatomite were investigated. The adsorption batch experiments were carried out as a function of initial herbicide concentrations, stirring speed, temperature and pH to determine the adsorption capacities of studied diatomaceous earth. The study of the pH effect showed a significant increase of adsorption as it passes from 6 to 9. The representation of the isotherms by the most commonly used models, Langmuir and Freundlich, showed that adsorption of the two selected phenylureas on diatomite obeys these two models. The adsorption mode of chlortoluron and isoproturon on diatomite could be primarily physical and under these conditions would lead to an exothermic retention process.

1. Introduction

Pesticides use has improved yields and crop diversity to meet the diet demand related to the increase in world population. However, this use has also caused indirect and adverse effects on the environment. Studies have shown the presence of pesticide residues in food [1] as well as the contamination of ground and surface water [2-3], so the environmental pollution by pesticides has become a serious problem. Chlortoluron and isoproturon which are phenylurea herbicides are widely used in cereal production to prevent weed proliferation. Many treatment processes have been proposed for the removal of environmental contaminants from aqueous solution. Adsorption process is one useful method and the most common commercially used adsorbent has been activated carbon [4-7]. However, the use of activated carbon has many drawbacks typically associated with its relatively high cost. The use of low cost materials as potential adsorbents for the removal of pollutants has been attempted to replace the activated carbon [8-22]. Nevertheless, the adsorption capacities of most of them were still limited. Diatomaceous earth or diatomite, one of the cheapest and most abundantly available adsorbents, is a siliceous sedimentary rock, it consists of an important quantities of silicon dioxide (SiO_2), with significant quantities of alumina (Al_2O_3) and ferric oxide (Fe_2O_3) [23]. Its porous structure, low density and fine particle size, resulted in a number of industrial applications, such as filter acid [24], insulting material [25], natural insecticides [26], catalyst support [27-28], drug delivery carrier [29] and template to fabricate porous materials [30]. Furthermore diatomite is approximately 500 times cheaper than activated carbon [31] and has the potential of being successfully used as a cost effective alternative to activated carbon.

Diatomite has a unique combination of physical and chemical properties which makes it applicable for the removal of heavy metals [32- 37], dyes [38- 52] and antibiotics [53]. However the adsorption characteristics of pesticides in aqueous solution onto diatomite have not been greatly investigated. Moreover few studies on the pesticide adsorption kinetics and its modeling were reported in the literature [54, 55]. Thus the objectives of this work were to examine the feasibility of using diatomaceous earth as an adsorbent for the removal of phenylurea herbicides, chlortoluron and isoproturon from aqueous solution. The effects of several factors, such as initial herbicide concentration, stirring speed, temperature and pH values were investigated. The use of pseudo-second order model for analyzing the adsorption systems between phenylurea herbicides and diatomite were evaluated and the applicability of common isotherm models (Langmuir and Freundlich) was investigated.

2. Materials and methods

2.1. *Materials*

Chlortoluron and isoproturon were obtained from Ridel – de Haen and were used without further purification (99 % purity). The chemical structures of studied compounds are shown in Fig. 1. Stock standard solution (1000 mg/L) of the two herbicides were prepared in methanol HPLC and stored at –4°C .Working standard solutions were prepared daily by diluting with deionized water. Diatomaceous earth, as adsorbent, was purchased from sigma-Aldrich-France. Before use, diatomaceous earth was dried in an oven at 100°C for 24 h.

An UNICO 2802 spectrophotometer fitted with a thermostated multiple cell compartment is used for all spectroscopic measurements.

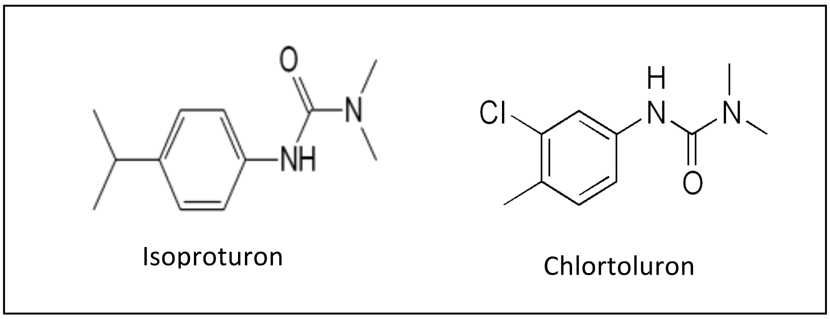

Figure 1: Structure of chlortoluron and isoproturon.

2.2. *Adsorption Kinetics*

All the experiments of adsorption kinetics were carried out by stirring 100 mg of diatomaceous earth with 200 mL of water spiked at different concentrations (0,5mg/L) of chlortoluron and isoproturon. The solution was filtered through a 0.45 µm membrane filter. Similar procedure was followed without diatomite to be used as a blank. The analysis was immediately made using a spectrophotometer at λ_{max} of 243 nm for chlortoluron and 239 nm for isoproturon.

The amount of adsorbed herbicide *qt* (mg/g), at time *t* (min), was obtained as follows

$$q_t = (C_0 - C_t) * \frac{V}{m} \qquad (1)$$

Where C_0 and C_t (mg/L) are the initial concentration and the concentration at time t respectively, m is the mass of diatomite; V is the volume of solution.

3. Results and discussion

3.1. *Characterization of diatomite*

Diatomite used in this work was characterized by scanning electron microscopy (SEM), X-ray diffraction and infrared absorption technique (IR). Fig. 2.a illustrates the MEB image of surface of tested diatomite. This figure shows a large amount of pores inside the skeleton of diatom with a wide variety of shape and size, typically 10- 200 µm [56]. The chemical composition of diatomite determined by X-ray diffraction is shown in Fig. 2.b. This figure shows that the main constituent of diatomite is SiO_2 quartz, tridymit and cristobalit. This result was observed with Jordanian diatomite [38] whose quantitative chemical analysis obtained by X-Ray florescence technique revealed 72% SiO_2, 11.42 Al_2O_3, 5.81% Fe_2O_3, 7.21% Na_2O and 1.48% CaO. Results of FT-IR (Fig. 2.c) show three absorption bands at 450 cm^{-1}, 800 cm^{-1} and 1075cm^{1}. The band at 450 cm^{-1} is corresponding to the vibration out plane of the oxygen of Si-O-Si. The band of deformation at 800 cm^{-1} is corresponding to the vibration of the oxygen in the plane of Si-O, this vibration is along the bisector of the angle Si-O-Si. The last band of elongation at 1075 cm^{-1} is corresponding to the vibration of the oxygen in the same plane Si-O but in a direction parallel to a line passing through the two silicon atoms.

3.2. *Adsorption Kinetics of chlortoluron and isoproturon onto diatomite*

3.2.1. *Contact time*

The adsorption of chlortoluron and isoproturon onto diatomite involves the determination of the contact time. The experimental process consists of contacting separately 5 mg/L of chlortoluron and isoproturon with

100 mg of diatomaceous earth at pH 5. The aqueous solutions were shaken at 120 trs/min and 25 °C. The residual concentrations of these substrates at different reaction times were determined. The obtained results are showed in Fig. 3. The adsorption of chlortoluron and isoproturon occurred after 60 and 30 min respectively. This process corresponds of the removal of 42.63% of chlortoluron and 50% of isoproturon. The extension of time up to 240 minutes does not lead to a significant improvement in the percentage of dispersion of these two herbicides.

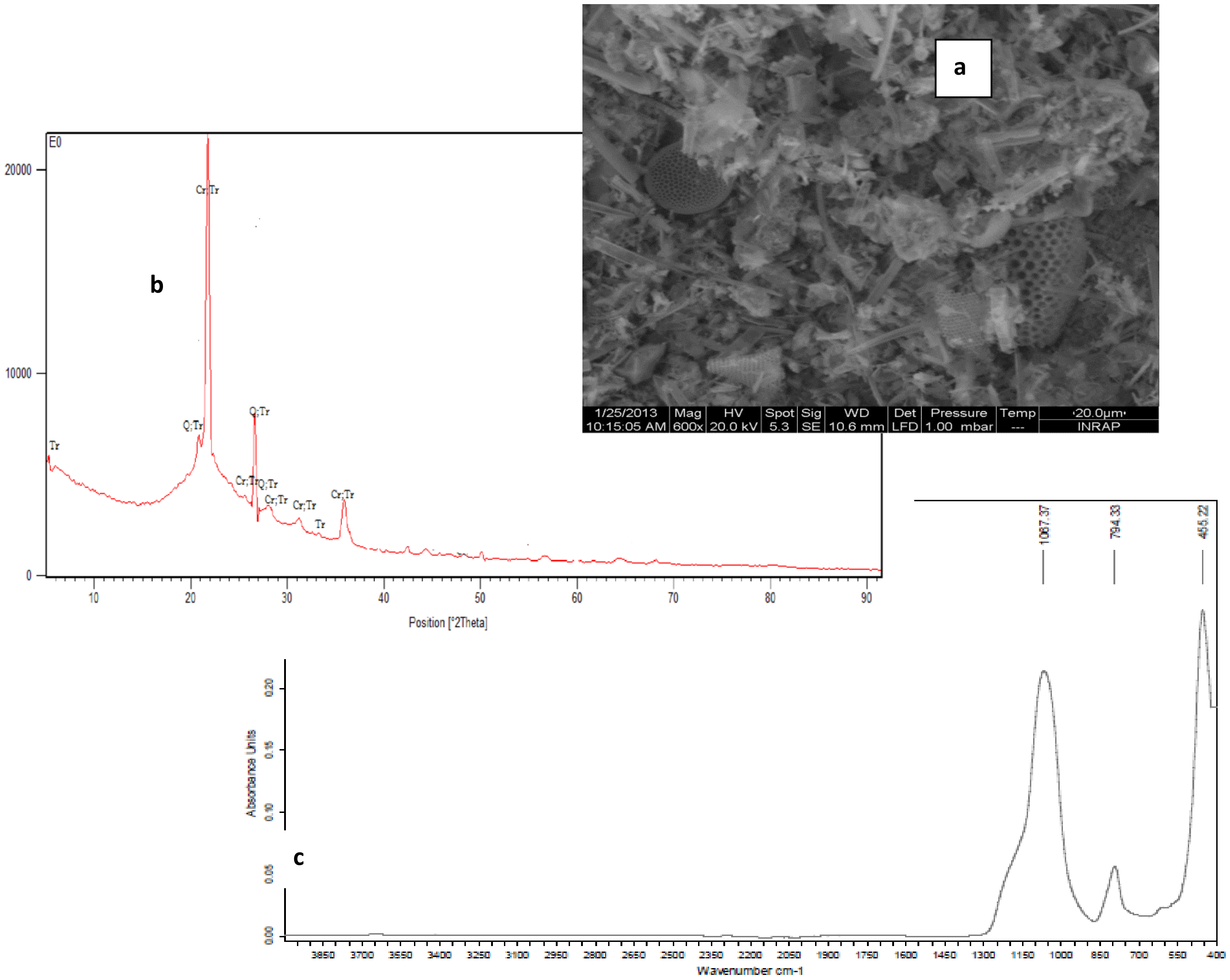

Figure 2: Characterization of diatomite.

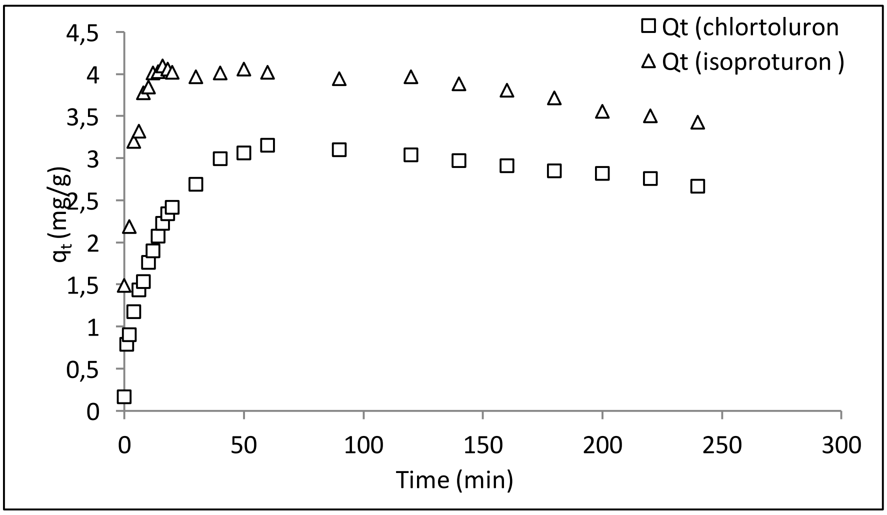

Figure 3: Plots of adsorbent chlortoluron and isoproturon (pH=5, C_0=5mg/L, v=120trs/min, T=25 °C).

3.2.2. *Effect of initial concentration*

The adsorption of chlortoluron and isoproturon was studied at different initial concentrations (5, 10, 20, 30, 50, 100 mg/L). The effect of initial concentration of the two herbicides on the rate of adsorption is shown in Fig. 4. The equilibrium adsorption capacity increased as the initial pesticide concentration increased from 5 to 100 mg/L, showing that the initial concentration provides a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases.

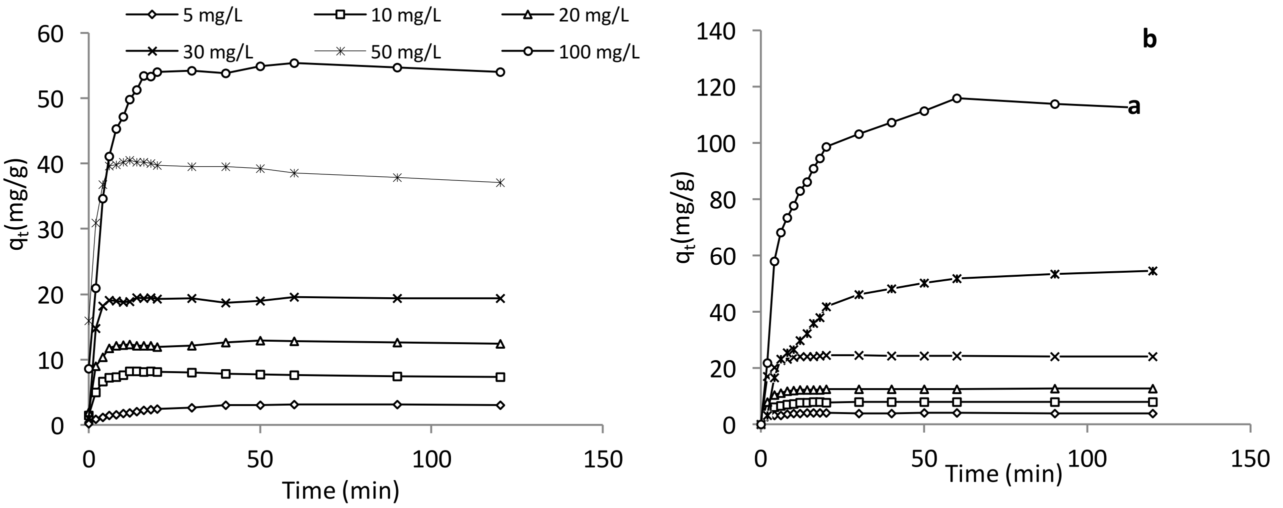

Figure 4: Effect of initial concentration of the adsorption rate of chlortoluron **(a)** and isoproturon **(b)** onto diatomite (pH=6, v=120trs/min, T=25 °C).

3.2.3. *Effect of agitation speed*

The effect of agitation speed on adsorption of chlortoluron and isoproturon onto diatomite is shown respectively in Fig. 5.a and b. The highest sorption for both chlortoluron and isoproturon were achieved at 550 trs/min. Therefore, 550 trs/min was selected as optimum agitation speed for further experiments.

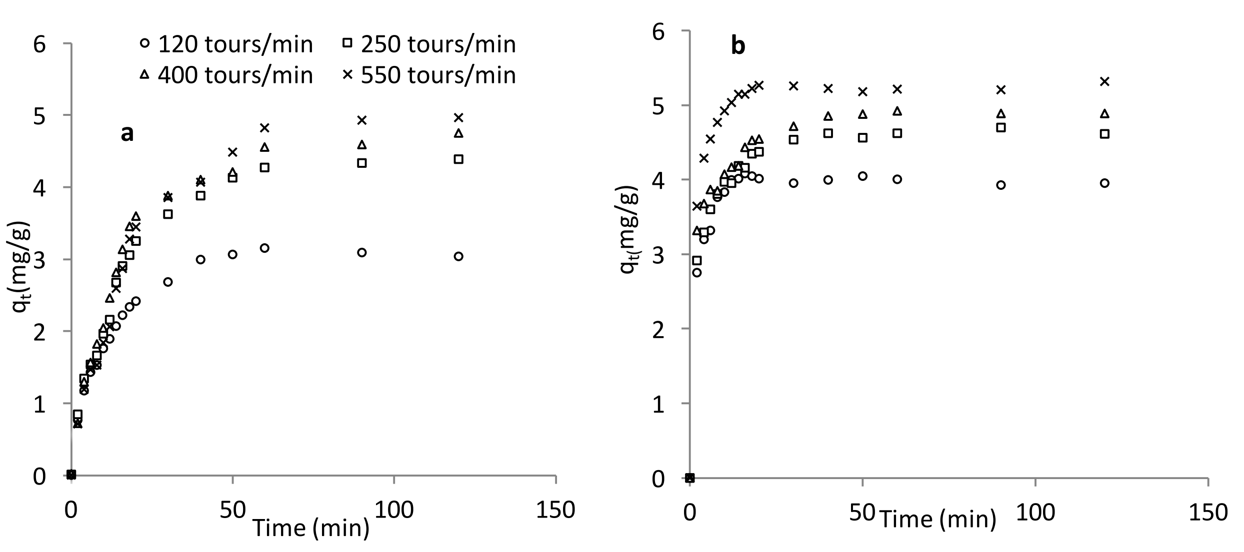

Figure 5: Effect of agitation speed on adsorption capacity of chlortoluron **(a)** and isoproturon **(b)** onto diatomite (pH=6, C_0=5mg/L, T=25 °C).

3.2.4. *Effect of Temperature*

The plots of □□ at various temperatures of chlortoluron and isoproturon are shown respectively in Fig. 6.a and b .It is clear that fitted adsorption capacity at equilibrium for each temperature decreased with increasing temperature. The obtained results were equivalent with those described in literature [48, 58].Consequently the main of the adsorption of chlortoluron and isoproturon onto diatomaceous earth should be physical adsorption and world lead to an exothermic retention process. Diatomite which consists of amorphous silica (SiO_2, nH_2O) contains many silanol groups (isolated silanols and siloxane bonds). The silanol group is very active and can react with phenylurea herbicide by the formation of hydrogen bond and Vander Waals interactions between the aromatic ring of the herbicide and the neutral site on the adsorbent surface.

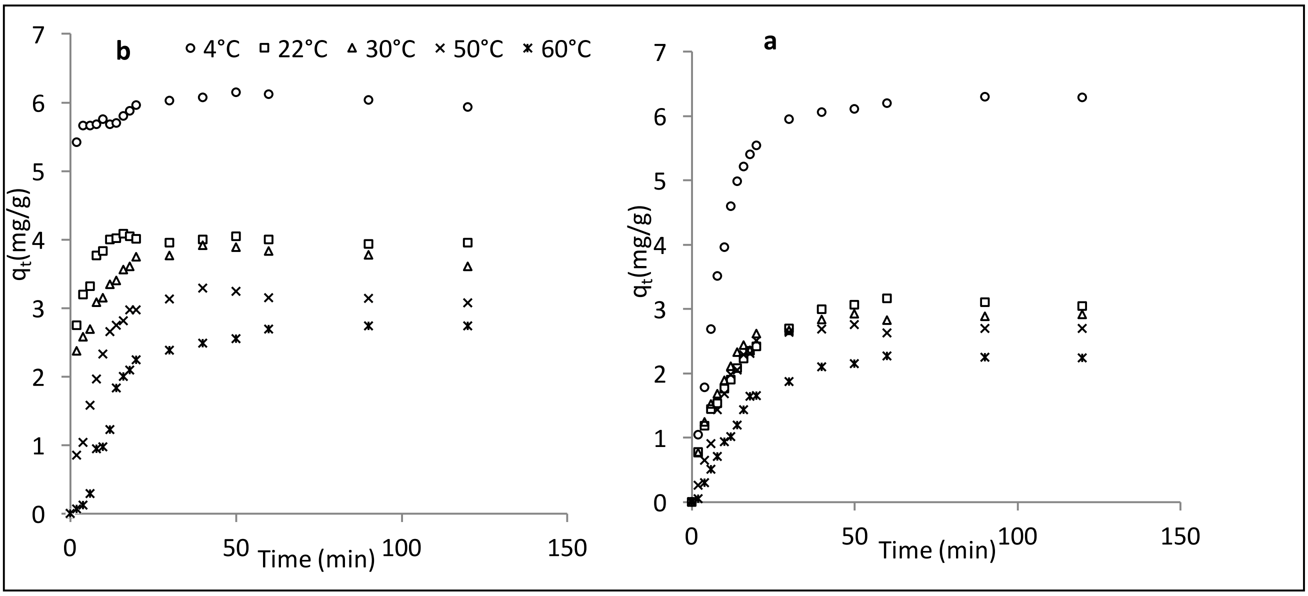

Figure 6: Effect of temperature of adsorption of chlortoluron **(a)** and isoproturon **(b)** onto diatomite (pH=6, C_0=5mg/L, v=120trs/min).

3.2.5. *Effect of pH*

The influence of pH was investigated in a range of 3 to 11. Fig. 7.a and b show the variation of the adsorbed amount in time at different pH values, respectively, for chlortoluron and isoproturon. The adsorption of isoproturon and chlortoluron increases with the increase of pH. A significant increase was observed when pH ranging from 6 to 9. These results are consistent with those studied by Tsai et al [58] when pH of point of zero charge (pH_{pzc}) of diatomaceous earth- water system was approximately 1.5 the surface of this diatomite at pH > 3 should exhibit negative charges mainly due to the variable charge from pH dependent surface hydroxyl sites [59].Those negative charge are available due to the loss of H^+ from the surface. So with the increase of pH the adsorbed amount of phenylurea herbicides increased in response to the increasing number of negatively charged sites.

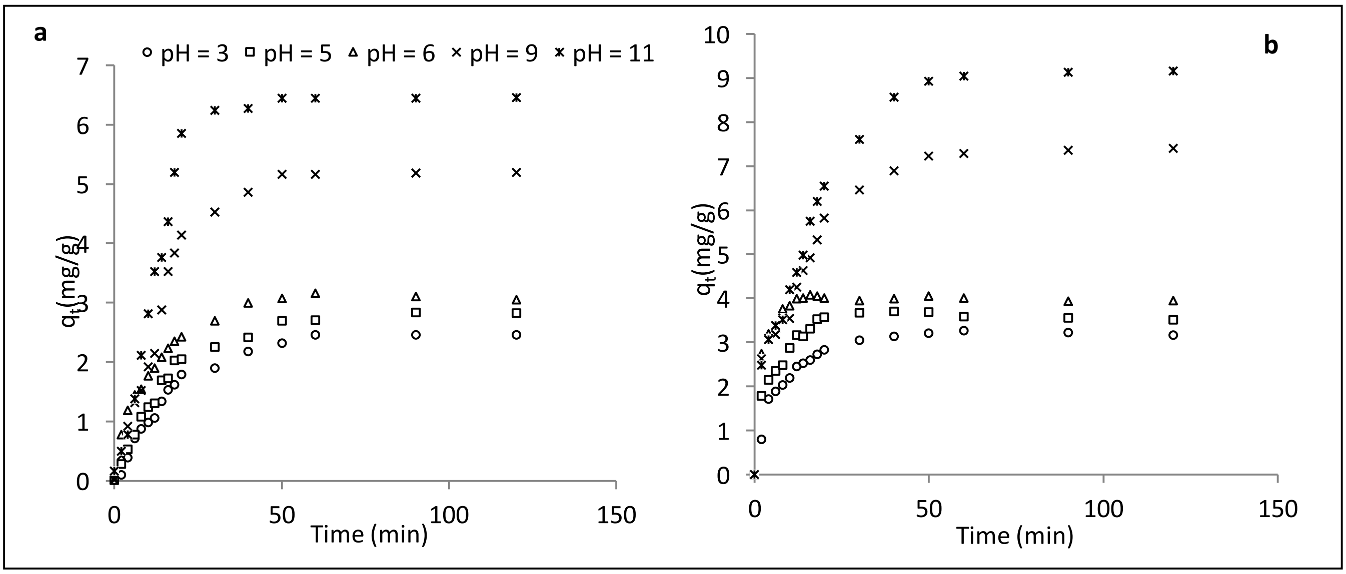

Figure 7: Effect of pH on adsorption capacity of chlortoluron **(a)** and isoproturon **(b)** onto diatomite (C_0=5mg/L, V=120trs/min, T=25 °C)

3.3. *Adsorption kinetic model*

In order to investigate the adsorption characteristics of chlortoluron and isoproturon on diatomite, the pseudo-second-order kinetics model was used to check the adsorption dynamics in this work because of its good applicability in most cases in comparison with pseudo first order model and intra-particle diffusion model [60-64]. The kinetics constants were calculated using the conventional kinetic model of pseudo-second-order equations:

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

where q_t and q_e (mg/g) are the adsorption capacity at time t (min) and equilibrium, respectively. k_2 (g/mg min) is the rate constant of the pseudo-second-order respectively.

Rate parameters k_2 and q_e and regression coefficient were displayed in table 1.Using the regression analysis the kinetics of phenylurea herbicides on diatomite follow the pseudo- second order adsorption model with regression coefficients higher than 0.994.The equilibrium adsorption capacity (q_e) increased as the initial pesticide concentration increased , showing that the initial concentration provides on powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases [65].

Table 1: Kinetic parameters of chlortoluron and isoproturon onto diatomite.

C (mg/L)	Chlortoluron			Isoproturon		
	k_2	q_e	r^2	k_2	q_e	r^2
5	0.057	3.165	0.995	1.524	4	0.999
10	1.965	7.519	0.996	1.74	8.130	0.999
20	0.208	1.658	0.999	0.125	12.658	0.999
30	0.217	19.608	0.999	0.240	24.390	0.999
50	0.061	38.462	0.998	$1.815.10^{-3}$	66.667	0.994
100	0.015	55.556	0.999	$2.041.10^{-3}$	142.857	0.998

3.4. *Adsorption isotherm*

Two common isotherm equations (Langmuir and Freundlich models) were applied in this study. Applicability of these isotherm equations was compared by calculating a correlation coefficient r^2.

Langmuir equation is commonly expressed as:

$$\frac{1}{q_e}=\left(\frac{1}{q_m}\right)+\left(\frac{1}{K_l.C_e.q_m}\right) \quad (3)$$

where q_e is defined in Eq. (2), C_e is the concentration of herbicide adsorbed at equilibrium, q_m is a constant related to the area occupied by a monolayer of absorbate reflecting the adsorption capacity (mg/g) and K_L is the Langmuir constant related to the affinity of binding sites.

The Freundlich isotherm equation is commonly given by :

$$qe=K_f.(C_e)^{\frac{1}{n}} \quad (4)$$

where q_e and C_e are defined in Eq. (4), K_f is Freundlich constant related to the bonding energy. It can be defined as adsorption or distribution coefficient and represents the quantity of herbicide adsorbed onto diatomite for unit equilibrium concentration (C_e = 1 mg/L). The slope $\frac{1}{n}$ ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [66]. A value for $\frac{1}{n}$ below one indicates a Langmuir-type isotherm since it comes difficult to adsorb additional contaminants at higher concentrations [67].

Table 2 presents the results of two isotherms fitted by using the data of adsorption capacity for diatomite. It can be seen that the Langmuir model yields a better fit than the Freundlich model as reflected with correlation coefficients r^2 of 0.967 versus 0.938 and 0.953 versus 0.818 for chlortoluron and isoproturon respectively.

Table 2: Parameters of Langmuir and Freundlich.

Herbicides	Langmuir Isotherm			Freundlich Isotherm		
	q_m (mg/g)	K_l (L/mg)	r^2	K_f [mg/g $(L/mg)^{\frac{1}{n}}$]	$\frac{1}{n}$	r^2
Chlortoluron	1000	0.001	0.967	1611	0.853	0.938
Isoproturon	250	0.006	0.953	1.162	1.188	0.818

4. Conclusion

The diatomite earth was used as an adsorbent for the removal of phenylurea herbicides, chlortoluron and isoproturon from water. Many factors affect the adsorption capacity on diatomite. The maximum adsorption capacity for chlortoluron and isoproturon was reached respectively after 60 and 30 min. The initial concentrations provide a powerful driving face to overcome the mass transfer resistance between the aqueous and solid phases. The effect of agitation speed on the adsorption behavior wasn't negligible and the adsorbed amount of herbicide increased as the agitation speed increased. The pH of phenylurea pesticide is very important parameter since it affects the herbicide adsorption capacity on diatomite. The adsorption process was found to be exothermic which means increasing the temperature will reduce the maximum loading capacity of the adsorbent. Furthermore the adsorption process follows the pseudo-second-order model. The adsorption isotherm data were well described by Langmuir adsorption isotherm model.

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