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ADSORPTION OF HUMIC ACID ONTO CHITOSAN: ISOTHERMAL AND KINETIC STUDIES

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Abstract – The increasing demand for low-cost adsorbents used in environmental protection processes and especially for water treatment processes has given rise to low-cost alternative adsorbents. Application of chitinous products as alternative adsorbents in water treatment has received considerable attention in recent years. Chitosan obtained from shrimp waste gives very good adsorbent proprieties with low cost. In the present work, the ability of chitosan as an adsorbent for humic acid in the form of sodium humate in aqueous solution was studied. For this batch adsorption tests were carried out at ambient temperature. The results of the adsorption kinetics showed very rapid adsorption of humic acid within a period of time which does not exceed 30 minutes with high removal that is 65%.

INTRODUCTION

Chitosan is a type of natural polyaminosaccharides, obtained from deacetylation of chitin which is among abundant biopolymer in nature.

Chitosan is considered as a cost-effective and environmentally friendly technology for the remediation of water polluted with organic pollutants.

Water contamination by organic macromolecules pollutants such as natural organic matter NOM increases the problems of water production for domestic use and deterioration of aquatic organisms. Therefore it is important that these waters should be, on the one hand, efficiently protected against any disturbance and, on the other hand, processed to produce water that satisfies the physical, chemical and biological norms of drinking water.

Humic substances are the major NOM groups in most lakes and rivers, in general, humic substances from soil organic matters, i.e., fulvic acid and humic acid, make up more than 70 % of aquatic NOM (Lawler and Kweon, 2004).

The chitosan, are biopolymer that comes from crustacean shells and has the ability to fix a great variety of heavy metals ions, dyes and organic solutes (Lin and Zhan, 2012).

During this work, we first made the preparation of the chitosan from marine products as an adsorbent, and then we realized adsorption tests to assess the ability and efficiency of chitosan for the removal of humic acid in aqueous solutions.

This work focuses on the chitosan is tested for humic acid removal from water by different conditions including the adsorbent dose, the contact time and the initial humic acid concentration, in order to investigate their effect on the retention capacity of the chitosan.

MATERIALS AND METHODS

Preparation of chitosan

The chitosan was prepared from Shrimp shell waste (Wan et al., 2013; Adarsh and Madhu, 2013) following the procedure described below:

Shrimp carapaces are added in an aqueous solution NaOH 2.5N with magnetic stirring for 6 hours at 75 °C. After decantation, the product obtained is washed with distilled water until the pH is stabilized and dried at 80 °C for 2 hours.

Next, demineralization followed the following protocol; the powder obtained after extraction of the proteins in a solution of HCl 1.7 N with magnetic stirring for 6 hours at room temperature. The material obtained is washed with distilled water and dried at 80 °C for 2 hours.

The discoloration of material obtained by oxidizing agent H_2O_2 (20%) and HCl. After the extraction of proteins, demineralization, and discoloration the material obtained is chitin. The chitin obtained is rinsed several times with distilled water until the pH is stabilized, and then dried at 50 °C for 24 hours.

The preparation of chitosan (deacetylation)In NaOH 50% solution with stirring the chitin at room temperature for 48 hours. After filtration, the product obtained is washed with distilled water until the pH is stabilized and then dried at 50 °C for 24hours. The resulting solids were crushed and sieved and stored in glass vials for later use.

Preparation of adsorbate

The Humic acid stock solution (100 mg/L) was prepared by dissolving 100 mg Humic acid in 20 mL NaOH (0.025 M) and completing at 1 L with deionized water. The experimental solutions of various initial concentrations (C_0) were prepared by diluting stock solution to the desired concentrations.

RESULTS AND DISCUSSION

FT-IR analysis

Chitosan were analyzed using infra-red analysis (FTIR):

The spectra show broad bands at 3100 cm^{-1} -3500 cm^{-1} corresponding to the (-NH) and (-OH) elongation vibrations including the hydrogen bonds which are especially present in the chitosan molecules.

There are also absorption peaks due to symmetric elongation vibrations of (-CH) and (-CH_2) at 1313 cm^{-1} and 2940 cm^{-1}.

Thus the peaks appeared at 1559 cm^{-1}, 1554 cm^{-1} and 1557 cm^{-1} due to the vibrations of the (- NH) bond of primary and secondary amine.

The absorption bands of the saccharide structure appear for bonds (C-O) at 1122 cm^{-1}, (C-O-C) at 1074 cm^{-1} and (C-N) at 1024 cm^{-1}.

Finally the spectrum has bands in the spectral region (500-900) cm^{-1} called region sensitive to the structure.

Adsorption kinetics studies

The knowledge of adsorption kinetics is important for designing removal of pollutants. In the present study, the rates of adsorption humic acid were determined with chitosan.

Kinetic experiments were carried out in erlenmeyer flasks containing saturated aqueous solutions of humic acid (100 mL) with 60 mg of the chitosan at 25 °C. Solutions were stirred at 300 rpm during a selected lapse of time. Then, the solution was centrifuged and analyzed using the UV-vis spectrometry. The humic acid adsorption capacity onto adsorbents at time t, q_t (mg/g) was calculated by the following mass balance relationship:

$$q_t = (C_0 - C_e) \times \frac{v}{m} \quad .. (1)$$

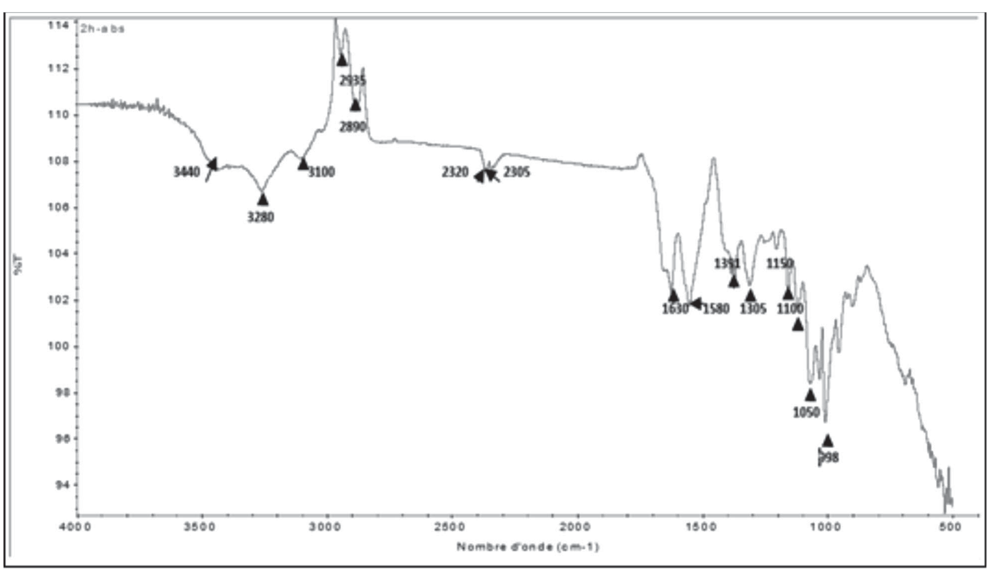

Fig. 1. Infrared spectra of chitosan

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad .. (2)$$

Where q_t is the adsorption capacity of the adsorbent, R (%) is the removal efficiency, C_o and C_e(mg/L) are the initial and equilibrium concentrations, respectively, of the adsorbate in the solution. V (L) the volume of the solution and m (g) is the mass of adsorbent used. This experiment was repeated for laps of time going up to 60 min.

Figure 1 presents the adsorption kinetics obtained at room temperature with the initial concentration of adsorbate being 10 mg/L solutions of humic acid. The mass of adsorbent was of 60 mg within all experiments.

Figure 2 shows the variation of the amount of humic acid adsorbed as function of time onto chitosan. It may be observed from the figure that the adsorption efficiency increases with the contact time because a large number of vacant surface sites are available for adsorption after some time equilibrium is reached.

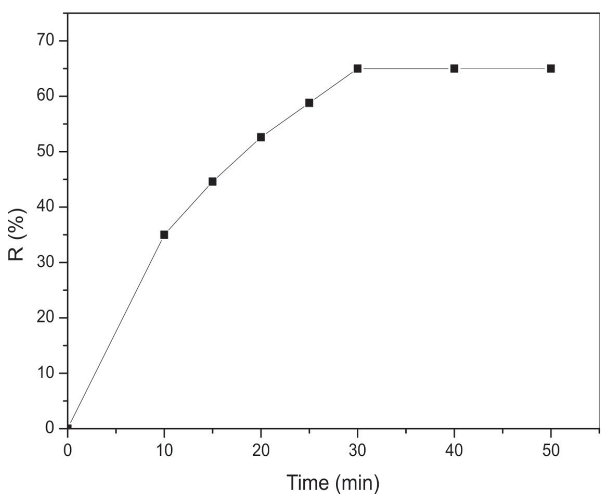

Fig. 2. Effect of contact time on the adsorption of humic acid

The best adsorption rate 65% is obtained for a contact time of 30 min. The adsorption kinetics obtained show that chitosan is a good adsorbent of humic acid.

In order to elucidate the adsorption process of humic acid on chitosan, two kinetic models including pseudo-first-order and pseudo-second-order models were selected to fit the kinetic data.

The first one was the pseudo first-order (Bougdah et al., 2017; Johnston et al.,2002), as expressed by the following equation:

$$Log(q_e - q_t) = Log(q_e) - (\frac{k_1}{2{,}303})t \qquad .. (3)$$

Where q_e and q_t are the amounts of a humic acid adsorbed at equilibrium and after time t respectively. The rate constant of adsorption was noted as k_1 (min^{-1}). If the plot of log ($q_e - q_t$) versus time is linear, then the value of k_1 may be directly obtained from the slope.

The pseudo-second –order model (Bousba, and Meniai, 2014; Bougdah et al., 2015) can be written as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad .. (4)$$

Where k_2 is the equilibrium rate constant of the pseudo-second order ($g.mg^{-1}min^{-1}$). Separating the variables in Eq. (4) and integrating for the boundary conditions q_t =0 to $q_t = q_t$ and t =0 to t = t yields an expression that may be rearranged to the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \qquad .. (5)$$

The slope and the intercept allow establishing q_e and k_2 respectively.

Different kinetic parameters of humic acid adsorption onto chitosan are shown in the table. 1.

For evaluating the kinetics of humic acid onto chitosan, the pseudo-first-order and pseudo-second-order were used to fit the experimental data.

q_e calculated determined from the pseudo-first-order model is not in a good agreement with the experimental value of q_e exp. Therefore, the adsorption of humic acid onto chitosan is not suitable for the pseudo-first-order reaction.

The pseudo-second-order rate constant k_1 and the value of q_e calculated were determined from the model and the results are presented in Table 1. The value of correlation coefficient is very high (R^2 = 0.99) and the calculated q_e value is closer to the experimental q_e value. In the view of these results, the pseudo-second-order kinetic model provided a

Table 1. Pseudo-first order and pseudo-second-order kinetics parameters

Adsorbent	$q_e$exp (mg/g)	Pseudo-first-order			Pseudo-second-order		
		K_1 (min^{-1})	q_e calc (mg/g)	R^2	K_2 ($g.mg^{-1}. min^{-1}$)	q_e calc (mg/g)	R^2
Chitosane	10.63	0.369	14.49	0.95	238.78	12.94	0.99

good correlation for the adsorption of humic acid onto chitosan.

Effect of adsorbent dose

Study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a humic acid from an economic point of view (Salleh et al., 2011).

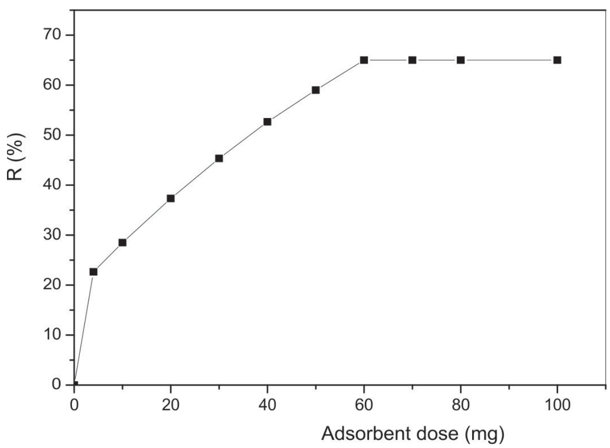

Fig. 3. Determination of the optimal dose of chitosan

The effect of adsorbent dose on the removal percentage (R %) of humic acid was studied and is shown in Figure. 3.

It was found in Figure 3 that the increase in the chitosan dose from 4 to 100 mg, the percentage of adsorbed humic acid increased from 22.66 % to 65%.

The increase in the percentage of humic acid removal with increasing adsorbent dosages is due to increase of sorption active sites at the adsorbent surface with increasing the dose.

Above 60 mg of adsorbent dose, there was no significant increase in the removal rate of humic acid. Considering R%, the adsorbent dose of 600 $mg.L^{-1}$ was found to be the optimum chitosan dose and was used for all other experiments.

Adsorption isotherms

The adsorption isotherm is a representative characteristic of the thermodynamic equilibrium between adsorbent and adsorbate. It is very useful for understanding the adsorption mechanism, it provides information on the affinity, on the binding energy between the adsorbate and the adsorbent and on the adsorption capacity, and it also allows advancing hypothesis about the adsorption mode.

Batch experiments were conducted by shaking 60 mg of chitosan with 100 mL aqueous solutions of HA at different concentrations (5-50 mg/L) was equilibrated during 30 min at 25 °C.

The Langmuir equation can be written as follows (Arias and Sen, 2009; Bhattacharya et al., 2006):

$$q_e = q_m \frac{K_L \times C_e}{1 + K_L.C_e} \quad .. (6)$$

Where q_m ($mg\ g^{-1}$) is the theoretical maximum monolayer adsorption capacity, and K_L ($L\ mg^{-1}$) is the Langmuir constant related to the energy of adsorption.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor R_L, which is expressed as:

$$R_L = \frac{1}{1 + K_L C_0} \quad .. (7)$$

Where C_o is the maximum initial HA concentration (mg/L). The value of R_L indicates the shape of Langmuir isotherm to be either unfavorable (R_L>1), linear (R_L=1), irreversible (R_L=0), or favorable (0<R_L<1). Also, the smaller R_L value indicates a highly favorable adsorption.

The Freundlich model is expressed as follows (Vimonses et al., 2009; Mohammad et al., 2010):

$$q_e = K_F C_e^{1/n} \quad .. (8)$$

Where K_F ($mg.g^{-1}$ $(l.mg^{-1})^{1/n}$) and 1/n are Freundlich constants related to the multilayer adsorption capacity and the surface heterogeneity, respectively. When (1/n >1) the adsorption is unfavorable, (1/n=1) the adsorption is homogeneous and (0<1/n<1) the adsorption is favorable.

The plot of q_e versus C_e for the adsorption of humic acid onto chitosan according to the non-linear form of Langmuir and Freundlich isotherm models were shown in Figure 4 and their parameters were calculated by non-linear regression analysis of the corresponding isotherms and are given in Table 2.

From Table 2 it can be seen, that the correlation

Table 2. Langmuir and Freundlich isotherm parameters for humic acid onto chitosan

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	K_L	q_m	R^2	K_F	n	R^2
chitosan	0.048 ±0.021	65.31 ± 16.35	0.97	3.83± 1.13	1.41±0.21	0.95

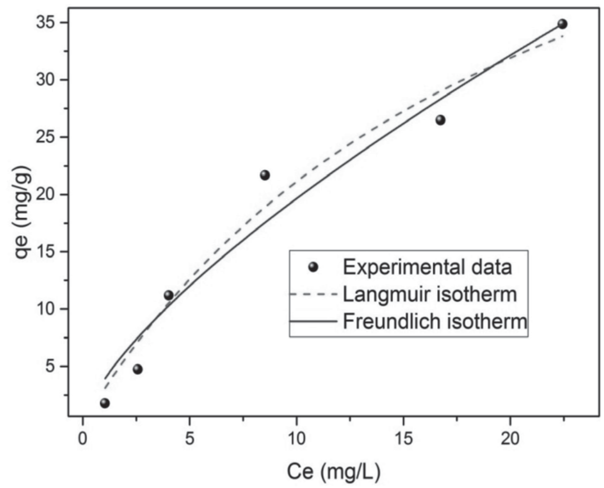

Fig. 4. Langmuir and Freundlich isotherm representation for the adsorption of HA onto chitosan

factor R^2 is high for both models, but with a better fit of the experimental data by means of Langmuir isotherm, indicating monolayer and a homogenous surface of chitosan adsorbent. The theoretical monolayer adsorption capacity q_m was found to be 65.35 mg/g of chitosan. Also, it can be seen that the values of R_L and 1/n were found to be within the range of 0–1, indicating that the adsorption of HA chitosan is favorable according to both Langmuir and Freundlich models. On the other hand, smallest values of R_L are obtained in the case of humic acid adsorption onto chitosan which indicates that the adsorption is more favorable in this case.

CONCLUSION

The work presented aims to contribute to the study of the removal of humic acid by chitosan. We have been able to determine the efficiency of removal according to several parameters such as the effect of contact time and effect of the initial concentration of humic acid. The best adsorption rate 65% is obtained for a contact time of 30 min.

Pseudo-first-order and second-order adsorption kinetics were studied, the second is most appropriate: q_e= 12.94 mg/g closer to experimental q_e= 10.629 mg/g with a high correlation coefficient of R^2=0.99 to describe the kinetics of removal of humic acid by chitosan. The Langmuir and Freundlich isotherms were studied and the straight line constants were determined under the operating conditions used in this work and the Langmuir model is more suitable with a correlation coefficient R^2= 0.97. It is concluded that the study is satisfactory for the removal of humic acid.

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