The Influence of the Chemical Structures of Chitosan and Acid Dye on the Adsorption Process

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Abstract: The objective of this paper is the study of the influence of the chemical structures of adsorbent and adsorbate on the adsorption process. By using of crab shell chitosan (CC) and deep-pink shrimp chitosan (CP) for removal of acid 183 and AR114 from aqueous solutions, it is shown that CP, which corresponds to the highest molecular weight, is the most efficient adsorbent material. In addition, the best extent of decolorization is obtained for AR 183 that is the smallest molecule. Langmuir model represents the best fit of the experimental data, indicating monolayer coverage of chitosan outer surface. Pseudo-second order kinetic model describes accurately the adsorption processes, suggesting chemical rate limiting steps. The positive values of the enthalpy changes indicated endothermic attachment of dyes to the biomaterials. CP/AR183 system corresponds to the most energetically favorable phenomenon. Besides, desorption of AR from chitosan was found to be very low in acidic aqueous medium for all couples.

Keywords: Crab shell Chitosan; Deep-pink shrimp shell Chitosan; AR 114; AR183; Adsorption isotherms; Kinetics.

Introduction

Due to its general interest in environment¹⁻⁴, the adsorption process for the removal of dyestuffs from textile effluents has been the subject of numerous studies. Their adsorption

onto activated carbon, which is the most efficient and expensive technique, has been widely used⁵⁻⁶. The presence of reactive amino groups in chitosan (Fig.1) gave it as a promising adsorbent⁷⁻¹⁹. The efficiency of this biopolymer could be affected by its Molecular weight and its degree of deacetylation⁴.

Several studies have been concerned with the adsorption of Acid dyes onto chitosan^{1, 4, 8, 16}. It is noteworthy that the studies of AR183/chitosan and AR 114/chitosan couples have never been reported onto this biomaterial.

The work presented here relates to the investigation of the effect of the chitosan molecular weight as well as the acid dye molecular structure on the adsorption process. We will report the comparative studies of the efficiency of chitosan, which derived from the shell chitin (CC) and the deep-pink shrimp chitin (CP), to remove AR183 and AR114 (Fig. 2) from aqueous solutions. Regarding storing of the modified chitosan, the study of the desorption phenomena of the adherent materials were also examined. The adsorption and desorption processes of AR/PAC couples were also studied.

Table 1. Langmuir isotherm constants of AR/ Adsorbent systems.

Dyes	$Q_{\max}$ (mg g ⁻¹)	K_L (L g ⁻¹)	a_L (L mg ⁻¹)	SSE
AR183/CC	347.374	14.045	0.040	0.072
AR183/CP				
AR183/PAC				
	446.75	103.092	0.23	0.006
	260.573	22.371	0.085	0.007
AR114/CC	327.974	17.421	0.053	0.001
AR114/CP				
AR114/PAC				
	439.8	76.335	0.173	0.001
	250.846	22.831	0.091	0.009

Experimental

Chitins were isolated from the crab shell (CC) and deep-pink shrimp shell (CP), respectively. The Corresponding chitosan were prepared by purification and deacetylation of chitins according to literature⁷. By means of FT-IR analysis of CP and CC^{20,21}, a degree of deacetylation (DD) of about 82 % was determined by Eq.1 for the two kind of chitosan.

$$DD = 100 - \left[\frac{A_{1654}}{A_{3450}} \right] \times 100 / 1.33 \quad (1)$$

Where A_{1654} and A_{3450} are the absorbance values of chitosan at 1654 cm⁻¹ and 3450 cm⁻¹, respectively. The average particles size of Chitosan is < 600µm. PAC (particle size < 250 µm) was purchased from Fluka. AR183 and AR114 (Aldrich chemical Co) were used

without purification. Their maximum wavelengths are 496 and 514 nm, respectively. The effects of the experiment parameters (pH, concentration, contact time and adsorbent dose) were studied. The pH of solution was adjusted with H_2SO_4 and NaOH solutions. Equilibrium adsorption isotherms were determined using bath solutions by UV-visible analysis. Adsorbent material (0.1g) and (50 ml) of dye ($50\text{--}500 \text{ mg L}^{-1}$) were mixed in conical flask (24 h), at 25, 35 and 45°C . For the kinetic studies, 0.2 g of adsorbents was added to 100 ml of dye solutions (500 mg L^{-1}). The amount of the adsorbed dye at equilibrium was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where C_o and C_e (mg L^{-1}), V (L) and m (g) are the initial and equilibrium dye concentrations in liquid phase, the volume of the treated solution and the weight of the adsorbent, respectively.

Figure 1. Chemical structure of chitosan.

Desorption of AR from adsorbents were studied at 25, 35 and 45°C . At $\text{pH}=3$, adsorbate/adsorbent samples were shaken with 100 ml of double distilled water in thermostatic shaker bath.

Results and discussion

Effect of experimental parameters on dyes adsorption

For CC/AR183, CC/AR114, CP/AR183, CP/AR114, PAC/AR183 and PAC/AR114, same S-form $q_e=f(\text{pH})$ curves have been obtained, evidencing three distinct shapes. A notably increasing of the amount of the adsorbed dye has been observed until $\text{pH}=3$, which corresponds to the optimum dye removals. The amino groups of chitosan are protonated and interact with sulfonyl groups of anionic dyes to form organic complex $(\text{NH}_3^+ \cdot \text{O}_3\text{SR})^{22,23}$, while more active acidic surface groups of PAC, such as carboxyl and lactone, facilitates electrostatic interactions^{7, 8, 24,25}.

Figure 2. Molecular structures of (a) AR183, (b) AR114.

Figure 3. The adsorption curves of (a) AR 183 and (b) AR114 dyes onto adsorbents.

As expected for the effect of adsorbent dose, the equilibrium uptakes of dye present optimum values for 0.1 g of adsorbents^{4,26}. Besides, the efficiency increases with temperature indicating endothermic incorporations of dyes into adsorbents, which could be considered as chemical adsorption²⁷.

Figure 4. Desorption profiles of (a) AR 183 and (b) AR114 onto adsorbents (C_t : the amount of dye adsorbed at any time).

Equilibrium modeling

The isotherms profiles of all adsorbent/ adsorbate couples show same shapes (Fig.3), with concavities and regular values. The equilibrium uptake increases with the initial dye concentration and the temperature, confirming the establishment of endothermic processes. Besides, the incorporation of both two kind of AR rises in the order $PAC < CC < CP$. This difference could be explained by the surface and micropore-macropore areas, structure and active sites dissimilarity. At the optimum conditions, the highest adsorption capacity is determined for CP/ AR183 couple (446.75 mg g^{-1}), while the lowest one is obtained for CC/ AR183 (301.59 mg g^{-1}). Since these biomaterials have similar DD%, this difference could be assigned to the effect of their molecular weights⁴, 550 g mol^{-1} for CP and 340 g mol^{-1} for CC. The degree of the adsorption of AR 183 and 114 are less important than this of Acid Orange 12 (973.3 mg g^{-1}), which is a smallest molecule and has only one sulfonated acid group⁴. In the literature, the difference in the degree of adsorption have be assigned to the molecular size or/and the number of sulphonate groups¹⁶. For AR 183 and AR114, the deeper penetration of the former dye into the internal pore structure of chitosan could be explained by its smallest molecule.

In order to describe the biosorption equilibrium, the experimental data were fitted to Langmuir^{28, 29}, Freundlich³⁰, Temkin²⁶ and generalized models³¹. To select of the most suitable one, the sums of the squares of errors between experimental and predicted values of q_e (Eq.3) were estimated¹⁶.

$$SSE = \sum_{i=1}^p (q_{e,calc} - q_{e,meas})_i^2 \quad (3)$$

The obtained results indicate that the most satisfactory equation is the Langmuir model (Eq. 4), which corresponds to the lowest SSE values indicating monolayer adsorption process and constants adsorption energy (Table.1). This fact may be due to homogeneous distribution of active sites on the material.

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (4)$$

$C_e \text{ (mmol L}^{-1}\text{)}$ and $q_e \text{ (mmol g}^{-1}\text{)}$ are the liquid and solid phase concentration of the adsorbate at equilibrium, respectively. $K_L \text{ (L g}^{-1}\text{)}$ and $a_L \text{ (L mg}^{-1}\text{)}$ are the Langmuir isotherm constants. $Q_{\max} / \text{mg g}^{-1} = K_L / a_L$ is a characteristic constant of the occupied area, which reflects the limited adsorption capacity.

Table 2. Pseudo second-order rate constant, calculated and experimental q_{eq} values obtained for initial AR concentration of 500 mg L⁻¹.

		AR 183			AR 114		
		25° C	35°C	45°C	25°C	35°C	45°C
CC	C_0 (mg L ⁻¹)	497	482.1	498.1	483.1	501.2	500.7
	$q_{e,exp}$ (mg g ⁻¹)	245.908	278.284	301.586	255.1	278.311	297.588
	K_{II}	9.333	10.8	18.166	10.8	12.675	20.333
	$q_{e,cal}$ (mg g ⁻¹)	243.902	277.777	303.03	256.41	277.777	285.741
	R^2	0.9995	0.9997	0.9998	0.9997	0.9997	0.9999
CP	C_0 (mg L ⁻¹)	497.5	499.5	502.2	489.4	500.1	501.2
	$q_{e,exp}$ (mg g ⁻¹)	367.388	412.611	446.755	388.544	412.336	439.818
	K_{II}	4.033	6.533	10.416	5.216	5.633	8.833
	$q_{e,cal}$ (mg g ⁻¹)	357.142	400	454.545	384.615	400	434.782
	R^2	0.9997	0.9997	0.9992	0.9993	0.9987	0.9997
PAC	C_0 (mg L ⁻¹)	482.3	483.4	485.5	481.1	483.4	483.7
	$q_{e,exp}$ (mg g ⁻¹)	226.576	239.386	250.83	210.877	228.122	243.09
	K_{II}	7.35	8.883	16.883	6.35	8.166	10
	$q_{e,cal}$ (mg g ⁻¹)	222.222	239.095	250	208.333	227.272	243.902
	R^2	0.9992	0.9982	0.9981	0.9999	0.994	0.9998

Kinetic modeling

Pseudo-first order and pseudo-second order models³²⁻³⁵ are usually used, for selecting the optimum operating conditions. For all couples, the kinetics of the adsorption fit well with the pseudo-second order model (Eq. 8), which predicts chemical adsorption involving valency force.

$$\frac{t}{q} = \frac{1}{q_e^2 K_{II}} + \frac{1}{q_e} t \quad (5)$$

q_e and q (mg g⁻¹) and K_{II} (g mg min⁻¹) are the amounts of the adsorbed dye (at equilibrium and after variable time contact) and the second order kinetic rate constant, respectively. K_{II} shows augmentation with the AR concentration and the temperature. These kinetics funding were in agreement with chemisorption rate controlling step³⁶⁻³⁸.

Table 3. Standard thermodynamic constants of AR/Adsorbent systems.

Systems	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (KJ mol ⁻¹ k ⁻¹)
AR183/ CC	-4.796	32.63	0.125
AR183/ CP	-6.72	75.555	0.275
AR183/ PAC	-4.846	45.273	0.169
AR114/CC	-5.42	26.45	0.108
AR114/CP	-6.64	64.84	0.239
AR114/PAC	-5.54	35.19	0.136

Thermodynamic modeling

The degree of spontaneity of the process could be indicated by Gibbs free energy, using the following equation³⁹ at 25°C:

$$\Delta G^\circ = -RT \ln k_L \quad (6)$$

where R, T and k_L are universal gas constant, temperature (K) and Langmuir equilibrium constant, respectively.

The enthalpy change (ΔH°) and the entropy change (ΔS°) can be determined using the van't Hoff equation:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

The thermodynamic characteristics could be estimated by determining the isotherms of the studied dye/adsorbent systems at different temperatures. In Table 3, the negative values of ΔG° at 25°C indicate that all the adsorption processes are spontaneous in nature, with high degrees of affinity of dye molecules for each adsorbent surface. The positive values of ΔH° suggest endothermic nature of adsorption. These results could be explained by strong bonding between dye and adsorbent. For ΔS° , the positive values reflect affinities of solid materials for AR and their structural changes. The highest negative values of ΔG° is obtained for CP/AR183 ($-6.72 \text{ kJ mol}^{-1}$). The difference in the thermodynamic characteristics between the adsorption process of CP/AR183 and CP/AR114 could be assigned to the dissimilarity of the chemical structures of dyes. In addition, CP shows the highest positive values of ΔH° and ΔS° , indicating that the most endothermic process corresponds to this adsorbent, which exhibits the highest increasing in randomness at solid /solution interface. Significant changes would occur in the internal structure of CP and dyes through the attachment of adsorbates⁴⁰.

Desorption studies

The nature of the adsorption process can also be elucidate by desorption studies⁴¹. In acidic medium, the kinetic curves show similar shapes with three periods of AR releases (Fig. 4). In the first one, slow deliveries take place; the amounts of dye desorbed are low. This behavior can be attributed to the fact that the main portion of the adsorbed dyes is chemically included in the adsorbents. In the second period (7-13 min), rapid releases are observed, which reach approximately 10% of the incorporated AR. After 13 min, desorption became independent to time, indicating a zero order kinetic processes. Lower percentages of acid dyes are eliminated from all adsorbents, confirming a strong interaction between SO_3^- group in AR (Fig.2) and NH_3^+ group in chitosan (Fig.1). Besides, the released quantities decrease from 25 to 45°C, suggesting the favorability of the adsorption processes at high temperature. These results confirm the chemisorption processes based on electrostatic attraction between the protonated amino cations and the sulfonate anions (scheme.1).

Scheme 1

Conclusion

Chemisorption processes based on electrostatic interaction between protonated amino groups of CP and CC and anionic sulfonate group of dye are suggested for the adsorption of AR 183 and AR114 onto chitosan. By this comparative study, we could assume that the molecular weight of chitosan, as well as the structure of textile dye, is important for the adsorption process. The efficiency of dye removal increases with the first factor, indicating the availability of more important site surface in adsorbent for the attachment of dye. Finally, highest uptake is obtained for the smallest dye molecule.

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