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Dyes Adsorption from Aqueous Solutions by Chitosan

Running title: DYES ADSORPTION BY CHITOSAN

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Abstract

In this study the ability of chitosan to remove acid, basic, reactive and direct dyestuffs by adsorption was studied. The effect of several factors influencing dye adsorption such as dye concentration, grain size, pH and temperature were investigated. Desorption of dyes at different pH was also examined. It was shown that the adsorption capacities of chitosan were comparatively high for acid and direct dyes and that the adsorption was controlled by the acidity of the solution. The kinetics of adsorption were found to be of pseudo second order. Batch isotherm studies showed that adsorption of dyes from aqueous solution by chitosan was described by the Langmuir equation.

Keywords: adsorption, chitosan, dyes, kinetics, textile wastewater

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INTRODUCTION

Dyes are widely used in the industry, such as textile, leather, plastics and paper one, to color the final products. Dye producers and users are interested in dye stability therefore dyestuffs always more difficult to degrade after use are being produced. Since many synthetic dye compounds are harmful to human beings, it is important to encourage industries to implement the color removal from wastewater before to discharge it. In particular, textile industries are water intensive because the specific water intake can vary between 95 to 200 m³/ton of treated fiber material, depending on the type of process used and water efficiency. In dyeing processes 10-15% of all dyestuffs, corresponding at about 100 kg COD/ton of treated fiber material, is being lost to wastewater and this material, or his degradation products, can be discharged in the environment with visual and environmental strong impact. Many dyes are toxic and some of them, such as those based on benzidine or arylamine are well known for their carcinogenity. A policy for rational use of water resources would allocate the pure water sources for direct human consumption and promote the development of effluent recycling processes to produce water for industrial application for which quality requirements are less stringent (e.g. softening is not necessary for all washing cycles). Among several chemical and physical methods, the adsorption process, either on activated carbon (1), fly ash (2) or chitin (3), is one of the most effective method to remove dyes from wastewater.

Chitosan appears to be economically attractive due to its origin. It is obtained, on industrial scale, by the alkaline deacetylation of chitin, the second most abundant polymer in nature after to cellulose (4). The main commercial sources of chitin are waste materials of the seafood industry,

mainly shell of crab and shrimp, that are treated with aqueous sodium hydroxide solutions (40-50%) at about 110°C.

One of the most interesting advantages of chitosan is its versatility. Indeed, this material can be readily modified preparing different polymer form such as beads (5), membranes (6), sponges (7). Other useful features of chitosan include non-toxicity, hydro-philicity, biocompatibility, biodegradability and anti-bacterial property (8) and currently it finds application in the industrial wastewater treatment and in the recovery of materials feed-grade from food-processing plants. Chitosan is effective material for sorption of metal ions and organic compounds such as phenols, polychlorinated biphenyls and proteins. This property is due to the amino and hydroxyl groups on polymer chains that can serve as coordination and electrostatic interaction sites, respectively (8). Critical reviews of published data about chitosan applications appeared in 2000 (8), 2003 (9) and in 2004 (10). Chitosan is versatile in sorbing metals, surfactants, detergents, etc. therefore can be considered as novel material to facilitate (increasing the size of the dissolved component) the treatment by membrane of wastewater (polymer enhanced filtration) and it also may provide new applications water treatment such as Boron (11) and Cyanotoxins (12) removal.

Chitosan has an extremely high affinity for many classes of dyes, except for basic dyes and it has a greater adsorption capacity compared to other poor materials. Therefore, chitosan appears to be economically attractive, more than activated carbon for dye removal from wastewater.

The equilibrium analysis is the most important study required for evaluating the affinity of a sorbent towards a reagent. Therefore, to assess chitosan suitability for application in the field of

textile wastewater treatment, in this study the ability of chitosan to remove acid, basic, reactive and direct dyestuffs by adsorption was studied.

MATERIALS AND METHODS

Chitosan (molecular weight: 400k, grain size: 66.9% <40 mesh, degree of deacetylation: 84-86% %) was supplied by Fluka while the commercial grade dyes were purchased from Dyestar and Chimica Tessile producers and used as received. The chitosan surface area (Quantachrome Nova 2200 surface area analyzer) obtained by the nitrogen adsorption method (BET), was 1.578 m²/g. The water content of this commercial chitosan determined by thermogravimetric analysis (TGA, Mettler Toledo TGA1) was 12,7% while the decomposition temperature was 292,12 °C. Starting from this chitosan, three grain size fractions (<0.420 mm, within 0.420÷0.707mm, >0.707mm) were obtained by sieve shaker in order to study the effect of grain size on the dye adsorption. The main characteristics of the dyes are reported in Table 1. The concentration of the dye solutions was analysed at a determinate wavelength (see Table 1) according to the calibration curve for each dye. Four different concentrations were prepared for each dye and the absorbance was measured by an UV-Vis spectrophotometer (VARIAN DMS 200). The TOC (Total Organic Carbon) was determined by an high temperature analyser (DC-190 Rosemont Analytical Inc.), anhydrous Dextrose (glucose) was used as TOC standard.

Dye aqueous solutions (100-300 mg/l) were prepared by dissolving the solutes into deionised water (Millipore Milli-Q) without pH adjustment. To obtain the equilibrium adsorption isotherms, a fixed amount (100 mg) of dry chitosan was placed in a 125 ml flask with the dye

solution (50 ml), stirred at 200 rpm and kept at 20 ± 0.5 °C. At fixed time intervals (within 0.5-11.5 hours), the solution was centrifuged and then an aqueous sample (0.5 ml) was withdrawn to determine the dye concentration.

The amount of adsorbed dye q_e (mg/g) was calculated as follows:

$$q_e = (C_0 - C_e)V/W$$

where C_0 and C_e were the initial and equilibrium (or at fixed time) concentrations (mg/l) of dye, respectively and V the volume of the solution (ml) and W the weight of chitosan (mg).

The experimental parameters included initial dye concentration, time, temperature, grain size and pH, adjusted by 0.1 M HCl and NaOH solutions.

Experiments with real wastewater coming from nylon fiber washing step were performed to verify the chitosan application to textile wastewater (chitosan=0.6g, $V=50$ ml, $\text{TOC}_i=889$ ppm, $\text{pH}=8.1$, $\text{Cl}=725$ ppm, $\text{SO}_4=192$ ppm, ionic surfactants=0.36 ppm, non ionic surfactants=7,09 ppm).

RESULTS AND DISCUSSION

Adsorption dynamics

It is well known that amine sites are the main reactive groups for ion sorption onto chitosan, though also hydroxyl groups (especially in the C-3 position) may contribute to the sorption (10).

The dye uptake by chitosan from solutions involves several steps needed for solute transfer from

the liquid phase to the specific sites inside the chitosan particles (e.g. external diffusion and intraparticle diffusion).

Since the chitosan chains have a large number and distribution of the $-NH_2$ and $-OH$ groups, the kinetic or mass transfer representation is likely to be global. In order to examine the mechanism of the dyes adsorption several kinetic models are used.

The pseudo-first-order equation described by Lagergren (13) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

A pseudo-second-order equation based on equilibrium adsorption capacity can be expressed in the following form (14):

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)t$$

Where q_e (mg/g) represents the amount of adsorbed dye at equilibrium, q_t (mg/g) is the amount of adsorbed dye at time t , k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are rate constants of pseudo first or pseudo second order kinetic models respectively.

Because the above two equations cannot give information about the adsorption mechanism, the simplified intraparticle diffusion model, according to Weber and Morris (15), was tested:

$$q_t = t^{1/2}$$

The fitting validity of these models can be checked by the slopes and intercepts of $\log(q_e - q_t)$ vs t , t/q_t vs t and q_t vs $t^{1/2}$ from each linear plot.

The results at different dye concentration according to the correlation coefficients (R^2) and the calculated and experimental adsorption capacity values are shown in Table 2.

The correlation coefficient R^2 for the pseudo second order adsorption model was high for the acid dye and its calculated equilibrium adsorption capacity $q_{e,cal}$ fits rather well with the experimental q_t values. These results suggest that a second order mechanism is predominant and that the overall rate of dye adsorption appears to be controlled by a chemisorption mechanism which fits the experimental data slightly better than the pseudo first order model.

The k_2 values tend to decrease with the increase of dye concentration. Although the adsorption seems to follow the kinetics of the pseudo second-order, it is expected that adsorbent and adsorbate interact with weak forces considering the nature of the adsorbent and of the dyes. This seems also confirmed by the fact that desorption is made possible by simple variation of pH. Although the activation energy is lower than that typical of chemisorption, in other papers the same observations were observed (5). The acid dye adsorption was very fast, the equilibrium times were short and with high adsorption capacity such behavior indicated a good affinity between the acid dye and chitosan.

Adsorption isotherms

To determine the maximum adsorption capacity of dyes by chitosan, a study of adsorption isotherm (Figure 1) was carried out, at pH=6÷7, by using the common models based on the Langmuir and Freundlich equations:

$$q_e = Q^\circ b C_{eq} / (1 + b C_{eq}) \quad \text{or, linearized} \quad 1/q_e = (1/Q^\circ k_L) (1/C_{eq}) + 1/Q^\circ \quad (\text{Langmuir})$$

$$q_e = k_F C_{eq}^{1/n} \quad \text{or, linearized} \quad \log q_e = \log k_F + 1/n \log C_{eq} \quad (\text{Freundlich})$$

where q_e (mg/g) is the amount at equilibrium of dye on the solid phase calculated using the mass balance, C_{eq} (mg/L) is the equilibrium concentration of dye in the aqueous phase. In addition, in Langmuir expression, Q° (mg/g) corresponds to available sites for complete coverage or to limiting adsorption capacity when the surface is fully covered with dye molecules while k_L is the Langmuir coefficient related to the affinity of the binding sites (16).

In Freundlich empirical equation, k_F and $1/n$ are empirical constants, determined by intercept and slope of the Freundlich equation in a logarithmic plot, representing the adsorption capacity and intensity, respectively.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L which is defined by McKay (17) as:

$$R_L = 1 / [1 + (k_L C_0)]$$

where C_0 is the highest initial dye concentration (mg/ml). R_L indicates the shape of the isotherm and the adsorption is unfavourable if $R_L > 1$, favourable if $0 < R_L < 1$, irreversible if $R_L = 0$ and linear if $R_L = 1$. In Table 3, the calculated separation factor values are reported for each dye. The low R_L values seem to confirm the high affinity between chitosan and all the tested dyes.

It was observed that the adsorption capacity (q_e), defined as the adsorbed dye amount at the isotherm plateau, depended on the nature of the dye. Under the same experimental conditions, the adsorption capacity decreased in the order Acid > Direct > Reactive > Basic dye, as reported in Table 3. This adsorption capacity is significantly greater than those obtained previously using adsorbent such as carbon (18), clay-carbon mixture (14), fly ash (2) and chitin (3).

The reactive dye q_e value, lower than acid and direct dye ones, could be explained by probable intramolecular interactions establishing between the SO_3^- and NH_2 groups, both positioned in the same benzenic ring of the dye (Figure in table 1). For this reason, the dye SO_3^- groups seem to have low effectiveness in electrostatic interaction with NH_3^+ groups of chitosan (19).

Therefore, the reactive dyes tend to react with the primary hydroxyl groups of chitosan as demonstrated by Gardner & Purves (20) for cellulose.

Effect of initial dye concentration

Figure 2 shows the effect of initial dye concentration on the adsorption kinetics of chitosan at 20°C. An increase in initial dye concentration led to an increase in the adsorption capacity of dyes as reported also by other authors (4,16, 21), this is due to the increase of driving force of the concentration gradient which promotes the intraparticle diffusion (21). Indeed, a rise in the

concentration gradient caused a rapid dye diffusion, a high dye adsorption and a longer time to reach the equilibrium. In particular, for 5 h with initial dye concentration ≥ 300 mg/l, the adsorption capacity were within 2÷4 times greater than at low concentration (about 100 mg/l). This indicates that the initial dye concentration played an important role in the adsorption capacity on chitosan as reported by Chiou et al (16).

Grain size effect

In Figure 3, the effect of grain size on the acid dye is reported. It can be observed that as the particle size decrease, the adsorption of dye increase.. This could be due to the high surface area of these particles that promotes the dye removal from solution in the initial stages of adsorption process. Such phenomenon, reported previously for adsorption of some dyes on chitin, chitosan (22) and Neem sawdust (3, 23), is further improved by the ability of the dye molecule to also penetrate into the internal structure of the chitosan.

Effect of pH

Figure 4 shows the effect of pH on adsorption of dyes onto chitosan flakes. It can be noted that dye uptake was in acidic and neutral solution much higher than in alkaline one, probably due to the prevalent negative charge of many dyes. Indeed, at low pH the amine groups of chitosan will be protonated ($R-NH_3^+$) to form a sort of polycation and then anions or Lewis bases adsorption will be promoted (10). On the contrary, since the free electron doublet of nitrogen is responsible for the cation adsorption, high pH will favor the adsorption of basic dyes. Since the value of pK_a of chitosan has been found to be 7.7 (24), a high number of protonated groups can be found even

at pH=6÷7. Therefore, the dye adsorption is due mainly to electrostatic interactions between two counter ions (25, 26). The electrostatic interactions can also explain the huge behavior difference between the basic dye and the other ones. Indeed, the Astrazon red dye, having positive $-R_4N^+$ groups, showed low adsorption onto chitosan.

Effect of temperature

The adsorption experiments were carried out at various temperature in the range of 283-323°K. In Table 4 the thermodynamic parameters related to the dye adsorption by chitosan, obtained from the experiments performed at the different temperatures, at pH 6 and with an initial dye concentration of 100 mg/l, are reported. For all dyes, the adsorption activation energies (obtained by the equation: $k = k_0 \exp(-E_a/RT)$ where k is the rate constant of sorption, k_0 is the temperature independent factor, E_a is the activation energy of adsorption, R is the gas constant and T is the solution temperature) seem to be small (0.289-36.94 J/mol) and the adsorption rate not very sensitive to temperature in the studied range. An increase of temperature leads to a slight increase in initial dye adsorption (data not shown). This behavior could be due to swelling effects of chitosan induced by the temperature increase thus enabling the dye ions to penetrate further within the internal chitosan structure indicating that dyes molecules interact with a larger portion of the polymer chain.

The changes in standard Gibbs free energy, standard enthalpy and standard entropy of the adsorption, obtained from the data at different temperature were determined according the following equation: $\Delta G^\circ = -RT \ln K$ where K is the adsorption equilibrium constant (5). ΔH and ΔS were calculated according to the van't Hoff plot. The values demonstrated that the dye-chitosan

interaction is thermodynamically favored. However the data indicated that the chitosan interactions with the basic dye (cationic) are less favorable than those of the other dyes. The values suggest that adsorption of dye onto chitosan is a spontaneous process and that the enthalpic contribution is much larger than that the entropic one.

Dye desorption

The regeneration of the sorbent is crucially important for keeping the process cost down. Therefore it is desirable to adsorb pollutants and to regenerate the material for many cycles of application. Since in basic solution the positively charged chitosan amino groups are deprotonated, the dye-chitosan electrostatic interactions become weaker and therefore the dye molecules leave the adsorption sites of chitosan allowing the chitosan reuse for several cycles. Therefore, the desorption can be easily obtained by pH variation as reported in the literature (5).

Table 5 shows the removal percentage (obtained by mass balance) after adsorption onto chitosan of the Direct and Acid dyes at pH=10 (0.1M NaOH) and at room temperature. The removal percentage of the charged material is about 55% for Direct dye and less than 10% for Acid dye. Higher pH and temperature could cause dye hydrolysis (5).

In the case of the Direct dye, different cycles of desorption were performed obtaining similar desorbed amount of dye. Chitosan seems to be useful for at least three cycles. This is a confirmation of the reversible deprotonation of chitosan amino groups.

Treatment of real wastewater

It is well known that certain additives such as salt and surfactants present in typical wastewater can either accelerate or retard dye adsorption processes. The effect of the typical wastewater contaminants on the discoloration efficiency was determined by using a real wastewater coming from the final washing step of nylon fiber having a TOC=889 ppm and pH=8.1 and containing mainly a reactive dye such as Remazol type series.

In Table 6 the dye and TOC removal percentage from real wastewater are reported. Utilizing wastewater, it was not possible to determine which was the contribution of the dye to the value of TOC but it was evident how the presence of other contaminants (stabilizer, detergents, etc.) did not reduce the dye removal. The TOC reduction was less than 40%, that corresponded to 255 mgTOC/g of chitosan of which 112 could be attributed to other pollutants.

Also the adsorption kinetics did not seem to be affected by the presence of other pollutants, this may favor the use of chitosan in the filtration process by reducing the cut-off of the membranes with significant cost savings. Moreover, the normal wastewater temperature variations (15-30°C) did not significantly affect the overall decoloration process.

CONCLUSIONS

The present study indicate suitability of applying chitosan in programs aimed at removing dyes from textile wastewater. The extreme variability of textile wastewater should be taken into account in the design of any decolorization system using chitosan, because the adsorption

capacity of chitosan was found to be depended on the nature and chemistry of the dyes as well as experimental conditions such as pH. The maximum dye adsorption followed the order Acid>Direct>Reactive>Basic dye and this is due to the highest reactivity of the acid dye with the protonated amine group of chitosan. For all dye types, the adsorption was optimum at $\text{pH} < 8$. The adsorption of all dyes by chitosan was initially rapid (up to 2 hours), particularly for the Acid dye, and then remained constant. For dye adsorption on chitosan, the Langmuir equation gave the best fit over the entire concentration range.

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TABLE 1 Main characteristics of selected “commercial grade” dyestuffs

Dye type	Commercial name and formula	Mw	Functional groups	λ_{\max} (nm)
Basic	Astrazon GTLN red 	416	$R_4N^+X^-$, NO_2 , $N=N$	485
Acid	Telon B red 	521	$-SO_3^-Na^+$, NH_2 , OH	493
Reactive	Remazol RR gran yellow 	751	$-SO_3^-Na^+$, NH_2 , 1,3,5-triazin	495
Direct	Scarlet red 23 	816	$-SO_3^-Na^+$, CO , OH , $N=N$	418

TABLE 2. Values of adsorption rate constants varying dye concentration, T=20°C, pH=6

		1 st order kinetic model			2 nd order kinetic model				Intrap. diffusion model	
Ci	q _t	k ₁	q _{e,cal}	R ²	k ₂	h	q _{e,cal}	R ²	k _i	R ²
(mg/l)	(mg/g)	(min ⁻¹)	(mg/g)		(g/mg min)	(mg/g min)	(mg/g)		(g/mg min)	
Acid dye										
341.3	170.6	2.9x10 ⁻²	301.8	0.858	4.1x10 ⁻⁴	12.69	175.2	0.999	1.68	0.683
218.3	109.1	3.4x10 ⁻²	76.2	0.522	2.3x10 ⁻³	28.25	109.9	1.000	0.43	0.538
117.0	58.5	5.7x10 ⁻³	109.1	0.481	2.9x10 ⁻³	0.46	84.3	1.000	0.061	0.501
Basic dye										
300.1	41.3	1.8x10 ⁻²	152.7	0.989	3.4x10 ⁻⁵	0.17	70.9	0.663	1.901	0.670
200.3	34.1	1.1x10 ⁻²	6.6	0.868	7.1x10 ⁻⁴	0.94	36.5	0.985	0.730	0.391
50.0	7.3	1.5x10 ⁻²	4.8	0.765	7.4x10 ⁻⁴	0.06	9.3	0.872	0.246	0.531
Direct dye										
328.9	157.3	2.3x10 ⁻²	563.1	0.880	4.5x10 ⁻⁶	0.39	294.1	0.585	6.64	0.936
187.2	86.5	1.4x10 ⁻²	366.8	0.939	3.5x10 ⁻⁵	0.47	116.3	0.971	3.32	0.940
105.9	52.3	1.8x10 ⁻²	293.1	0.943	1.6x10 ⁻⁴	0.58	60.2	0.995	1.53	0.887

Reactive dye

300.0	88.8	1.1×10^{-2}	36.7	0.241	4.5×10^{-4}	3.86	92.6	0.994	1.53	0.370
200.0	90.6	1.8×10^{-2}	165.4	0.965	2.0×10^{-4}	1.91	98.1	0.996	2.19	0.694
100.0	50.4	1.7×10^{-2}	37.2	0.938	8.5×10^{-4}	2.31	52.4	0.999	0.74	0.664

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TABLE 3 Langmuir and Freundlich isotherm parameters at 20°C

Dye	Langmuir				Freundlich		
	q_e (mg/g)	k_L	R^2	R_L	K_F (mg/g)	1/n	R^2
Basic	58.82	0.9541	0.9958	3.5×10^{-3}	3.45	0.5073	0.9358
Acid	144.9	0.0104	0.9888	0.219	61.48	0.2536	0.9613
Reactive	98.04	0.1346	0.9945	2.4×10^{-2}	42.14	0.3073	0.9925
Direct	142.8	0.0176	0.9106	0.159	46.23	0.3486	0.7056

TABLE 4 Activation energies according to the Arrhenius plots, Gibbs energy ($\Delta G^\circ = -RT \ln K$) and van't Hoff plots

dye	-Ea (J/mol)	ln <i>K</i>	- ΔG° (kJ/mol)	- ΔH° (kJ/mol)	ΔS° (J/Kmol)	dye	-Ea (J/mol)	ln <i>K</i>	- ΔG° (kJ/mol)	- ΔH° (kJ/mol)	ΔS° (J/Kmol)
Basic	13,08	2,84	0,114	4,273	4,406	Reactive	0,289	0,89	4,885	0,455	15,12
Acid	12,92	7,88	10,364	1,226	0,141	Direct	36,44	16,11	10,058	2,635	0,440

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TABLE 5 Desorption experiments (%) of the Direct (D) and Acid (A) dyes performed at pH=10. Chitosan= 100 mg, Dye=100 mg/l

Time (min)	I cycle (D)	II cycle (D)	III cycle (D)	I cycle (A)
30	45.7	36.7	26.8	8.7
60	52.3	46.3	39.8	8.8
180	54.8	48.7	45.7	8.9
300	54.8	50.4	48.5	9.2
720	54.8	51.7	49.0	9.4

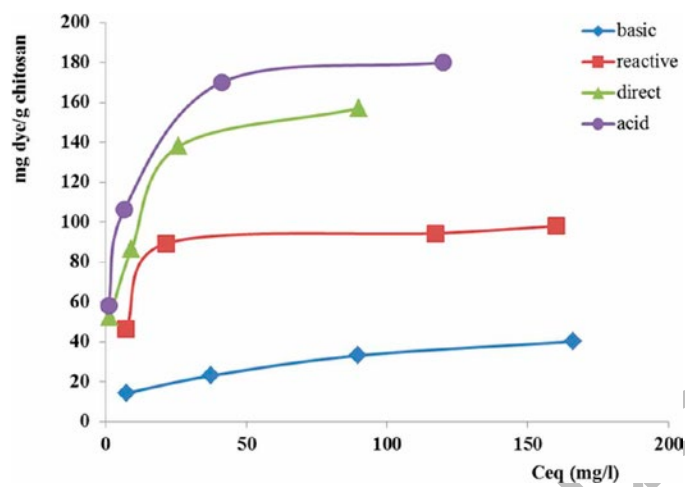
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TABLE 6 Dye and TOC removal % from wastewater. TOC i=889 ppm, V=50 ml, Chitosan=0.6 g

Time (min)	Dye removal %	TOC removal %
30	86.5	3.2
90	93.3	5.0
300	96.3	38.3

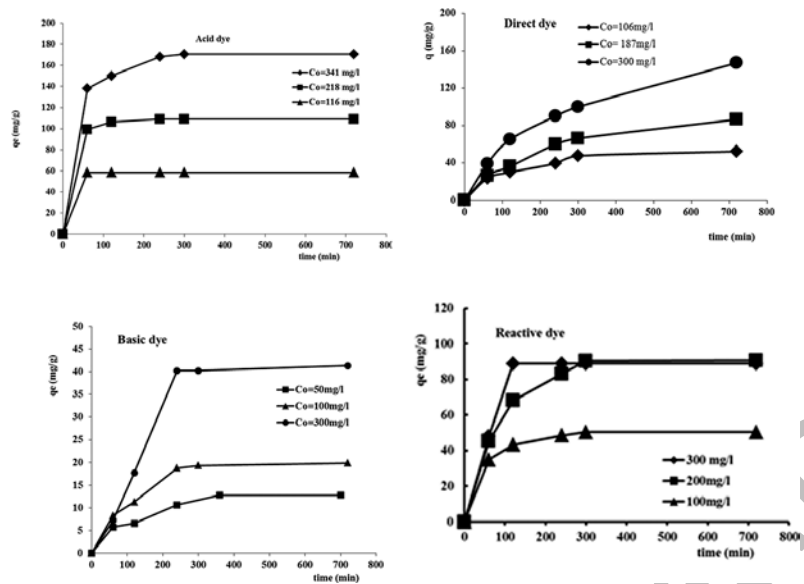
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FIG. 1. Adsorption isotherms. V=50 ml, chitosan=100 mg



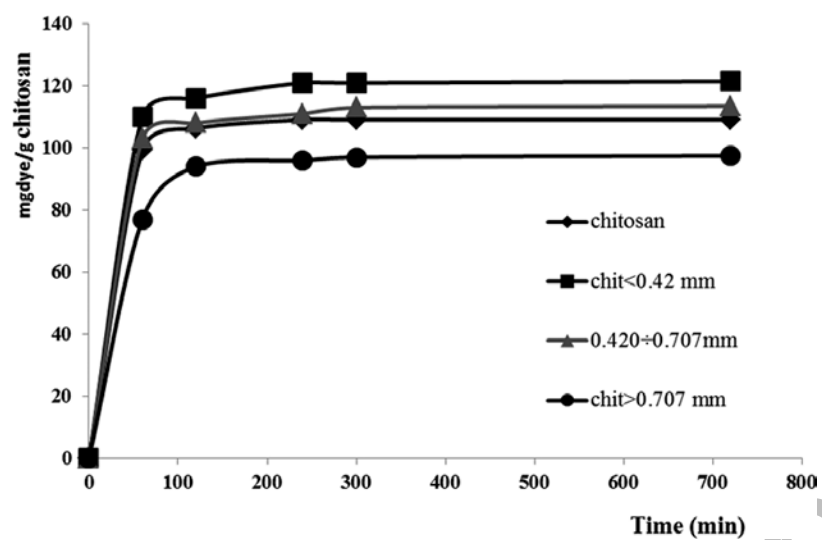
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FIG. 2. The effect of initial dye concentration on the adsorption kinetics. $V=50$ ml, chitosan=100 mg



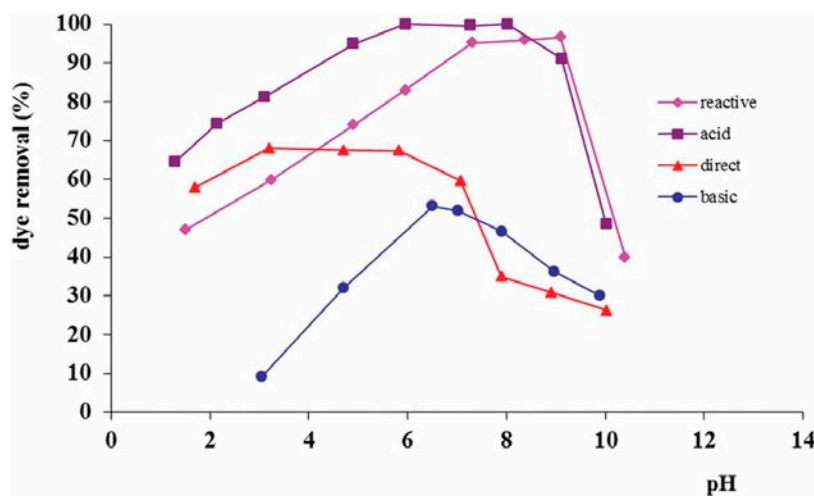
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FIG. 3. Grain size effect on Acid dye adsorption. $T=20^{\circ}\text{C}$, $C_i=220\text{ mg/l}$



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FIG. 4. pH effect on dye adsorption. T=20°C, Ci=100 mg/l, Chitosan=100 mg



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