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Adsorption of acid yellow dye on flakes of chitosan prepared from fishery wastes

Javed Iqbal ^a, Feroza Hamid Wattoo ^{b,*}, Muhammad Hamid Sarwar Wattoo ^c,
Rukhsana Malik ^a, Syed Ahmad Tirmizi ^c, Muhammad Imran ^a,
Allah Bux Ghangro ^d

^a Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan

^b Department of Biochemistry, Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi 46300, Pakistan

^c Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

^d Institute of Biochemistry, University of Sindh, Jamshoro 76080, Pakistan

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Abstract Chitosan flakes, extracted from prawns and labeo rohita scales, with high adsorption capacity were prepared after chemical treatment and were used to remove acid yellow dye from water. The results showed that adsorption capacity is dependent on pH, initial concentration of dye, BET, Langmuir surface area and pore volume of the adsorbent. In acidic conditions, the polymer amino groups were protonated (positively charged polymer chain), which showed attraction with negative ions of anionic dye. Chitosan from prawns scales showed higher dye adsorption under the same experimental conditions. Adsorption isotherms were developed and equilibrium data fitted well to Langmuir and Freundlich isotherm models.

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1. Introduction

Acid yellow dye ($C_{20}H_{10}Na_2O_5$, molecular weight: 376.27594, melting point: 320 °C) is mainly used in detergent, soap, silk, woolen and cosmetic industries. It is usually marketed with the synonyms like fluorescein, disodium salt, uranin, acid yellow 73, fluorescein sodium and D & C Yellow #8. Fig. 1 shows the structure of this anionic dye. The dye synergizes dermatitis to sensitive skin and causes irritation to eyes. When heated to decomposition, it emits toxic fumes of CO, CO₂ and Na₂O. Acid yellow 73 is mutagenic for bacteria, yeast and mammalian somatic cells, toxic to female reproductive system, crosses the human placenta and excreted in human breast milk when applied to eyes as a topical ophthalmic solution. It may cause

* Corresponding author.

E-mail address: dfhwattoo@gmail.com (F.H. Wattoo).



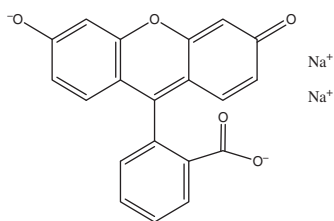


Figure 1 Structure of acid yellow 73 (fluorescein sodium).

adverse reproductive effects, i.e., maternal, affects genetic material and causes cancer, i.e., tumorigenic. It may also affect the behaviour, respiration (dyspnea), cardiovascular system, blood and sense organs of humans (NOAA, 2007).

Removal of dyes from waste water of concerned industries in an economic fashion remains a major problem of the present scenario (Sanghi and Bhattacharya, 2006; Crini, 2006). For industrial liquid effluents, colour is the first indication of water pollution. The industrial dumping of effluents containing dyes not only mars the natural beauty of the rivers but also is extremely toxic to aquatic life interfering in the transmission of sunlight and thus reducing the action of photosynthesis (Crini and Badot, 2008).

Adsorption appears to be good for the treatment of effluents (Sananmuang and Cha-un, 2007). The first thing for an efficient adsorption process is the search for a low cost adsorbent with high adsorption capacity and second it should be biodegradable (Iqbal et al., 2005). The activated carbon has been till now the most used adsorbent but is expensive to use on a large scale (Akmil-Basar et al., 2005; Figueiredo et al., 2000; Reddy et al., 2008; Voudrias et al., 2002) and the idea of using natural adsorbents from waste material rises in this perspective.

Chitin is a biopolymer and is a major structural component of exoskeleton of lobster, shrimp, prawn, cuttle fish, etc. (Longhinotti et al., 1998). Chitosan naturally exists only in some species of fungi and can be produced by deacetylation of chitin with alkali solutions at elevated temperature (Kasaai, 2008; Kumar, 2000; Rinaudo, 2006). Chitin and chitosan (Fig. 2) are potentially useful adsorbent materials to remove dyes from industrial waste water but chitosan is more active adsorbent than chitin (Uzun, 2006). So chitin is converted into chitosan after the chemical treatment (Iqbal et al., 2005). Other useful features of chitosan include its abundance, low cost, non-toxicity, biocompatibility, biodegradability and anti-bacterial properties (Cestari et al., 2004; Chion et al., 2003, 2004; Kim and Cho, 2005; Yoshida et al., 1993). In the present study, the chitosan flakes were used as dyes' adsorbent.

Chitosan is the deacetylated form of chitin and is a linear polymer of acetylamino D-glucose. Its natural abundance is next to that of cellulose. In Pakistan, various types of fish scales are readily available. These fish scales are wasted with-

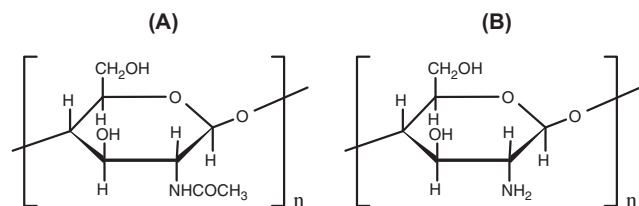


Figure 2 Structure of (A) chitin and (B) chitosan.

out proper treatment and cause environmental pollution such as bad smell. The aim of the present study is to investigate the adsorption behaviour of acid yellow 73 on low cost chitosan adsorbent under different experimental conditions. The chitin obtained from fish scale is converted into chitosan after chemical treatment (Iqbal et al., 2005) and used as low cost, environment-friendly adsorbent. The effect of solution pH, initial dye concentration, adsorbent particle size and competitive adsorption of chitosan extracted from prawn and labeo rohita fish scales would be discussed here.

2. Experimental methods

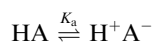
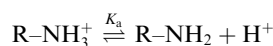
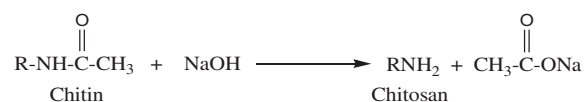
2.1. Materials

Acid yellow 73 dye studied was of the practical grade and was used as received. The dye solution was prepared in distilled water in different concentrations, ranging from 0.3 to 0.9 mg/L, by vigorous stirring at 50 °C for 30 min to reach complete dissolution. All other chemicals used were of AR grade purity. Deaerated high purity demineralized double distilled water was used for solution preparations.

2.2. Extraction of chitosan

Exoskeleton (scales) of prawn (*Nephrops norvegicus*) and labeo rohita (local name Raho fish) were collected from the local fish market and were washed with deionised water before use. These fish scales were then treated with NaOH (1 mol L⁻¹) at room temperature for 24 h and washed with distilled water until the pH became neutral, and demineralization was then carried out with HCl (2 mol L⁻¹) at room temperature. The material was again washed with distilled water until the pH became neutral. The skin pigments were oxidized on treatment with NaClO (1%, w/v) for 15 min and the material was washed until its pH became neutral. The material was then dried at 80 °C in an oven for eight hours and pulverised to get chitosan flakes. Degree of deacetylation of the chitin was determined by the method as reported by (Iqbal et al., 2005) using the following relationship and was found to be 45%:

$$\% \text{ Deacetylation} = \left(1 - \frac{A_{1558}}{A_{2852}} \right) \times 100$$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The adsorbent's specific surface area (BET multipoint and single point surface area – m²/g), Langmuir surface area (m²/g) and total pore volume (m³/g) were determined by using

Chemisorb-2750 in a physisorption mod. BET equation was used to calculate the specific surface area. All samples were degassed at 35 °C for 3 h.

2.3. Effect of pH

Samples of 100 mg of chitosan flakes were placed in a conical flask with 25 ml of dye solution. The pH was adjusted to the desired value by the addition of acid or alkaline solution and medium ionic strength was achieved by the addition of NaCl (0.10 mol L⁻¹). Flask was then stoppered and placed in a water bath controlled by a thermostat at 25.0 ± 0.5 °C for 4 h. After this contact period, supernatants were separated from the solid phase by centrifugation and the concentration of dye in solution was determined by spectrophotometer. The quantity of dye adsorbed was determined by the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e is amount of dye adsorbed at equilibrium (mg/g), C_0 is the initial dye concentration in liquid phase (mg/L), C_e is liquid-phase dye concentration at equilibrium (mg/L), V is the volume of dye solution (L) and m is the mass of adsorbent (chitosan flakes) used in g.

2.4. Adsorption isotherms

The adsorption isotherms were obtained by employing 100 mg of chitin and 25 mL of dye solution with different concentrations. These solutions were buffered at an optimum pH (pH 4) for adsorption and stirred in a mechanical shaker until they reached adsorption equilibrium, i.e., 80 min. The adsorbent biopolymer (chitosan) was separated by centrifugation. The quantity of dye adsorbed was determined by employing the UV/Visible spectrophotometer Hitachi U-2000, at λ_{\max} of 488 nm.

3. Results and discussion

3.1. Effect of solution pH on adsorption

pK_a of $-\text{NH}_3^+$ group of chitosan is 6.1. The protonation of chitosan in acidic solution is interesting for the electrostatic attraction of anionic dyes. Fig. 3 shows a tendency towards greater adsorption for anionic dye (acid yellow 73) in the pH

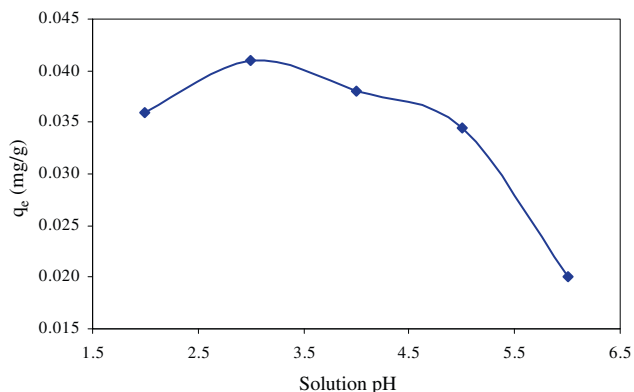


Figure 3 Effect of solution pH of acid yellow 73 on adsorption.

range of 3–4. At pH below 3, the anions in the solution compete with the anionic dye and hence decreasing the adsorption. This has also been observed in alkaline pH (results not shown) since the amino groups of the polymer are deprotonated. In general, the uptakes are much higher in acidic conditions:

$$[\text{RNH}_2] = \frac{K_a}{K_a + [\text{H}^+]} \times [\text{RNH}_2]_{\text{Total}}$$

In surface adsorption mechanism, a molecule is attracted to a charged surface without the exchange of ions or electrons. Sakkayawong et al. (2005) reported that the mechanism of adsorption by chitosan under acidic conditions is by chemisorption, while under caustic conditions it is both by physical interaction (rapid surface adsorption) and chemical adsorption. Uzun and Guzel (2005) reported that both physical adsorption and chemisorption occurred simultaneously between anionic dye and chitosan. They concluded that physical surface interaction occurring with multilayer adsorption played an important role in the adsorption of anionic dye.

Tables 1 and 2 show that chitosan flakes extracted from prawn fish scales show higher surface area and total pore volume. Surface area and total pore volume increase linearly with pH for chitosan flakes extracted from labeo rohita fish scales and are maximum at pH 3 for chitosan flakes extracted from prawn fish scales. This evidence that low pH not only increases surface area of the adsorbent but also increases dye adsorption on chitosan flakes. When the BET analyses are performed, the access of nitrogen molecules becomes difficult due to the small size of the pores at very low pH. After increasing the pH, there is a small increase in the crystallinity of chitosan flakes and also an increase in the free RNH_2 sites to the small pores of the chitosan flakes that show higher surface area and pore volume. This is due to the fact that higher pH (lower acidity) not only maintains stronger mechanical properties of chitosan flakes but also gives higher surface areas and hence physical adsorption increases as the surface area of the adsorbent is increased.

Chitosan flakes are insoluble in aqueous solutions of various acids, but chitosan molecules have no amphiphilicity and cannot form micelles in water. The effect of different pH values on the adsorption of dye by chitosan is given in Fig. 3. The observed data indicate that the adsorption capacity of dyes on chitosan is dependent on pH. This biopolymer adsorbent (chitosan) has functional groups OH, NHCOCH_3 and NH_2 . According to Longhinotti et al. (1998), the hydroxyl groups of pyranoside ring are strongly hydrated and are virtually incapable of forming hydrogen bonds with dyes; nevertheless they can adsorb by the formation of a hydrogen bond, by van der Waals interactions and also by ion exchange with other groups. Also the pK_a of NH_3^+ groups of chitosan strongly depends on the degree of deacetylation of the polymer and charge neutralization in the solution.

In the present study, the BET specific surface area of chitosan flakes is very low, so the mechanism of anionic dye (acid yellow 73) is mainly controlled by surface diffusion. At lower temperatures, this surface diffusion is even more dominant. Depending on the pH in water, the polymers containing the amino groups are neutral ($-\text{NH}_2$) or cationic ($-\text{NH}_3^+$). These groups are protonated at higher pH and negative counter-ions are adsorbed to maintain neutrality in an aqueous environment. These ions are freely moveable and are exchanged by the dye-ions at appropriate pH.

Table 1 Physisorption characteristics of chitosan flakes extracted from labeo rohita scales at 25 mg/L dye concentrations, different pH levels and 30 °C.

pH	BET _M SA (m ² /g)	BET _S SA (m ² /g)	Langmuir SA (m ² /g)	Total pore volume (m ² /g)
2	4.09 ± 0.29	3.29	9.27 ± 2.25	0.0017
3	8.93 ± 0.04	7.29	19.34 ± 2.29	0.0037
4	12.97 ± 2.63	9.18	40.38 ± 25.87	0.0046

BET_M SA, BET multipoint surface area; BET_S SA, BET single point surface area.

Table 2 Physisorption characteristics of chitosan flakes extracted from prawn scales at 25 mg/L dye concentrations, different pH levels and 30 °C.

pH	BET _M SA (m ² /g)	BET _S SA (m ² /g)	Langmuir SA (m ² /g)	Total pore volume (m ² /g)
2	12.81 ± 1.17	10.14	29.87 ± 8.48	0.0051
3	15.51 ± 0.27	12.87	32.82 ± 4.51	0.0065
4	14.35 ± 0.359	11.78	30.98 ± 4.74	0.0059

BET_M SA, BET multipoint surface area; BET_S SA, BET single point surface area.

In this ion-exchange process, electrostatic interactions are also involved which are responsible for dye adsorption. Juang et al. (2002) carried out different studies to challenge the theory that amino groups were primarily responsible for dye binding in chitosan and reported that electrostatic properties of chitosan are pH responsive and the pH play an important role in chitosan-based adsorbent processes.

3.2. Effect of dye concentration on adsorption

Fig. 4 shows equilibrium adsorption isotherm of acid yellow 73 on chitosan flakes at 30 °C and keeping the pH constant (pH 3). The equilibrium adsorption density q_e is increased with the increase in dye concentration. At low equilibrium dye concentrations C_e , the equilibrium adsorption densities q_e of the chitosan flakes reach almost the same q_e as those at high equilibrium dye concentrations. It indicates that chitosan flakes have high adsorption density even at low equilibrium dye concentrations.

Tables 3 and 4 indicate that increasing the dye concentration increases the lattice of chitosan flakes which results in not only increased dye adsorption but also increases surface area and total pore volume. This is a positive advantage of

chitosan flakes to be used as good candidate for anionic dyes in acidic media. It is suggested that the increase in adsorption depends on the properties of the adsorbent surface and the dye structure. It is also observed that the time required to reach equilibrium decreases at higher doses of adsorbent and the results will be reported elsewhere. Crini (2006) observed that the increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface and availability of more adsorption sites. However, if the adsorption capacity is expressed in mg adsorbed per gram of material, the capacity decreased with the increasing amount of sorbent. This may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length.

3.3. Isotherms data

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The adsorption curves were applied to both the Langmuir and Freundlich equations. The Freundlich isotherm model, which assumes that the adsorption occurs on heterogeneous surfaces, is often expressed as;

$$q_e = K_F [C_e]^{1/n} \quad (2)$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (3)$$

where K_F is Freundlich isotherm constant (L/g) and n_F is Freundlich isotherm exponent. Values of K_F and n_F were calculated from the intercept and slope of plots $\ln q_e$ vs $\ln C_e$ and a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The value of n_F should be greater than one confirming good adsorption of dye onto chitosan.

Langmuir isotherm, which assume that a monolayer of dye is formed on a relatively regular polymer surface, using the

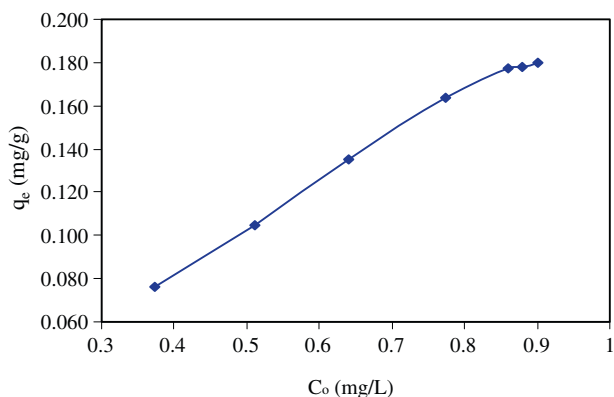
**Figure 4** Equilibrium adsorption isotherm of acid yellow 73 on chitosan flakes.

Table 3 Physisorption characteristics of chitosan flakes extracted from *labeo rohita* scales at pH 3 and 30 °C: after adsorption of different dye concentrations.

q_e (mg/g)	BET _M SA (m ² /g)	BET _S SA (m ² /g)	Langmuir SA (m ² /g)	Total pore volume (m ² /g)
0.076	7.89 ± 0.07	6.35	17.52 ± 1.69	0.0032
0.105	10.11 ± 0.06	7.91	23.38 ± 1.47	0.0040
0.135	10.39 ± 0.04	8.78	21.26 ± 2.41	0.0044
0.164	13.68 ± 2.13	10.03	38.24 ± 18.18	0.0050

q_e , Amount of dye adsorbed at equilibrium; BET_M SA, BET multipoint surface area; BET_S SA, BET single point surface area.

Table 4 Physisorption characteristics of chitosan flakes extracted from prawn scales at pH 3 and 30 °C: after adsorption of different dye concentrations.

q_e (mg/g)	BET _M SA (m ² /g)	BET _S SA (m ² /g)	Langmuir SA (m ² /g)	Total pore volume (m ² /g)
0.076	7.67 ± 0.08	6.19	16.96 ± 2.22	0.0031
0.105	8.48 ± 0.16	6.73	19.43 ± 2.89	0.0034
0.135	9.77 ± 0.32	7.99	20.98 ± 1.15	0.0040
0.164	10.75 ± 0.05	8.68	23.77 ± 2.87	0.0044
0.177	15.25 ± 2.44	12.35	32.76 ± 5.26	0.0062
0.178	16.45 ± 1.14	13.41	36.16 ± 8.34	0.0067
0.180	18.25 ± 1.22	15.13	38.17 ± 0.07	0.0076

q_e , Amount of dye adsorbed at equilibrium; BET_M SA, BET multipoint surface area; BET_S SA, BET single point surface area.

partially protonated groups of the chitosan. The Langmuir isotherm has been successfully applied to many real sorption processes and is expressed as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{4}$$

The linear transformation of the Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} \times C_e \tag{5}$$

where K_L and a_L are Langmuir isotherm constants (L/g). From the data C_e/q_e vs C_e , K_L and a_L can be determined from the slope and intercept.

The dotted lines in Figs. 5 and 6 represent a linear regression fit to the results for both isotherms. However, since adsorption data are of a nonlinear nature, nonlinear regressions are also performed on each set of data points. These non-

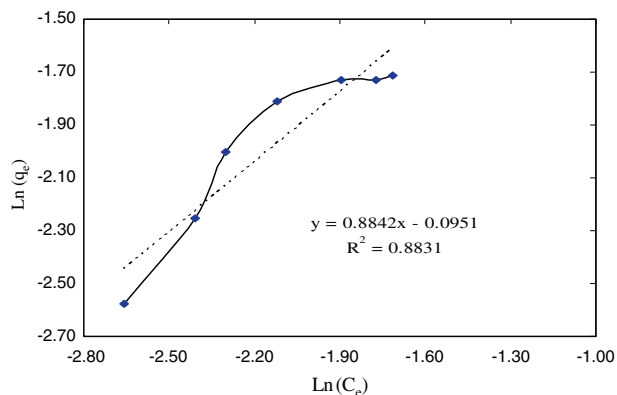


Figure 5 Freundlich adsorption isotherm at 30 ± 0.5 °C.

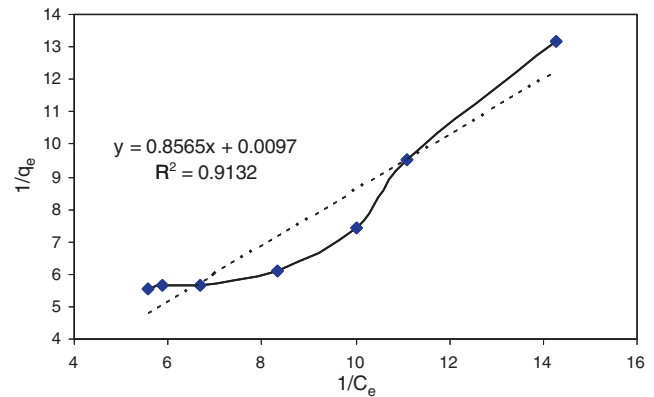


Figure 6 Langmuir adsorption isotherm at 30 ± 0.5 °C.

linear regression fits are represented as solid lines in Figs. 5 and 6. The correlation coefficients obtained with both kinds of regression for both adsorption isotherms are summarized in Table 5. The correlation coefficient values in Table 2 indicate that the data fit the Freundlich isotherm better than the Langmuir isotherm, both in case of linear and nonlinear regressions.

Fig. 7 shows the effect of dye concentration on chitosan adsorption. An increase in initial concentration of dye led to an increase in the adsorption capacity of dye on chitosan. This indicates that the initial concentration of dye played an important role in the adsorption capacity of acid yellow 73 on chitosan.

3.4. Changes of free energy

The free energy changes ΔG° for adsorption of anionic dye in acidic pH 3 at 30 °C were evaluated using the following equations (Chion et al., 2004):

$$K_C = \frac{C_{Ae}}{C_e} \tag{6}$$

$$\Delta G^\circ = -RT \ln K_C \tag{7}$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \tag{8}$$

Table 5 Freundlich and Langmuir adsorption isotherm constants for acid yellow 73 dye at 30 ± 0.5 °C, pH 3.

Freundlich isotherm			Langmuir isotherm		
K_F (L/mg)	n_F (L/mg)	R^2	a_L (L/mg)	K_L (L/mg)	R^2
0.9093	1.131	0.8831	0.0113	1.1675	0.9132

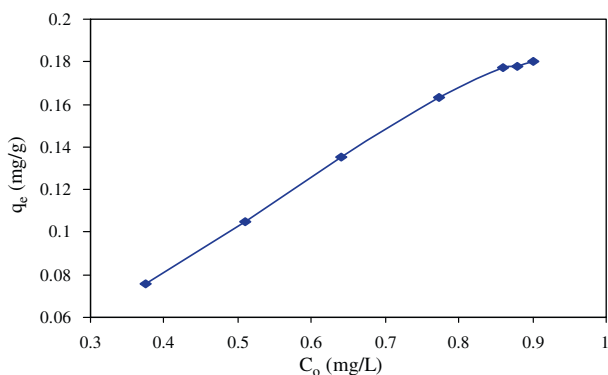


Figure 7 Effect of dye concentration on chitosan adsorption.

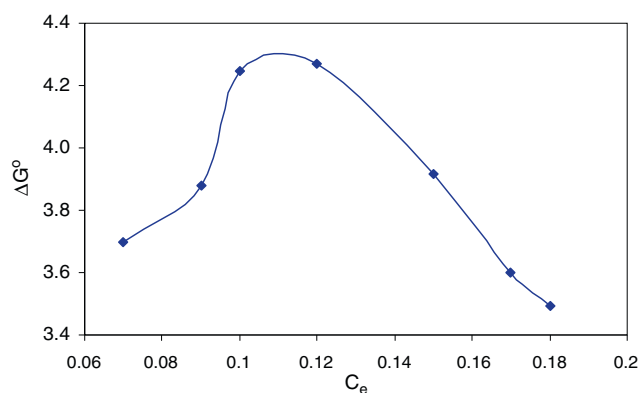


Figure 8 Changes in free energy with respect to different equilibrium concentrations for the adsorption of acid yellow 73 on chitosan flakes at 30 °C.

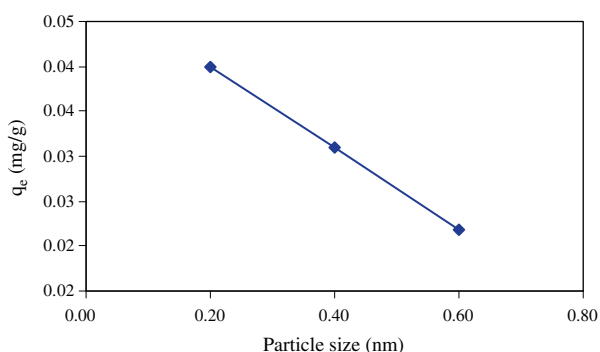


Figure 9 Effect of particle size.

where K_C is the equilibrium concentration, C_{Ae} is the amount of dye (mg) adsorbed on the adsorbent per dm^3 of the solution at equilibrium, C_e is the equilibrium (mg/ dm^3) of the dye in the solution, T is the solution temperature on Kelvin scale (K) and R is the gas constant. The isotherm data in Fig. 7 were applied to compute the changes of free energy. Fig. 8 shows the plot of ΔG° vs C_e for adsorption of acid yellow 73 dye. The positive values of ΔG° indicate that overall adsorption process is non-spontaneous. At low equilibrium concentration C_e of the dye solution, shown in Fig. 8, the more positive values of ΔG° imply the less driving force of adsorption process than that at higher C_e .

3.5. Effect of particle size

Particle size of an adsorbent played a very important role in the adsorption capacity of dye. Fig. 9 shows the effect of particle size on dye adsorption. Minimum particle size showed greater adsorption than larger size. Small size of adsorbent increases the surface area for adsorption. The increase in adsorption capacity with decreasing particle size suggests that the dye preferentially adsorbed on the outer surface and did not fully penetrate the particle due to steric hindrance of large dye molecules. The relationship of adsorption capacity to particle size depends on two criteria: (i) the chemical structure of the dye molecule (its ionic charge) and its chemistry (its ability to form hydrolyzed species) and (ii) the intrinsic characteristic of the adsorbent (its crystallinity, porosity and rigidity of the polymeric chains). As adsorption is a surface phenomenon, this can be attributed to the relationship between the effective specific surface area of the adsorbent particles and their sizes (Fig. 9). Guibal et al. (2005) also showed that more dye was absorbed when the particle size was small.

Table 6 shows physisorption characteristics of different grade chitosan flakes extracted from prawn fish scales. The dye uptake is increased with a decrease in the particle size since the effective surface area is higher for the same mass of smaller particles. The surface area values usually increased as the particle size decreased and as a consequence, the saturation capacity per unit mass of adsorbent increased. Decreasing the size of particles improves the adsorption properties of the chitosan, due to the expansion of the chitosan network and the increase in the specific surface area.

3.6. Competitive dye adsorption

Fig. 10 shows competitive dye adsorption on chitosan. Two types of fish scales were studied, i.e., prawn and labeo rohita. Conditions were kept same for both types of scales. Results showed that chitosan obtained from prawn scales has much greater adsorption than labeo rohita.

Table 6 Physisorption characteristics of different grade chitosan flakes extracted from prawn scales.

Particle size (μm)	BET _M SA (m^2/g)	BET _S SA (m^2/g)	Langmuir SA (m^2/g)	Total pore volume (m^3/g)
0.20	32.19 ± 3.42	26.88	66.18 ± 4.24	0.0135
0.40	15.91 ± 1.06	12.48	37.67 ± 9.10	0.0063
0.60	7.99 ± 0.141	6.36	18.23 ± 2.67	0.0032

BET_M SA, BET multipoint surface area; BET_S SA, BET single point surface area.

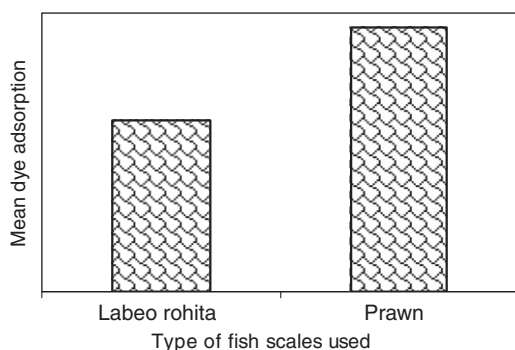


Figure 10 Competitive dye adsorption.

4. Conclusion

Chitosan is widely used to remove colour from dye solution and chitosan–dye interactions are very interesting for the sorption of dyes on solid chitosan flakes using sulphuric acid for pH control. The chitosan flakes used in this study show promising adsorption capacities. The adsorption capacities are significantly affected by the initial dye concentration, pH and particle size. The uptake increased with increase in initial dye concentration and with decrease in pH and particles sizes. The chitosan flakes exhibited excellent performance for adsorption of acid yellow 73. The strong electrostatic interaction between NH_3 of chitosan and dye anions can be used to explain the high adsorption capacity of anionic dye on chitosan competitive adsorption with two different types of scales. Prawn scales showed greater adsorption power than the labeo rohita scales. At low pH, the amino groups are protonated (NH_3^+) and form interaction with dye anions. The results show a tendency towards greater adsorption for anionic dye in the pH range of 3–4. It has also been observed in alkaline pH since lot of amino groups of the polymer are deprotonated.

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