Kinetic and Equilibrium Studies of Adsorption of Reactive Red 120 on Chitin

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ABSTRACT

Chitin is a natural compound that can be extracted from various organisms that is used in various applications from medicine to environmental applications. In this study, effect of chitin is followed for adsorption of reactive red 120 textile dye from water at different conditions such as pH, initial concentration of dye, ionic strength, initial concentration of chitin, effect of temperature, effect of contact time. Characterization of the adsorption were recorded by Fourier Transform Infrared (FT-IR) spectroscopy.

Keywords:
Chitin; Textile Dye Removal; Adsorption.

INTRODUCTION

The increase in population brings contamination of water with time. Textile dyes are great environmental problem for the environemnt since they change the quality of water as well as color of water. Their complicated structure with multiple aromatic compounds makes these contaminats resistance for degradation in water and under sunlight, their photolytic conversion to more toxic compounds is possible. Dyes have been widely used in different industries. As a result of dyeing process in textile industry, high amount of pollutant formed in liquid form [1]. Due to their highly brilliant colors, azo dyes the most important groups of dyes used in the textile dyeing processes [2]. Azo dyes, contains one or more azo (−N=N−) bonds in their structure [3]. Azo dyes are widely used in various industries such as textile, cosmetics, food, paper printing etc.. Because of complex structure of azo dyes, they are resistant to ozone, light, biodegradation and other environmental conditions. Thus treated of these dyes with conventional treatment methods remains ineffective [4].

Untreated dye contained effluents cause several adverse effects such as decrease photosynthetic activity by means of reduce penetration of light, reduce dissolved oxygen, reduce water quality, dyes and breakdown products have toxic effects on aquatic flora and fauna [1]. Azo dyes are large group of carcinogenic and mutagenic pollutants [5]. Various kind of physico-chemical methods have been used for treat dye contained waste water, including activated carbon adsorption, membrane filtration, oxidation, ozonation, and coagulation/flocculation. These physico-chemical methods have disadvantages, they have high operation costs and applicability are limited [1,6]. The use of biomass as a sorbent for treatment of wastewater is an effective alternative processes [7].

Chitin, poly (b-(1-4)-N-acetyl-D-glucosamine) is the most abundant biopolymer after cellulose. Chitin is found in the exoskeleton of arthropods and cell wall of fungi [8]. Chitin is a good biosorbent for environmental pollutants. Cadmium ions were removed from aqueous solution by chitin particles [9]. Another study showed that chitin adsorb zinc and arsenate ions effectively [10]. Chitin can adsorb reactive black 5 and reactive yellow 2 dyes [11]. Previous study reported that chitin adsorbed anionic dyes orange G, orange IV and xylenol orange [12].

The main objective of this study is to investigate biosorption of the dye reactive red 120 by the biopolymer chitin. The effect of initial pH, dye concentration, salt concentration, chitin dosage, and temperature and contact time was evaluated. Kinetic and thermodynamic parameters will be detected as well as with adsorption isotherms.

MATERIALS AND METHODS

Dye and Chitin

Reactive red 120 (CAS Number 61951-82-4) and chitin (CAS Number 1398-61-4) were obtained from Sigma-Aldrich.

Removal of Dye

The removal of dye was determined spectrophotometrically at 553 nm wave length with shimadzu Shimadzu UV-1700 spectrophotometer. The adsorption of dye capacity was calculated by following equation:

$$q = (C_i - C_e)\frac{V}{m} \tag{1}$$

in which q is adsorption capacity, Cf and Ci are initial dye concentrations, respectively. V is the volume of dye solution and m is the mass of the adsorbent that is chitin here.

Biosorption Experiments

Biosorption of dye reactive red 120 experiments were carried out in 250 ml Erlenmeyer flasks containing 100 ml dye solution. In order to reveal effect of initial pH on dye biosorption by chitin, 50 mg L^{-1} dye contained mediums were adjusted to pH 2-9 range using 1M HCl and 1M NaOH. Then 0.1 g chitin added into flasks and flasks were shaken on an orbital shaker at 150 rpm and 30°C for 24 h. The effect of initial dye concentration was also evaluated, different dye concentration was studied in the concentration range of 10-150 mg L^{-1} dye. The influence of chitin dosage was studied in the range of 0.025-0.2 g. In order to determine effect of contact time on removal of dye, samples were taken different time intervals (0-1440 min). The influence of temperature on dye removal was studied in different temperatures (20-60° C). To determine effect of salt on removal of dye, different NaCl so-
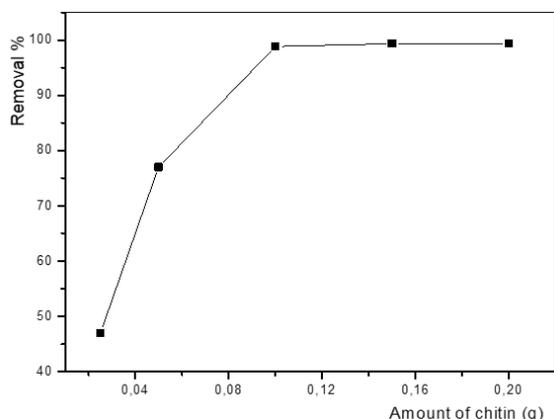

Figure 1. Effect of chitin amount on percent removal of reactive red 120.
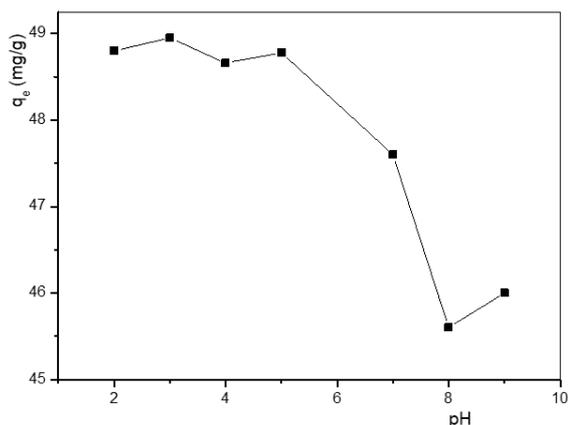

Figure 2. Effect of pH on adsorption capacity of chitin at equlibrium.

lutions (1-5 % m/v) were used. Unless otherwise stated, all experiments were carried out same conditions, (0,1 g chitin, pH 3, 50 mg l^{-1} dye conc., 30°C, 150 rpm, 24 h).

Spectroscopic Analyses

Characterization of the adsorption were recorded Fourier Transform Infrared (FT-IR) spectroscopy in ATR mode by Thermo instruments.

RESULTS AND DISCUSSION

Effect of Chitin Amount

The effect of adsorbent amount was followed in 50 ppm dye solution at pH 3 and 30°C. The amounts of chitin ranges from 0.025 g to 0.2 g (Fig. 1). It is clear that 0.1 g chitin is enough to remove nearly 99% of the dye from solution which is used for further experiments.

Effect of pH

The effect of initial pH on adsorption capacity at equilibrium is shown in Fig. 2. There is no strong effect on adsorption capacity of chitin since its change is narrow with wide pH change at 30°C for 50 ppm dye, 0.g chitin and 24 hours contact time. This is attributed to the rigid structure of chitin.

Effect of Salt

The adsorption of reactive red 120 by chitin is followed for 50 ppm dye solution at pH 3 and 30°C for different concenrations of salt from 1% to 5% by mass. Sodium chloride was used to observe the effect of ionic strength. The change in the ionic strength is not effective for the equilibrium adsorption capacity since the change adsorption capacity is minor (Fig. 3).
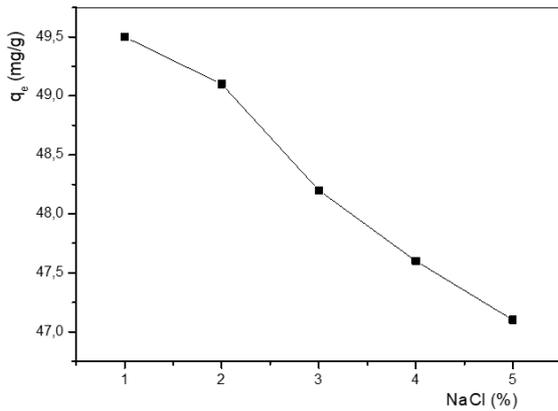
Figure 3. Effect of ionic strength on adsoption capacity of chitin at equlibrium.

Figure 5. Effect of temperature on adsorption capacity of chitin at equlibrium.

Effect of Contact Time

The change in the adsoption capacity with different contact times for 50 ppm dye solution at pH 3 and 30⁰C is shown in Fig. 4. Dye adsorption is high up to 180 minutes and reaches equilibrium for further contact times finally all dye is adsorbed.

Effect of Temperature

The effect of temperature on adsorption of dye is given in Fig. 5 at pH 3 for 50 ppm dye and various temperatures at 20°C, 30°C, 40°C and 60°C. The adsorption capacity increased only 5% with temperature since the polymeric chains in chitin becomes more flexible with temperature and the diffusion of dye is more possible through the chains.

Effect of Initial Dye Concentration

Fig. 6 shows the effect of initial dye concentration on adsorption capacity on 0.1 gram of chitin. There is an increase in adsorption capacity with increase in chitin concentration upto 100 ppm initial chitin concentration and
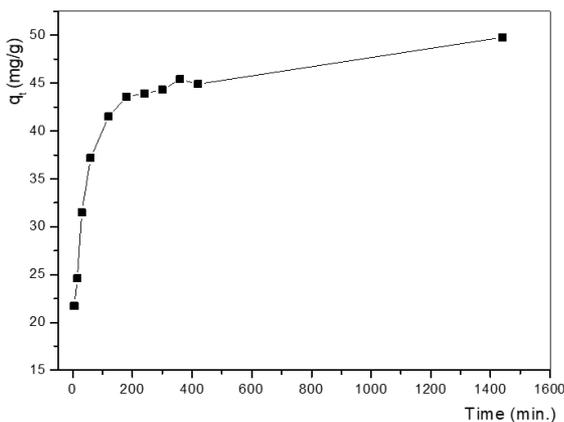
it seems to be constant above this value. The active sites of the chitin may be filled with textile dyes upto 100 ppm initial textile dye for 0.1 g chitin sample.

Equilibrium Isotherms

There are several isotherm equations that are used to analyze the experimental adsorption paramerers in which well known are Langmuir and Freundlich models. Langmuir isotherm model depends on the homogeneous finite number of active sites on the adsorbent that corresponds monolayer adsorption with no interaction between adsorbed species [13].

The linear form of the Langmuir equation follows the expressed equation:

$$C_e / q_e = C_e / q_m + 1 / \left(q_m K_a \right) \qquad (2)$$

q_e is the amount of dye adsorbed per gram of adsorbent (mg/g), C_e is the equilibrium concentration of dye (mg/L), q_m is the maximum adsorption capacity (mg/g) and K_a is adsorption equilibrium constant (L/mg). Langmuir isotherm that is fitted linear is given in Fig. 7 with some analytical parameters and from the isotherm q_m is 5.92
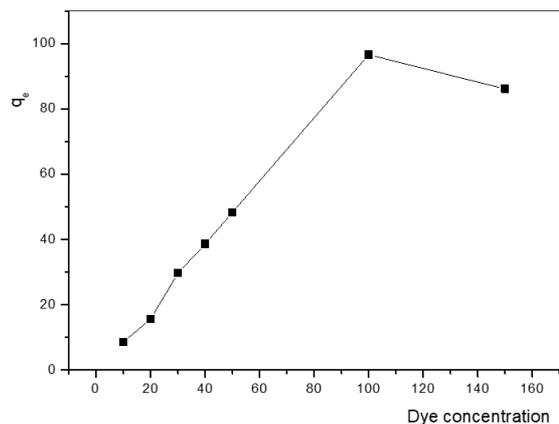

Figure 4. Effect of contact time on adsoption capacity of chitin at equlibrium.

Figure 6. Effect of initial dye concentration on adsorption capacity of chitin at equlibrium.

Figure 7. Langmuir isotherms for the adsorption of Reactive Red 120 on chitin.

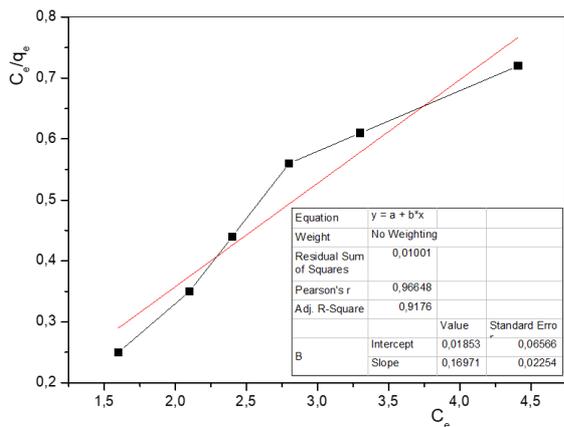**Figure 8.** Freundlich isotherms for the adsorption of Reactive Red 120 on chitin.

mg/g as well as K_a is 9.12 L/mg. Dimensionless separation factor (K_R) is one of the essential parameter of the Langmuir isotherm that indicates the characteristic of isotherm [14].

$$K_R = 1/(1 + K_a C_o) \tag{3}$$

where C_o is the initial concentration of the dye. K_R values are between 0 and 1 ($0 < K_R < 1$) that indicates favorable adsorption (Table 1) at pH 3 and 30°C.

The Freundlich isotherm is one of the widely used model for adsorption studies. It generally applies on heterogeneous surfaces that is in contact with adsorbed molecules. Freundlich isotherm differs from Langmuir isotherm that is not restricted with monolayer coverage The widely used expression for Freundlich isotherm model is [15].

$$log(q_e) = log K_f + (1/n) log C_e \tag{4}$$

where K_f is Freundlich constant, n is relates the deviation of the adsorption from linearity. The Freundlich isotherm was also evaluated for adsorption of reactive red 120 on chitin but this model fails for our data especially for higher concentrations as in literature. The data for dilute dye was used to evaluate the parameters of Freundlich isotherm (Fig. 8) which are 4.12 and 2.29 for K_f and n, respectively at pH 3 and 30°C. Adsorption is favorable if Freundlich isotherm is assumed since n value is greater

than one [16], same was assumed as in the case of Langmuir. Correlation coefficient, r^2 is higher for Freundlich isotherm that means in dilute solutions, the adsorption of reactive red 120 on chitin is expressed as Freundlich model rather than Langmuir model.

Kinetic Studies

The kinetics of adsorption of reactive red 120 on chitin was also followed at pH 3 and 30°C for 50 ppm dye and 0.1 gram of chitin. The pseudo-first order and pseudo-second order diffusion models were applied for linear region of the plots. The first order rate equation is followed for pseudo-first order formula derived by Lagergren [17].

$$ln(q_e - q_t) = ln q_e - kt \tag{5}$$

where q_t is the amount of dye adsorbed at any time t (mg/g) and k is the rate constant for pseudo-first order assumption. The adsorption data of reactive red on chitin is not a linear line for pseudo-first order assumption. A pseudo-second order model for adsorption of solute on adsorbent is proposed by Ho [18] (Fig. 9) and adsorption of dye on chitin in this study follows this model.
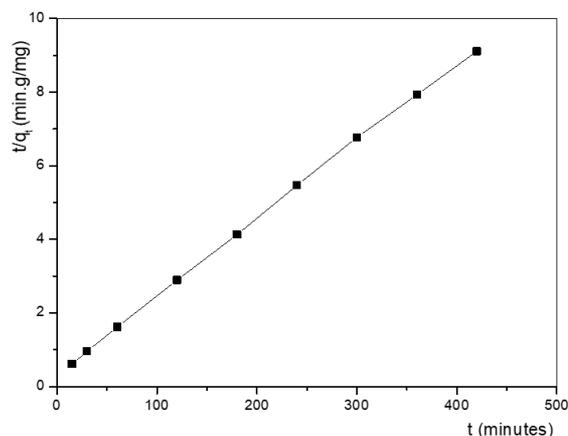
Figure 9. Pseudo-second order kinetic evaluation of adsorption of reactive red 120 on chitin.

Table 1. K_r values of the Langmuir isotherm at different initial concentrations.

Initial concentration (C_o)	Dimensionless seperation factor (K_R)
10	0.0108
20	0.00545
30	0.00364
40	0.00273
50	0.00218
100	0.00109

$$t / q_t = 1 / \left(k q_e^{\,2}\right) + t / q_e \qquad (6)$$

where t is time elapsed for adsorption (min.), q_t is the amount of dye adsorbed at any time t (mg/g) and k is the adsorption rate constant. From expressed graph, equilibrium amount of adsorbed dye (q_e) was found as 47.6 mg/g where this value is found as 46.1 experimentally. The close value of experimental q_e and its value expressed from the graph proves that the adsorption of reactive red 120 on chitin obeys the pseudo-second order model suggested by Ho. The adsorption rate constant (k) was found as 0.0013 g/(mg.min.).

SPECTROSCOPIC CHARACTERIZATION (FTIR-ATR)

The FTIR-ATR spectrum of the chitin after absorption of reactive red 120 is given in Fig. 10. The characteristic peaks of chitin are O-H stretching at 3433 cm⁻¹, N-H stretching at 3255 cm⁻¹ and 3099 cm⁻¹, C=O amide stretching at at 1650 cm⁻¹ and 1620 cm⁻¹, C-O-C stretching for bridge oxygen at 1152 cm⁻¹ and N-acetylglucosamine in ring stretching mode at 1115 cm⁻¹ were observed in the spectra. The peaks from reactive red 120 are N-H stretching of seconder aromatic amine that overlaps with chitin O-H stretching at 3436 cm⁻¹, C=O stretching frequency of hydrazone at 1735 cm⁻¹, 1020 cm⁻¹ and 1045 cm⁻¹ is O-H from phenol, the peaks at 1205 cm⁻¹ is due to aromatic C-O and 1670 cm⁻¹ is from N=N.

CONCLUSION

Chitin is one of the most produced natural polymer with variety of applications. In this study, chitin from crab shells was used to remove reactive red 120 dye from water that is more than 95%. There is no significant change in adsorption of reactive red 120 by chitin when pH, io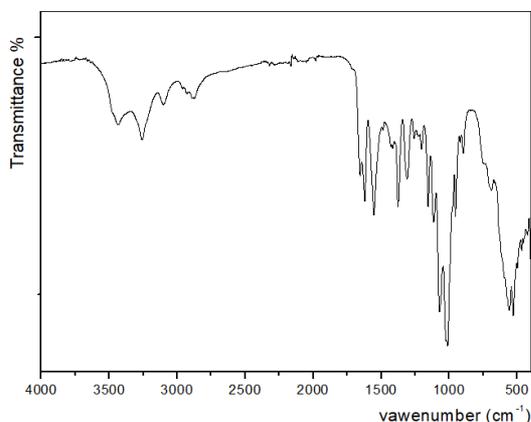nic strength and temperature changes since the rigid structure of chitin. The increase in chitin amount increases the adsorption as well as the same is for contact time up to a special time that equilibrium is established. The adsorption models were evaluated for Langmuir and Freundlich models, although adsorption process obeys both of the models, the linearity was observed for Freundlich model rather well. The adsorption kinetics were observed as pseudo-second order diffusion. FTIR-ATR spectra were evaluated for spectroscopic characterization.

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Figure 10. FTIR-ATR spectrum of the chitin after absorption of reactive red 120.