Kinetic and equilibrium studies on the removal of Congo red from aqueous solution by biosorption on crosslinked chitosan- ECH nanoparticles

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Abstract:The nanoparticles of templated crosslinked chitosan, was prepared through using ECH as a crosslinker. The nanoparticles exhibited significantly higher adsorption capacities from the congo red dye than other adsorbent formed without a crosslinker. The adsorption of the dyes on the nanoparticles was affected by the initial pH, dye concentration, and temperature. The results were in accordance with the second-order adsorption models. The E_a values of the dyes calculated using the Arrhenius's equation revealed that the adsorption process may be due to the dual nature of the process, physisorption and chemisorption, and that adsorption was predominant in the chemisorption process. The adsorption processes in the nanoparticles were spontaneous and exothermic.

Keywords: Adsorption kinetics, Congo Red, Crosslinked Chitosan-ECH nanoparticles.

INTRODUCTION

Azo dyes are the largest class of dyes with the greatest variety of colours - approximately 10–15 % of the dyes are released into the environment during dyeing of different substrates, such as synthetic and natural textile fibres, plastics, leather, paper, mineral oils, waxes, and even foodstuffs and cosmetics [17]. Dyeing effluents have a serious environmental impact because disposal of these effluents into the receiving water body (causes damage to aquatic biota or humans by mutagenic and carcinogenic effects) [9]. Treatment of effluent containing synthetic dyestuffs is very difficult, since the dyes are stable in conditions of light and heat, the presence of oxidizing agents and are resistant to aerobic digestion [14, 18].

Several physical, chemical and biological treatment methods (e.g., adsorption, coagulation-flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods) have been applied to remove dye molecules from such effluent [9]. However, these processes vary in their effectiveness, cost and environmental impact. Adsorption is a more competitive treatment process for dye removal because of its simplicity, high efficiency, and wide-ranging availability [1,11].

Approximately, half of all known dyes are azo dyes, which are the major group of colorants used in textile industries [3]. Congo red (CR) dye is a benzidine-based anionic bisazo dye. This dye is known to metabolize to benzidine, and as a human carcinogenic and mutagenic. It is a potential danger of bioaccumulation and exposure to this dye can creates allergic problems [6, 16].

A number of low cost adsorbents, such as coir pith [15], rice hull ash [8], rice husk [13], leaf [2], and fungi [3,10], have been used for the removal of CR from aqueous solutions. However, the low adsorption capacities of these adsorbents for CR limit their application in the practical field. Hence, there is a need to search for adsorbents that are more effective, since the water treatment industry requires highly effective, ecofriendly, and low cost adsorbents that are available in tonnage quantities. Chitosan (CS), a linear biopolymer of glucosamine, exhibits a high adsorption capacity towards many classes of dyes especially anionic dyes because of its high amino and hydroxyl functional group content [9]. Recently, CS has become very useful for the removal of metals [12], dyes [9], and other simple anionic molecules [6]. Some cross-linking reagents [19] have been used to stabilize chitosan in acid solutions. Cross-linked chitosan is not only insoluble in an acid solution but is also endowed with stronger mechanical properties.

The aim of this research, is the investigation of the adsorption ability of the chitosan nanoparticles and also the finding of appropriate conditions for carrying out the adsorption process of anionic dye congo red in acid solutions. The effects of solution pH on

adsorption capacity were also studied. The batch process behaviors of the adsorption at different temperatures and different initial dye concentration were measured.The adsorption rates were determined quantitatively and stimulated by the nonlinear first-order and second-order models.

EXPERIMENTAL
1. Materials and methods
1.1. Chemicals
Chitosan was purchased from Sigma–Aldrich Co., USA. The degree of deacetylation (DD=79.1%) was determined by ^{1}H NMR spectroscopy. Congo Red with 97% purity (Mw = 696.66 g/mol) and ECH with 98% purity were purchased from Fluka. Pentasodium triphosphate (TP) with 98% purity was purchased from Sigma–Aldrich Co., USA.
1.2. Preparation
The nanoparticles of the templated crosslinked CS-ECH-TP was prepared according to the procedure described by Chen et al.[7].
A solution with 50 mg of chitosan dissolved into a 50 mL aqueous solution of acetic acid (0.5%, v/v) was prepared. A 5 mL aqueous solution of CR dye (8.7 mg) was added, and the mixture was stirred for 30 min. A 5.0 mL aqueous solution of ECH was added dropwise, and the mixture was stirred for 2 h at 50°C. Using a syringe, 30 mL of 1.45% TP solution was slowly dropped into the chitosan solution by mechanical stirring (1000 rpm) to obtain a milky emulsion. The resulting emulsion was frozen at −4°C and then thawed in the atmosphere to produce nanoparticle precipitates, which were collected using a centrifuge. Finally, the nanoparticle precipitates were stirred with a pH 10.0 NaOH solution to remove the dye. This stage was monitored by a UV/visible spectrophotometer. The process was followed by collecting the precipitates with a centrifuge and by intensive washing of the nanoparticle precipitates with distilled water to remove any unreacted ECH.
1.3. Batch kinetics
The adsorption kinetics of the CR dyes on the nanoparticles was carried out in a batch process. The variable parameters were studied, including the initial pH values, initial concentrations of dye, and temperatures. In each test, 20 mL (0.5% CH$_3$COOH) of the nanoparticles (7×10^{-3} g/mL) was added into 5 mL of aqueous solution of the dye with a known concentration. Whenever necessary, the pH value was adjusted with diluted NaOH or HCl solutions. Then 0.1 mL aliquots of the solution were added to 10mL distilled water at different time intervals. The mixture solution was centrifuged to remove adsorbents. The filtrate was adjusted to correct pH. The dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}, at different pH using a spectrophotometer.

RESULTS AND DISCUSSION
The cross-linked nanoparticles were synthesized by mixing chitosan and ECH.Chitosan solution changed from a clear solution to an opalescent suspension when TPP was added. This transformation indicated that ionic gelation occurred between chitosan-ECH and TPP, and nanoparticles were formed.The chitosan nanoparticles obtained as a white powder could be dispersed in water, dilute acidic and alkali solutions without aggregation.
The efficiency of dye adsorption from aqueous solution using adsorbent depends on various factors like contact time, pH, temperature of the solution, equilibrium time of adsorption, agitation speed, initial concentration of dye and amount of adsorbent dose. The effect of contact time on the removal of CR is given in Fig. 1. The contact time curves show rapid adsorption of CR in the first 250 min. It is well known that pH plays a significant role in adsorption of dyes. It has been observed that with increase in pH from 3 to 4, the the adsorption capacities decreases slowly from 115 mg g^{-1} to 105 mg g^{-1} and then decreases with the further rise of pH till 9 (Fig. 2).The biopolymeric adsorbent, chitosan

have functional groups like –OH, –NHCOCH$_3$ and –NH$^+_3$.The hydroxyl groups of the polymer are strongly hydrated and are virtually incapable of forming hydrogen bonds with dyes. However, they can adsorb by the formation of hydrogen bonds, by Van der Waals interactions and also by ion exchange with other groups.
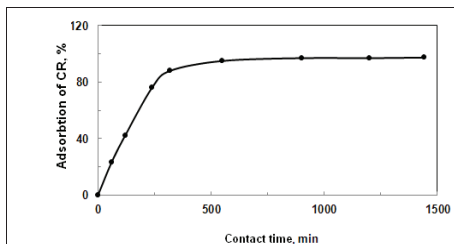

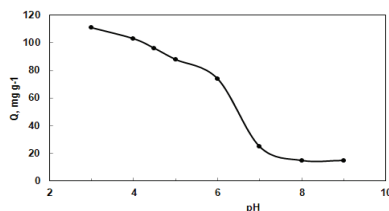Fig. 1. Effect of contact time and initial dye concentration on Congo Red removal.

Fig. 2. Effect of pH on Congo Red removal.

To measure the rate-controlling and mass transfer mechanism, kinetic data were correlated to linear forms of the first-order equation:

$$\ln(Q_{eq} - Q_t) = \ln(Q_{eq}) - K_{1,ad}$$ (1)

and the second-order equation:

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_{eq}^2} + \frac{1}{Q_{eq}}t$$ (2)

where: Q_{eq} and Q_t are the adsorption capacities of dye (mg/g) at equilibrium and at a given time t, respectively; and $k_{1,ad}$ (min^{-1}) and $k_{2.ad}$ (g/(mg min)) are the first-order and the second-order rate constants, respectively. According to Eq. (1), the plot of $\ln(Q_{eq} - Q_t)$ versus t yields a straight line with a slope of $-k_{1,ad}$ and an intercept of $\ln Q_{eq}$. In Equation (2), the plot of t/Q_t versus t gives a straight line with a slope of $1/Q_{eq}$ and an intercept of $1/(k_{2,ad}Q^2_{eq})$. These mathematical equations are presented on the Figures 3,4 and Table 1.
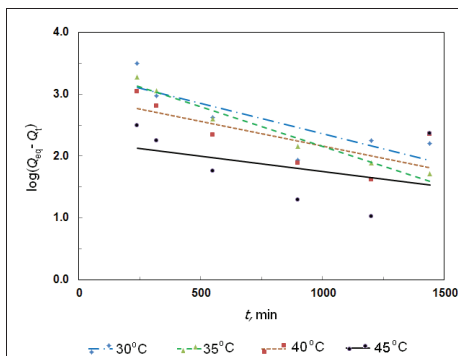

Fig. 3. A plot of log(Q_{eq}-Q_t) against the time at different temperatures.
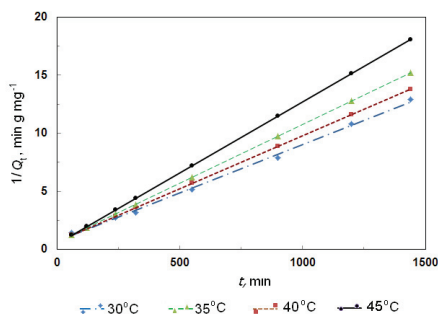
Fig.4. A plot of 1/Q_t against the time at different temperatures.

Table 1. Comparison of the first-order, second-order adsorption, and intraparticle diffusionrate constants, calculated Q_{eq} and experimental $Q_{eq\,exp}$ values for different initial dye concentrations, temperatures.

t °C	C_o mg dm^{-3}	$Q_{eq\,exp}$ mg g^{-1}	First-order kinetic model			Second-order kinetic model		
			$K_{1\,ads}$ min^{-1}	$Q_{eq\,calc}$ mg g^{-1}	R^2	$k_{2\,ads}$ g mg^{-1} min^{-1}	$Q_{eq\,calc}$ mg g^{-1}	R^2
30	800	111.43	1.50×10^{-3}	49.69	0.4477	9.146×10^{-5}	120.48	0.9976
	600	110.25	1.42×10^{-3}	40.45	0.9513	8.824×10^{-5}	108.51	0.9991
	400	82.65	6.33×10^{-3}	42.69	0.8635	1.517×10^{-4}	80.25	0.9990
	200	63.24	4.86×10^{-2}	52.68	0.9155	8.564×10^{-4}	63.56	0.9991
35	800	111.63	1.60×10^{-3}	44.77	0.9153	1.235×10^{-4}	109.89	0.9964
	600	108.44	1.40×10^{-3}	50.12	0.9732	1.798×10^{-4}	116.42	0.9931
	400	80.42	5.40×10^{-2}	59.45	0.8117	3.198×10^{-4}	82.45	0.9994
	200	62.45	7.17×10^{-2}	49.52	0.9664	1.420×10^{-3}	61.86	0.9996
40	800	108.85	1.31×10^{-3}	31.69	0.9478	1.847×10^{-4}	99.010	0.9984
	600	106.12	1.52×10^{-3}	38.12	0.5699	3.010×10^{-4}	109.00	0.9952
	400	84.65	9.96×10^{-3}	50.49	0.9765	5.010×10^{-4}	83.10	0.9989
	200	58.85	9.53×10^{-3}	55.74	0.9839	1.901×10^{-3}	59.75	0.9997
45	800	105.45	1.10×10^{-3}	17.82	0.9478	2.900×10^{-4}	81.96	0.9971
	600	99.35	1.80×10^{-3}	20.12	0.8819	6.197×10^{-4}	100.44	0.9988
	400	82.56	8.40×10^{-3}	38.15	0.9566	1.220×10^{-3}	82.95	0.9994
	200	54.98	8.65×10^{-3}	43.86	0.9753	3.720×10^{-3}	55.86	0.9998

In order to determine the activation energy of adsorption Ea (J/mol), the data should be fitted with Arrhenius's equation

$$k = A\,E\exp\left(-\frac{E_a}{RT}\right)$$

(3)

where A is a pre-exponential factor (g/g min), R is the gas constant and T is the absolute temperature. Taking logarithm from both sides of Eq. (3) we obtain the next linear equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

(4)

Having the values of the rate constant k, determined at different temperatures T, and plotting ln k against $1/T$, the activation energy E_a and pre-exponential factor A can be determined from the slope and the intercept of the straight line, respectively (Fig.5). The positive value of E_a means the existence of an energy barrier. According Cagnon et al. [4] an activation energy lower than 25–30 kJ/mol could mean that the adsorption process is controlled by intra-particle diffusion.
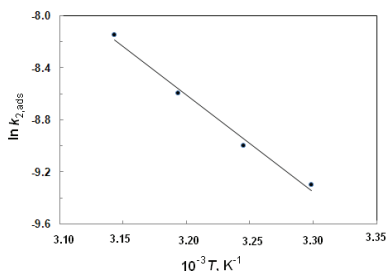

Fig.5. A plot of ln $K_{2ads.}$ against the temperature.

CONCLUSION:

Appropriate conditions for congo red dye adsorption on the chitosan-ECH nanoparticle were established. The results obtained are in accordance with the second-order adsorption model. The E_a values of the dyes calculated using the Arrhenius's equation revealed that the adsorption process may be due to the dual nature of the process, physisorption and chemisorption, and that adsorption is predominant in the chemisorption process. The adsorption processes in the nanoparticles are spontaneous and exothermic.

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This paper has been reviewed