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Removal of methyl orange dye from textile effluent using adsorption on chitosan hydrogel beads

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Abstract

Pollution is a worldwide problem that has led to a corresponding interest in pollution control. With the positive influence, dyes are widely used in many fields such as textiles, paper, plastic, food, painting, and medicine. Most synthetic dyes are toxic and can bring serious problem of water pollution. The removal of such type of dye-stuffs from effluent is necessary as such effluents cause abnormal coloration to the surface water and block photosynthetic bacteria and aquatic plants from sunlight. Methyl orange (MO) is an azo dye having high solubility in aqueous solution and is mutagenic, human carcinogen. MO mainly occurs in the effluents discharge from textiles, paper, printing, leather industries etc. Adsorption has been recognized as the most popular treatment process for the removal of dyes from an aqueous solution due to its simplicity, high efficiency, easy recovery and the reusability of the adsorbent. In recent years, low-cost absorbents for waste water treatment have attracted a lot of attention.

Chitosan (CS), the deacetylated product of chitin, exhibits a high adsorption capacity towards many classes of dye. CS based hydrogel beads have shown the highest adsorption capacity for numerous dyes. We attempted to prepare chitosan hydrogel beads crosslinked with glutaraldehyde as an adsorbent to remove MO from waste water effluents.

A Batch adsorption study was conducted as a function of contact time. Dye concentration was determined by spectrophotometric titration at λ_{max} 375 nm. The equilibrium adsorption capacity was reached with in 24 hrs and the maximum adsorption capacity was around 155 mg/g at 30^{o}C. The data was treated for pseudo first order, pseudo second order and also for intra particle diffusion equation to study kinetic parameters.

Color removal efficiency were calculated as function of pH, temperature and initial concentration of MO dye solutions. The CRE decrease with increasing pH while increase with increasing temperature and initial concentration. The results show that CS is an effective adsorbent for MO dye from waste water effluents.

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Introduction

Pollution is worldwide problem that has created interest in pollution control. On the positive side, dyes can give beautiful color to various products, and therefore they are widely used in many fields such as textiles, paper, plastic, food, painting, and medicine (Altinisik *et al*., 2010; Safa and Bhatti, 2011). However, the waste water from industries using dye may still contain up to 15 % of the dye (Moussavi and Khosravi, 2011). Most synthetic dyes are toxic and can bring about serious water pollution, destroy community structure of aquatic organisms, and further become a hazard to all mankind. It is reported that around 25 % of diseases facing humans suffering today because of long-term exposure to environmental pollution (Tang *et al*., 2012; Matta, *et al*., 2016).

Azo dyes represent about 50 % of all dye varieties and these dyes are of great environmental concern due to their huge applications and recalcitrance. The removal of such type of dye-stuffs from effluent before discharging into neutral water bodies is extremely important from an environmental point of view. Such effluents cause abnormal coloration to the surface water and block photosynthetic bacteria and aquatic plants from sunlight (Cheung *et al*., 2009).

Methyl orange (MO) (Sodium 4-[(4-dimethyl amino) phenyl di azienyl] benzene sulphonate) is an azo dye and it was selected in this study as a model anionic dye because of mutagenic in nature, highly soluble in aqueous solution and its persistence, once it is discharge into natural environment. MO mainly occurs in the effluents discharge from textiles, paper, printing, leather industries etc. (Han *et al*., 2008) and during dyeing operation about 10 % of MO ends up in waste waters. There are many processes to remove MO molecules from colored effluents and the treatment methods can be divided into three catagories: (1) physical methods such as adsorption (Namasivayam and Kavitha, 2002; Chatterjee *et al*., 2009b): (2) chemical methods such as ozonation (Gharbani *et al*., 2008; Khadhraoui *et al*., 2009), photo degradation and electrochemical process (Elahmadi *et al*., 2009); and (3) biodegradation (Gopinath *et al*., 2009; Matta and Gjyli, 2016).

Adsorption has been found to be a more feasible process for pollutants removal from industrial effluents in comparison to other existing methods (Jain and Sikarwar, 2008). The reason is, the most of those processes involve high costs and low efficiency. Nowadays, adsorption has been recognized as the most popular treatment process for the removal of dyes from an aqueous solution due to its simplicity, high efficiency, easy recovery and the reusability of the adsorbent (Garg *et al*., 2003; Aksu, 2005; Matta, *et al*., 2016). Activated carbon is the most popular adsorbent due to its excellent performances in adsorption (Baccar *et al*., 2009). However, its high cost and difficulty in regeneration limits its applicability (Mahmoodi *et al*., 2011). In recent years, low-cost absorbents for waste water treatment have attracted a lot of attention. Agricultural wastes (Bhattacharyya and Sharma 2005; Vadivelan and Kumar 2005) and industrial by-products (Batzias and Sidiras 2007; Hamdaoui 2006; Jain and Jayaram 2010; Kumar and

Sivanesan 2007), activated carbon prepared from coir pith, clay minerals (Gurses *et al*., 2004), rice husk, leaf powder (Bhattacharyya and Sharma 2004), fly ash (Acemigolu, 2004), bacterial bio sorbents and fungus (Fu and Viraraghavan, 2002) have been studied in detail for the removal of dyes in aqueous media. However, low adsorption capacities of these adsorbents towards dyes limit their applications in practical field.

Chitosan (CS), the deacetylated product of chitin, exhibits a high adsorption capacity towards many classes of dye due to its multiple functional groups, biocompatibility and biodegradability. CS-based adsorbents are versatile materials in view of their use in different forms; from flake or powder to hydrogel bead types. Recent review papers reported that CS-based adsorbents that are usually used in the form of hydrogel beads have shown the highest adsorption capacity for numerous dyes (Crini and Badot, 2008). However, low mechanical strength of CS hydrogel beads limits their commercial application as an adsorbent. Several chemical modification steps, including chemical cross-linking (Chiou *et al*., 2004), poly amination and carboxy alkyl substitution, have been performed to increase the mechanical strength of CS hydrogel beads.

We attempted to prepare chitosan hydrogel beads crosslinked with glutaraldehyde as an adsorbent to remove MO from waste water effluents.

Materials and Method

Materials

Chitosan, a natural polymer of animal origin was purchased by India Sea Food, Kerala, and was used as received. Its percentage of deacetylation after drying was 89%. Glutaraldehyde was procured from Loba Chemie Pvt. Ltd, India and used as a crosslinking agent between chitosan chain units of polymer. Methyl orange was obtained from Merck, India. All other chemicals like acetic acid, methanol, NaOH, HCl, KCl, KH_2PO_4 etc. were used of analytical grade. Double distilled water was used throughout the studies.

Methods

Preparation of chitosan beads

Chitosan (1.0 g) was dissolved in 40 ml of 2% acetic acid under stirring condition for 3h at room temperature. The homogeneous mixture was extruded in the form of droplets using a syringe into NaOH-methanol solution (1:20 (w/w)) under stirring condition at 400 rpm. The resultant beads were then placed in a water jacket containing glutaraldehyde maintained at 50^oC for about 10 minutes. Finally the beads were washed with hot and cold water successively and then vacuum dried.

Color removal efficiency (CRE) & Adsorption studies

10 ml dye solution of known concentration with 0.2 g of beads was taken in conical flask at desired temperature and pH. It was shaken for 10 min and then kept for 24 h and lastly the remaining concentration of dye was estimated spectrophotometrically at λ_{max} (375 nm) of MO dye. The CRE (%) for CS beads was calculated by given formula-

$$CRE\ (\%) = (1 - Ac/Ai)\ X\ 100$$

Where, Ai and Ac are the absorbance of the dye solution before and after the adsorption process.

A Batch adsorption study was conducted as a function of contact time. The equilibrium adsorption capacity was reached with in 24 h. Adsorption is calculated by given formula-

$$qe = (Co - Ceq) \times V/W$$

Where, qe is the adsorption of dye per gram dry weight of the adsorbent in mg/g, C_o is the initial concentration of MO in the solution in mg/l, C_{eq} is the equilibrium concentration of MO in the solution in mg/l, V is the volume of the solution in ml and W is the dry weight of the hydrogel beads in g.

Results and Discussion

The CS hydrogel beads cross-linked with glutaraldehyde was used for the study of the influence of contact time for adsorbing MO. The effect of the contact time on the adsorption capacity of CS hydrogel beads for MO is shown in Figure 1. The contact time varied in the range 0 – 24 h, and the initial concentration of dyes was fixed at 5000 mg/l. As Figure 1 shows, the time required to achieve the equilibrium at temperature 30˚C was about 24 hrs.

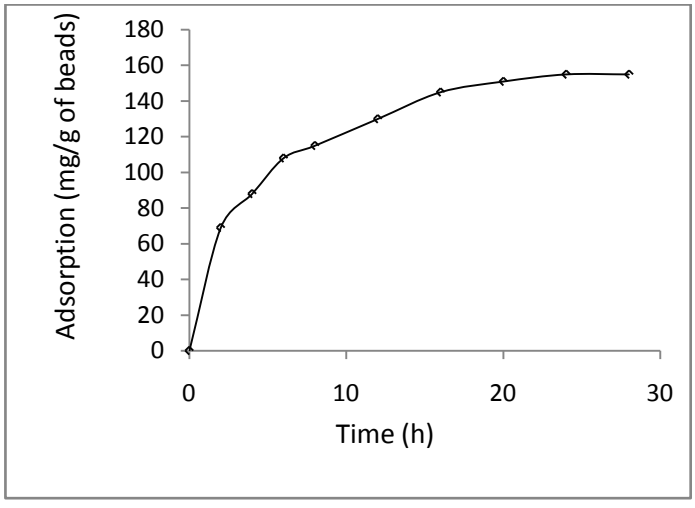

Figure 1: Adsorption of MO dye onto CS hydrogel beads as a function of contact time at initial concentration of 5000 mg/l.

The kinetics of dye adsorption on the CS hydrogel beads was determined with three different kinetic models, i.e., the pseudo-first order, pseudo-second order and the intra-particle diffusion model.

The pseudo-first order equation of Lagergren is one of the most widely used equation, being the first rate equation developed for sorption in solid/liquid systems.

$$\log (qe - qt) = \log qe - \frac{K_1}{2.303} t$$

Where, qe and qt are the amounts of dyes adsorbed at equilibrium and at time t, k_1 is the rate constant of the pseudo-first order kinetics. The slopes and intercepts of the plots log (qe− qt) versus t (Figure 2) were used to determine the pseudo-first order rate constant, k_1, and qe, the values obtained being presented in Table 1.

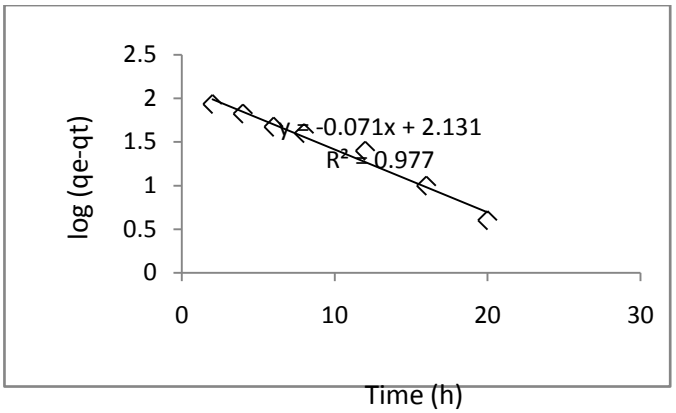

Figure 2. Pseudo-first order model fitted for the adsorption of MO on the CS hydrogel beads.

The adsorption data were also treated according to the pseudo-second order kinetics using t, which is proposed by Ho and McKay

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Where, k_2 is the rate constant of the pseudo-second order kinetics. The values of k_2 and qe were obtained from the intercept and slope of the straight lines resulted by plotting t/qt against t (Figure 3).

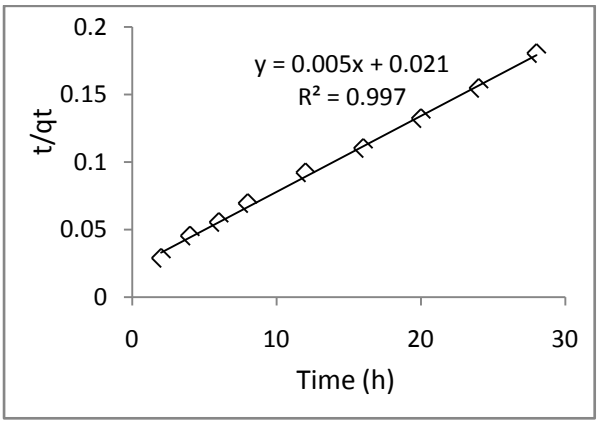

Figure 3. Pseudo-second order model fitted for the adsorption of MO on the CS hydrogel beads.

In order to assess the nature of the diffusion process reasonable for the adsorption of dyes onto the CS hydrogel beads, attempts were made to calculate the pore diffusion coefficients. The intra-particle diffusion model was proposed by Weber and Morris. The initial rate of intra-particle diffusion is calculated by linearization of the curve.

$q = f(t^{0.5})$

$qt = K_{id}\ t^{0.5}$

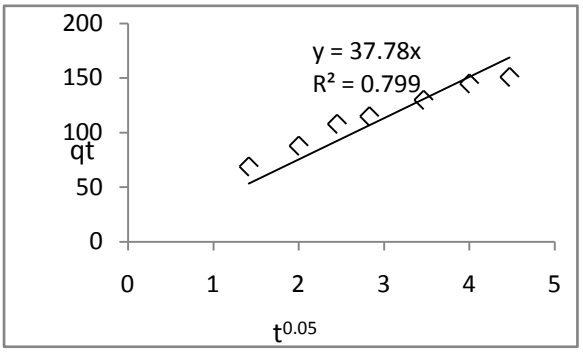

Figure 4. Weber and Morris intra-particle diffusion model fitted for the adsorption of MO on CS hydrogel beads.

Generally, the intercept of the plot of qt versus $t^{0.5}$ gives an idea about the boundary layer thickness, the larger the value of the intercept, the greater the boundary layer diffusion effect is. The values of intra-particle diffusion rate constant are presented in Table-1.

Kinetic model	**Parameter value**		
Pseudo-first-order equation	$qe_{(cal)}$ (mg g^{-1})	$K_1(h^{-1})$	R^2
	126.18	16.35 x 10^{-2}	0.977
Pseudo-second-order equation	$qe_{(cal)}$ (mg g^{-1})	K_2(g $mg^{-1}h^{-1}$)	R^2
	200.0	1.19 x 10^{-3}	0.997
Intra-particle diffusion	K_p(g $mg^{-1}min^{-1}$)		R^2
	37.78		0.799

Table 1: Constants of different rate models for CS beads at the initial concentration of 5000 mg/l

If the regression of qt versus $t^{0.5}$ is linear and passes through the origin, then the intra-particle diffusion is the sole rate-limiting step. The deviation of the straight line from the origin indicates that this process is not the rate-limiting step.

The effect of temperature, initial concentration and pH on the adsorption of MO onto CS hydrogel beads.

It is evident from table 2 that % CRE decreases with increasing pH of the dye solution. The % CRE increased with increasing initial concentration of methyl orange dye. Color removal of dyes occurred due to the adsorption of dye molecules onto chitosan beads hence adsorption of dye on chitosan beads increased with increase of initial concentration of dye and temperature while decreased with increase of pH.

Initial conc. Of dye MO (x 10^{-4}M)	% CRE (pH 5.0)		% CRE (pH 7.0)	
	30°C	40°C	30°C	40°C
3.59	59.2	80.7	50.8	74.8
1.795	29.6	51.8	23.8	42.5

Table 2: Illustrates the effect of temperature, pH and conc. on the removal of CR chitosan hydrogel beads

Conclusion

In this study, the capacity of CS hydrogel beads to adsorb MO from aqueous solutions was examined. Kinetic data were successfully fitted by the pseudo-second order equation, which gave the best correlation with experimental data, for the studied systems. The increase of temperature and initial dye concentration led to the increase of the CRE for dye while increasing pH decreases the CRE of dye.

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