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DYE REMOVAL FROM AQUEOUS SOLUTION BY MAGNETIC HYDROGEL

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Abstract: *For coloration of products, dyes are used in various industries such as pulp, paper, leather, pharmaceuticals, and textiles. Disposal of colored textile wastewater into the environment, without efficient treatment, imposes serious damages to aquatic life by reducing sunlight penetration to water. Different treatment techniques including chemical coagulation, electrochemical coagulation, advanced oxidation processes, membrane technology, and adsorption have been applied to remove dyes from industrial wastewater. Among these, adsorption is an easy-operating, effective, and cost-effective option. Activated carbon has been employed for removal of various pollutants from wastewater, but it has high cost of regeneration. Hence low-cost adsorbents alternative to activated carbon are gaining attention in recent years. In the present study methylene blue was selected as the model dye molecule. Methylene blue adsorption kinetics and equilibrium of poly(viny) alcohol hydrogel films containing different amounts of magnetic particles were investigated. The hydrogels were synthesised by freezing-thawing method. The amounts of dye adsorbed by the hydrogels at equilibrium were in the range of 2.5–3.4 mg/g almost independent of the hydrogel magnetic particle content. The MB adsorption kinetics of the magnetic hydrogels can be represented by the pseudo-second order kinetic model and the model parameters were determined. It was not possible to desorb all the adsorbed dye by contacting the saturated hydrogels with water at 25 ℃.*

Key words: *magnetic particles, magnetic hydrogel, dye adsorption, poly(vinyl) alcohol*

1. INTRODUCTION

Many industries including textile industry use dyes extensively in different unit operations to colour their products, and as a result they generate substantial amount of colored effluent. The removal of dyes from the effluents is extremely desirable, and adsorption of dyes by low-cost and efficient adsorbents was considered as a simple and economical method for this purpose [1, 2]. In recent years, magnetic adsorbents have received increasing attention due to their facile recovery by magnetic separation from the water after the adsorption [3-6]. In the present study, authors used previously synthesized and characterized magnetic PVA hydrogels [7] with different concentrations of magnetic particles (MPs) to investigate their dye removal efficiency. Methylene blue (MB) was selected as a model dye molecule. MB adsorption by the magnetic hydrogels was studied in batch mode by contacting 5 g of hydrogel with 1 liter of the dye solution with initial concentration of 25 ppm at 25 °C for 24 hours.

2. EXPERIMENTAL PART

2.1 Dye Adsorption

MB (3,7-bis{dimethylamino}-phenazathionium chloride, $C_{16}H_{18}ClN_3S$, C.I.52015, CAS number: 61-73-4)) was obtained from Merck. The magnetic hydrogels were prepared by freezing-thawing (freezing at -20 °C for 16 hours and thawing at room temperature for 8 hours) of aqueous poly(vinyl) alcohol (PVA) solutions containing different amounts of MPs. The MPs were synthesised by co-precipitation method. The dried hydrogel discs were contacted with aqueous MB solutions with the initial concentration of 30 mg/L in the adsorbent/solution ratio of 5 g/L in a thermostated water bath (NB303, N-Biotek) at 25 ºC and shaking speed of 180 rpm for 24 hours. During the adsorption 1 mL samples taken from the supernatants at specific time intervals were analysed using UV-VIS spectrophotometer (UV-1280, Shimadzu) and the absorbance values at 668 nm were recorded. The hydrogel with the highest MP content (Film 4) was also tested for MB adsorption capacity after chopping the film and then sieving to particle size range of 150-250 μm to investigate the effect of adsorbent particle size on the adsorption kinetics. The particles obtained in this manner were labelled as Film 4-s. The synthesized MP was also contacted with the MB solution under the same conditions as for the films. At the end of the adsorption period of 24 hours, the adsorbents were separated from the solution and dried at 40 ºC until constant mass.

The amount of MB adsorbed at any time (q_t, mg MB/g adsorbent) was calculated from the following equation:

$$q_t = \left(\frac{C_o - C_t}{m} \right) V \quad \textbf{(1)}$$

where C_t is the MB concentration in the solution at time t (mg/L), C_o is the initial MB concentration in solution (mg/L), V is the volume of the dye solution (mL), and m is the adsorbent mass (g).

Table 1:*Adsorption kinetic models investigated*

Kinetic model	Equation
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
Intraparticle diffusion	$q_t = k_i \sqrt{t} + c$

Kinetic modelling gives information about adsorption mechanisms and possible rate-controlling steps such as mass transport or chemical reaction processes. For this purpose, the dye adsorption kinetics of the films was analysed using the kinetic models given in Table 1. The goodness of the fit of the experimental data to the models were deduced based on the linear regression coefficients (r^2) for the $\log(q_e\text{-}q_t)$ versus t, t/q_t versus t, and q_t versus $t^{1/2}$ plots, respectively for the pseudo-first, pseudo-second order and intraparticle diffusion models, respectively. In the model equations k_1, k_2 and k_i are the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic rate constants, respectively.

The percent MB removal at equilibrium was calculated as,

$$\text{Percent dye removal} = \left(\frac{C_e - C_o}{C_o} \right) \times 100 \quad \textbf{(2)}$$

where C_e is the dye concentration in solution at equilibrium.

2.2 Desorption Studies

To test the recyclability of hydrogels in dye adsorption, the films after the adsorption were immersed into 30 mL deionized water at 25 °C and agitated at 180 rpm. During desorption, the samples taken from the supernatants were analyzed for the absorbance values at 668 nm.Desorption efficiency (*DE*, %) was determined by the following equation,

$$DE(\%) = \frac{q_{des}}{q_{ads}} \times 100 \quad \textbf{(3)}$$

where q_{ads} and q_{des} are the amounts of dye adsorbed and desorbed by the films, respectively.

3. RESULTS AND DISCUSSION

3.1. Dye Adsorption

The MB concentration in the adsorption solution and amount of MB adsorbed by the films as well as by the MPs during the adsorption as a function of time are shown in Fig. 1. It can be seen that the adsorption equilibrium has been reached after the first hour of contact.

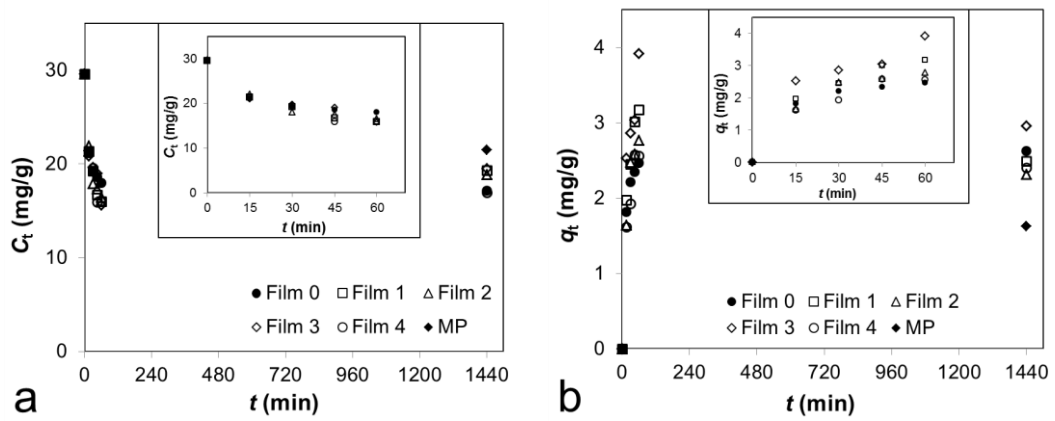

Fig. 1*: Solution MB concentration (a) and amount of MB adsorbed (b) as a function of time during adsorption (data for first 60 min of the adsorption is given in the insets).*

The amounts of adsorbed MB and percent removal values for the films and MPs at equilibrium (after 24 hours) are given in Table 2. Addition of MPs did not result in significnt change in the amount of dye adsorbed at equilibrium. Moreover the MPs added to the hydrogel did not affect the percent dye removal values remarkably. The equilibrium MB adsorption capacity of the synthesized MPs was 1.63 mg/g, lower than the PVA hydrogel without magnetic particles (Film 0). The reduction of the particle size of the Film 4 resulted in a significant decrease (46 %) in the dye adsorption capacity of the film.

Table 2: *Amounts of adsorbed MB and percent removal by the films and MPs at equilibrium*

Film	MP content of dry films (wt %)	q_e (mg/g)	removal (%)
0	0	2.55	40.4
1	2.1	2.83	40.4
2	4.0	2.56	40.4
3	6.2	3.44	40.7
4	8.1	2.52	44.2
4-s	8.1	1.37	25.7
MP	100	1.63	27.5

From the regression coefficients (r^2) for the investigated adsorption kinetic models (Table 3), it was concluded that the MB adsorption by the hydrogels can be represented by the pseudo-second kinetic model. This indicated role of interactions between the functional groups of the hydrogels and dye molecules [8]. The pseudo-second order kinetic model fittings are shown in Fig. 2 and the model parameters are given in Table 4. The data for Film 4-s was also reported.The initial dye adsorption rate (h) was calculated as follows,

$$h = k_2 q_e^2 \quad \textbf{(4)}$$

The rate of MB adsorption decreased with the MPs content of the films but increased with the size reduction of Film 4. The q_e values determined from the model fitting were found to be in good agreement with the experimental q_e values previously given in Table 2.

Table 3: *Regression coefficients (r^2) for the investigated adsorption kinetic models*

Film	Regression coefficients (r^2)		
	Pseudo-first order	Pseudo-second order	Intraparticle diffusion control
0	0.980	1.000	0.461
1	0.989	0.991	0.003
2	0.947	0.989	0.002
3	0.899	0.917	0.001
4	0.947	0.965	0.114
4-s	0.304	0.986	0.135

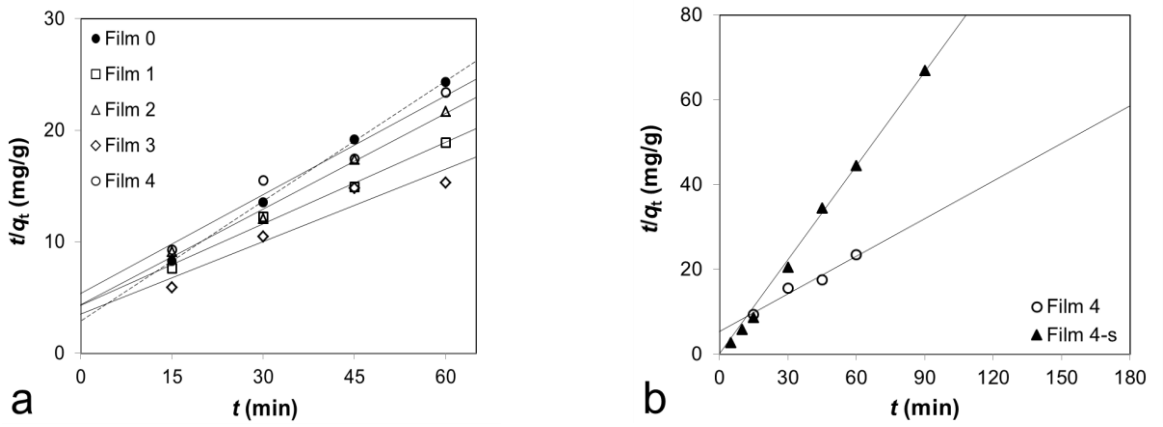

Fig. 2: *Pseudo-second order model fittings for the films (a) and for the two forms of Film 4.*

Table 4:*Pseudo-second order kinetic model fitting parameters*

Film	$q_{e,model}$ (mg/g)	k_2 (g/mg·min)	h (mL/g·min)
0	2.64	0.050	0.349
1	2.48	0.038	0.234
2	2.31	0.043	0.229
3	2.95	0.033	0.286
4	2.41	0.032	0.187
4-s	1.35	4.097	7.509

The photos of the films after crosslinking (wet), drying, swelling and MB adsorption are shown in Fig. 3. The volume of the films increased remarkably after swelling and the colourhas changed notably after the dye adsorption.

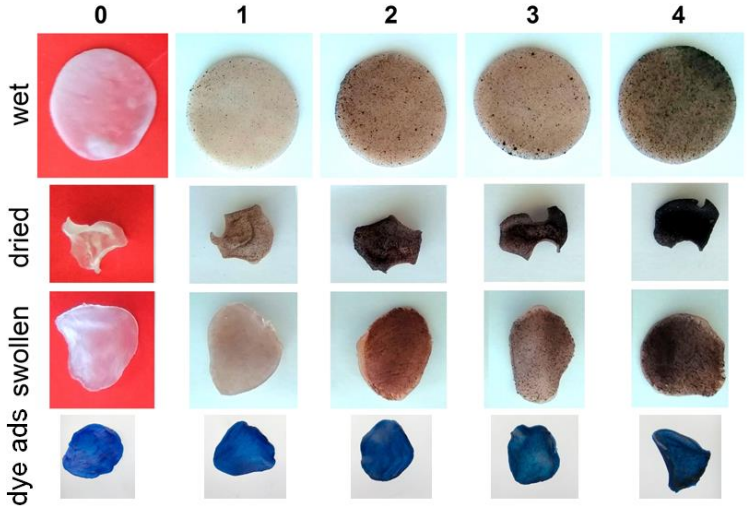

Fig. 3*: Photos of the films after crosslinking, drying, swelling and MB adsorption.*

3.2. Desorption Studies

The dye desorption efficiencies of the films were found to almost independent of the MP content (Table 5). Approximately 20 % of the dye adsorbed could be desorbed under the desorption conditions.

Table 5: *Desorption efficiency*

Films	Desorption efficiency (%)
0	19.0
1	19.5
2	22.5
3	18.4
4	19.5

4. CONCLUSIONS

The amounts of dye adsorbed by the hydrogels at equilibrium were between 2.5 mg/g and 3.4 mg/g, almost independent of the hydrogel MPs content. The equilibrium MB adsorption capacity of the synthesized MPs was 1.63 mg/g, lower than the hydrogel without the MPs. The MB adsorption kinetics of the magnetic hydrogels can be represented by the pseudo-second order kinetic model and the model parameters were determined.

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