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Studies on the Sorption Behavior of Dyes on Cross-linked Chitosan Beads in Acid Medium

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Abstract. The deacetylated chitosan(HDC) beads, cross-linked HDC-TPP beads and chemical cross-linked HDC-ECH were used to study the adsorption behavior of anionic dye (congo red or direct red 28) and cationic dye (methylene blue or basic blue 9). The adsorption studies with respect to pH, adsorbent dosage, contact time, initial dye concentration and temperature were investigated. Anionic dye removal of 87.2% by HDC-ECH beads and 81.9% by HDC-TPP beads were achieved with an optimal dosage of 3.5 g at the optimum pH of 4 in contact time, 60 min. At this pH, the highest percent dye removal of cationic dye was about 49% for HDC-ECH beads and 42% for HDC-TPP beads. The pseudo-first-order, second-order and intraparticle diffusion models were used and the rate constants and initial adsorption rates were evaluated. The data fit well with the pseudo-second-order kinetic model. The second order rate constants for HDC-ECH beads were found to be 0.0011 g mg^{-1} min^{-1}, 0.0019 g mg^{-1} min^{-1} and 0.0025 g mg^{-1} min^{-1} at 40°C, 60 °C and 80 °C respectively. For HDC-TPP beads, 0.0017 g mg^{-1} min^{-1}, 0.0029 g $mg^{-1}$$min^{-1}$ and 0.0072 g mg^{-1} min^{-1} were obtained. It was found that the rate constants increase with increasing temperature.

Keywords: Highly deacetylated chitosan beads, Cross-linking reagent, Anionic dye, Cationic dye, Adsorption.

1. Introduction

Synthetic dyestuffs in industrial effluents cause toxic to creatures in water.Hence the removal of dyes from waste effluents becomes important. Various dye removal methods are chemical oxidation by ozone, UV plus H_2O_2, anaerobic bioremediation, adsorption etc. Among them, adsorption process is one of the effective methods to remove dye from waste water. The adsorption mechanism is attributed to the gradual transition of the dye from the solution onto the surface of the adsorbent reaches a point after which distribution of the dye between the adsorbent and the solution remains constant. Suitable adsorbents used in dye adsorption process are activated carbon, silica, rice husk, coconut husk, saw dust, chitin, chitosan, cross-linked chitosan beads, etc. Many adsorbents have been tested for their removal ability but most of them are non-regenerable throwaway products. However, cross-linked chitosan beads can be easily regenerated to absorb the dye.

Chitosan is the deacetylated form of chitin and contains high contents of active sites, amino and hydroxyl functional groups. It has also high potentials of the adsorption of dyes.Other useful features include its abundance, non-toxicity, hydrophilicity, biocompatibility, biodegradability and anti-bacterial property.In acid solutions, the amino groups of chitosan are much easier to be cationized and they adsorb the dye anions strongly by electrostatic attraction. However, chitosan formed gel below pH 6. To obtain more rigid beads, the ionic cross-linker sodium tripolyphosphate (TPP) can be used. To obtain more stable and strengthen beads, the chemical cross-linkers, epichlorohydrin, glutaraldehyde, ethylene glycol diglycidyl ether can be used. In this study, cross-linker epichlorohydrin (ECH) was used.ECH cross-links chitosan molecules by

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connecting mostly with the –OH group of chitosan.Therefore, ECH does not reduce the major adsorption site (-NH3+) on chitosan attracting the anion of dye via electrostatic interaction.

In this research, the main aim is to study the adsorption behavior of dyes on cross- linked chitosan beads in acid medium then the percent dye removal from aqueous solution by using chitosan beads in industrial textile dye effluents were comparatively studied. In addition to this, the dye adsorbed beads were also recycled.

2. Experimental Procedure

Commercial chitosan was used in experimental work and the apparatus used were Mettler (Gottigen, Germany), Viscometer (Technico, England), pH meter (Jenway, England), Magnetic stirrer (Bibby Sterilin, England), Water bath (Rikakikai Co. Ltd., Japan), Spectrophotometer 259 (Ciba- Corning), Shaker bath SBS 30 (Bibby, England). The preparation, determinations and analysis were carried out according to the recommended standard procedures. During the experiments, the equipment together with the supporting facilities was used at the Department of Chemistry, Yangon University.

A batch system was applied to study the adsorption of anionic and cationic dyes from aqueous solutions by cross-linked HDC beads. More rigid chitosan beads were prepared using sodium tripolyphosphate (TPP) in acid solutions and chemical cross-linking reagent, epichlorohydrin (ECH) was used to get highest adsorption capacity. Factors affecting on the adsorption kinetics at different pH, adsorbent dosage, contact time, and temperature were determined. The six adsorption/desorption cycles of dye adsorbed chitosan beads were done. The effect of pH and adsorbent dosage on the percent dye removal of the cross-linked HDC and non-cross-linked HDC beads in ITDE solution were determined.

3. Results and Discussion

In this section, the resultant data from studies on the adsorption behavior of dyes on cross-linked chitosan beads were summerised. Anionic dye removal of 87.2% by HDC-ECH beads and 81.9% by HDC-TPP beads were achieved with an optimal dosage of 3.5 g at the optimum pH of 4 in contact time, 60 min were noted in Table 3.1 and Figure 3.1.

Table 3.1 Experimental data for adsorption of anionic dye (congo red) at different adsorbent dosages

No	Dose (g)	HDC-TPP		HDC-ECH	
		C_e (mgL^{-1})	% removal	C_e (mgL^{-1})	% removal
1	0.5	35.0	65.0	23.5	76.5
2	1.0	29.5	70.2	19.0	81.0
3	1.5	25.2	74.8	16.5	83.5
4	2.0	20.7	79.3	13.6	86.4
5	2.5	18.8	81.2	12.9	87.1
6	3.0	18.5	81.5	12.8	87.2
7	3.5	18.1	81.9	12.8	87.2

At this pH, the highest percent dye removal of cationic dye was about 49% for HDC-ECH beads and 42% for HDC-TPP beads. The data fit well with the pseudo-second-order kinetic model. The second order rate constants for HDC-ECH beads were found to be 0.0011 g mg-1 min-1, 0.0019 g mg-1 min-1 and 0.0025 g mg-1 min-1 at 40°C, 60 °C and 80 °C respectively. For HDC-TPP beads, 0.0017 g mg-1 min-1, 0.0029 g mg-1 min-1 and 0.0072 g mg-1 min-1 were obtained. The rate constants increase with increasing temperature. The thermodynamic parameter, activation energy of adsorption (Ea) was also determined. The Ea value of second-order kinetic adsorption reaction with anionic dye was found to be -17.06 kJmol-1 for HDC-ECH beads and 34.96 kJmol-1 for HDC-TPP beads. For cationic dye Ea was found to be -62.07 kJ mol-1 for HDC-ECH beads and -20.87 kJ mol-1 for HDC-TPP beads as shown in Table 3.2, Figure 3.2 and 3.3.

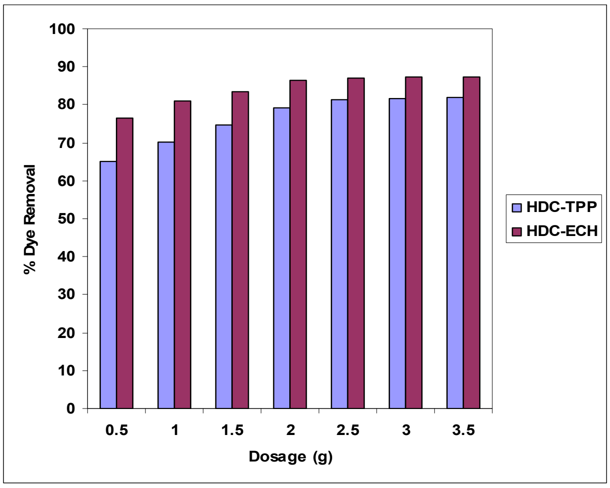

Figure 3.1 Effect of adsorbent dosage on the removal of anionic dye by HDC-TPP and HDC-ECH beads

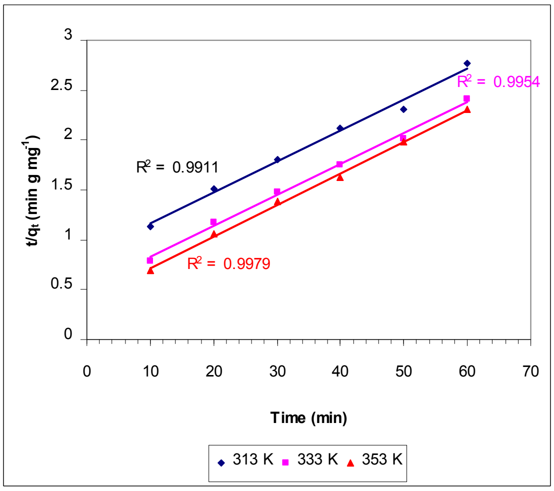

Figure 3.2 Reciprocal of dye adsorbed with contact time for anionic dye by HDC-ECH beads at different temperatures

Table 3.2 (a) Kinetic and thermodynamic data for the adsorption of anionic dye on HDC-TPP

Temp (K)	HDC-TPP		
	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	k_i (g mg^{-1} min^{-1})
353	0.0072	3.186	1.2493
333	0.0029	1.580	1.2596
313	0.0018	0.957	2.1158
E_a (kJmol^{-1})		- 34.96	

Table 3.2 (b) Kinetic and thermodynamic data for the adsorption of anionic dye on HDC-ECH beads

Temp (K)	HDC-ECH		
	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	k_i (g mg^{-1} min^{-1})
353	0.0025	2.516	2.8249
333	0.0019	1.950	3.1129
313	0.0011	1.179	3.2257
E_a (kJmol^{-1})		- 17.06	

4. Conclusion

The percent removal of typical dye such as anionic dye (congo red) and cationic dye (methylene blue) were controlled by the factors affecting on adsorption capacity such as pH, adsorbent dosage, contact time, and temperature. The adsorption capacity increases largely with decreasing pH of the dye solution. The highest percent removal of anionic dye achieved at pH 4, in contact time of 60 min, by adsorbent dose of

3.5g used and 100mg/L of initial dye concentration. When 3.0 g absorbent and 20 mg/L of initial dye concentration was used and at contact time of 60 min, the highest percent removal of cationic dye of 48.1% can be achieved. It can be concluded that the high adsorption capacity of the cross-linked chitosan beads in

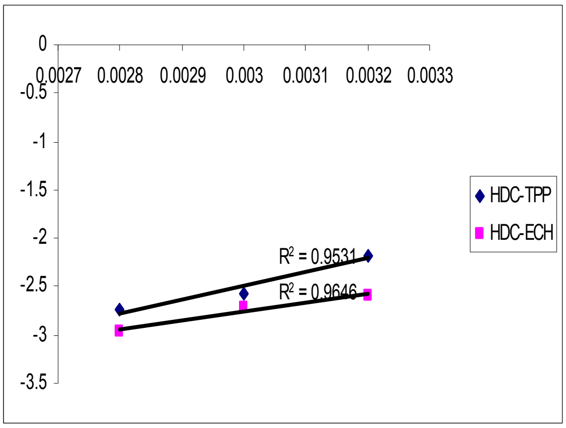

Figure 3.3 Relationship between the natural logarithm of the absorption rate constant and the reciprocal of the absolute temperature.

acidic solutions is due to the strong electrostatic interactions between its adsorption site $–NH_3^+$.The effect of temperature on adsorption was found to be an increase in the temperature leads to an increase in initial adsorption rate but the adsorption capacities at 60 min are close to each other.

The highest correlation coefficient R^2 was suggested that the dye adsorption process is predominant by the pseudo-second-order adsorption mechanism at the high temperature. The second order rate constant, k_2 increases with an increasing temperature. It was also found that the initial adsorption rate increases by one step which varies with the temperature. The intraparticle diffusion had occurred since the intraparticle diffusion rate constants (k_i) also varies with the temperature.In this study the anionic dyed loaded beads were used for recycling study by adjusting the pH at 10 where the dye uptake was minimal. It can be concluded that the decrease in efficiency was not due to deactivation of the binding sites, but due to the loss of adsorbent mass itself during the desorption process.

In the comparative study of adsorption of ITDE it was found that HDC-ECH beads has higher percent dye removal (90%) than the non- cross-linked HDC beads for dye removal(69%).

5. Recommendation

- Different cross-linkers should be applied in the preparation of cross-linked chitosan beads for further efficiency.
- Adsorption / desorption should be studied by using wet cross-linked chitosan beads
- Adsorption of cationic dyes on cross-linked chitosan beads in basic medium

6. Acknowledgement

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7. References

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