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REMOVAL OF METHYLENE BLUE DYE FROM WASTEWATER BY ADSORPTION ONTO SEMI-INPENETRATING POLYMER NETWORK HYDROGELS COMPOSED OF ACRYLAMIDE AND ACRYLIC ACID COPOLYMER AND POLYVINYL ALCOHOL

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ABSTRACT
Dye removal from wastewater has received considerable attention with several classes of dye being investigated. Methylene blue has wide applications and can cause some harmful effects in humans. The use of clean technology of low-priced and biodegradable absorbents could be a good tool to minimize the environmental impact caused by dye manufacturing and textile effluents.The present study deals with the preparation of a novel sIPN (semi interpenetrating) hydrogel composed of copolymer of acrylamide and acrylicacid with poly vinyl alcohol as linear polymer there in. The adsorption abilities of hydrogels with different molar ratios for removal of methylene blue from aqueous solutions were investigated. A weighed quantity of dry hybrid hydrogel was immersed in 50 ppm MB solution and kept at 37 ^oC. The amount of MB adsorbed was measured spectrophotometrically (λ= 661.6 nm) in periodically taken solution samples. The maximum dye adsorption concentration for hydrogel composites was 95% and no dye desorption of MB/polymer solutions was observed. Hence, the composites can be used as good membranes for removal of cationic dyes from aqueous solutions while they do not release harmful materials into water.

Key words: Hydrogel; Adsorption; Methylene blue; Semi-inpenetrating polymer network

INTRODUCTION
Methylene blue (MB) has wide applications, which include paper coloring, temporary hair colorant, dying cottons, and wools. Although not strongly hazardous, it can cause some harmful effects in humans such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis. The effluents of the manufacturing and textile industries are discarded into rivers and lakes, changing their biological life (Ho and McKay, 1998; Walker *et al*., 2003; Stydini *et al*., 2004). The problems associated with dye pollution could be reduced or minimized by physical, chemical and biological processes; for example, by microbial degradation, chemical oxidation, coagulation, or filtration and membrane separation (Gupta *et al*., 2006; Han *et al*., 2007).

Use of clean methods of low-priced and biodegradable adsorbents could be a good tool to minimize the environmental impact caused by dye manufacturing and textile effluents. Currently, adsorption process have been studied because of their low cost, easy access and effective dye removal by adsorption process in which dissolved dye compounds attach themselves to the surface of adsorbents.

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Researchers have exploited many biodegradable and effective adsorbents obtainable from natural resources for the removal of different dyes from aqueous solutions at different operating conditions. Particular attention has been paid to superadsorbent hydrogel (SAH) (Bell and Peppas, 1995; Buchholz and Graham, 1998; Crini, 2005; Sannino *et al*., 2005; Yi and Zhang, 2008). The SAH is formed of three-dimensional cross-linked polymer networks of flexible chains that are able to absorb and retain water and solute molecules. The higher water content and porous structure networks allow solute diffusion through the hydrogel structure (Bell and Peppas, 1995).

As SAH hydrogels possess ionic functional groups, they can adsorb and trap ionic dyes, such as MB, from wastewaters. The dye molecules, upon contact with water may penetrate into hydrogel, depending on physiochemical interactions that are established between dye molecules and polymer networks.

The present study deals with the preparation of a novel Semi-interpenetrating hydrogel composed of poly (acrylamide-co-acrylic acid) and polyvinylalcohol. Then the adsorption ability of the hydrogel for removal of MB from aqueous solutions was investigated. Linear polyvinyl alcohol monomers increase the strength of the gel by forming semi-interpenetrating polymer networks (sIPN). The effects of changes in the amount of acrylamide monomer, natural acrylic acid, polyvinyl alcohol (PVA) and cross linking agent on the adsorption of methylene blue have been studied. At the end, the best composition for a rigid network with a high adsorption efficiency has been determined.

MATERIALS AND METHODS

Materials

Acrylamide (AM), acrylic acid (AA), potassium hydroxide (KOH), N,N′-methylene bis acrylamide (Bis), N,N,N′,N′-tetra methyl ethylene diamine (TMED), ammonium persulfate (APS), methylene blue dye were supplied by Merck co. and polyvinyl alcohol (PVA) was purchased from Fluka. All materials were used with out further purification.

Synthesis of poly (acrylamide-co-acrylic acid) and polyvinylalcohol hydrogels

Hydrogels were synthesised through free radical polymerisation with various molar composition of acrylamide, potassium acrylate, polyvinyl alcohol and the cross linking agent. As it is demonstrated in Table 1, in each step after adding specific amounts of acrylamide, bis-potassium acrylate and polyvinyl alcohol to water, solution was mixed 30 minutes by a 300 rpm magnetic mixer. Solution was deoxygenated by means of nitrogen during the mixing process. Casting process started after adding accelerator and initiator to the solution. Total volume of solution was 15 mL in each step. PVC disk shape casts (L/D=1) were used for gel-casting. Gels were separated from the moulds two to five minutes after gel-casting; their surface were rinsed with high amounts of distilled water and were dried 72 to 96 hours in laboratory condition.

Adsorption of methylene blue

A weighed quantity of dry hybrid hydrogel (0.2 g) with different compositions was immersed in enough methylene blue (50 ppm) and kept at 37^{o}C. The amount of MB adsorbed was measured spectrophotometrically (λ: 661.6 nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant.

RESULTS

Morphology

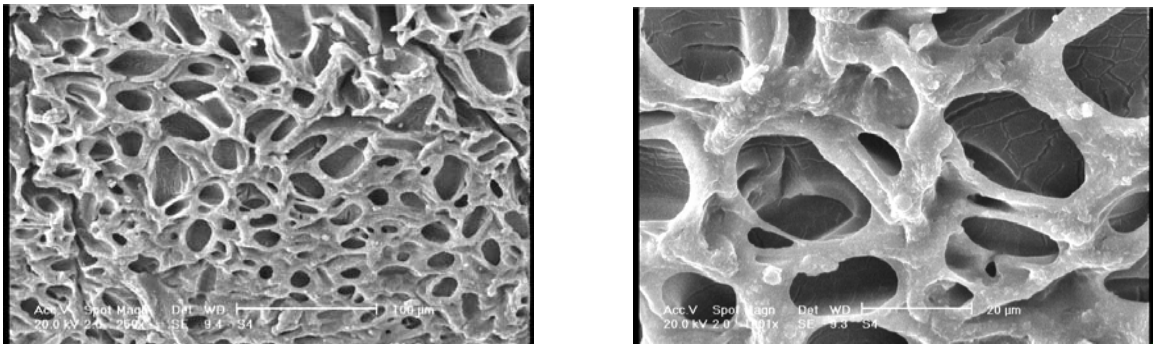
The morphology of dry poly (acrylamide-co-acrylic acid) and polyvinylalcohol hydrogels was observed using Scanning Electron Microscope (SEM). SEM observation shows the uniform and porous structure for poly (acrylamide-co-acrylic acid) and polyvinylalcohol. Figs.1a and 1b, respectively.

Effect of acrylamide on adsorption of methylene blue

A sample with the molar ratio of acrylamide ranging from 0-2.5 was used to study the effect of the amount of acrylamide on the network and adsorption of MB. Fig. 2 demonstrates the concentration of adsorbed MB or removal

Table1: Composition (Molar ratios) of reactants hydrogels

Sample code	Acrylamide molar ratio	Acrylic acid molar ratio	PVA awmolar ratio	Bis-acrylamide molar ratio
1-1	0	1	2×10^{-4}	0.05
1-2	0.5	1	2×10^{-4}	0.05
1-3	1	1	2×10^{-4}	0.05
1-4	1.5	1	2×10^{-4}	0.05
1-5	2	1	2×10^{-4}	0.05
1-6	2.5	1	2×10^{-4}	0.05
2-1	1.5	0	2×10^{-4}	0.05
2-2	1.5	0.5	2×10^{-4}	0.05
2-3	1.5	1	2×10^{-4}	0.05
2-4	1.5	1.5	2×10^{-4}	0.05
2-5	1.5	2	2×10^{-4}	0.05
2-6	1.5	2.5	2×10^{-4}	0.05
3-1	1.5	2	0	0.05
3-2	1.5	2	1×10^{-4}	0.05
3-3	1.5	2	2×10^{-4}	0.05
3-4	1.5	2	3×10^{-4}	0.05
3-5	1.5	2	4×10^{-4}	0.05
3-6	1.5	2	5×10^{-4}	0.05
4-1	1.5	2	2×10^{-4}	0.05
4-2	1.5	2	2×10^{-4}	1
4-3	1.5	2	2×10^{-4}	0.15
4-4	1.5	2	2×10^{-4}	0.2



(a) **(b)**

Fig. 1: SEM photographs of sIPN with the best molar ratio, a): poly (acrylamide-co-acrylicacid) and b): poly (acrylamide-co-acrylicacid) with close view

efficiency for different acrylamide composition versus time. As it is shown, the adsorption rate increased as the amount of acrylamide increased upto molar ratio of 1.5 for higher molar ratios, the adsorption rate decreased. Therefore, molar ratio of 1.5 led to maximum amount of adsorption rate.

Effect of acrylic acid on adsorption of methylene blue

Fig.3 demonstrates the adsorption rate of network versus time for different compositions of acrylic acid. As the amount of acrylic acid increases to 2 percent, the adsorption rate increased. It seems, increasing of adsorption was because of increasing the COO^- groups in polymer network. In addition, formation of electrostatistic repellent

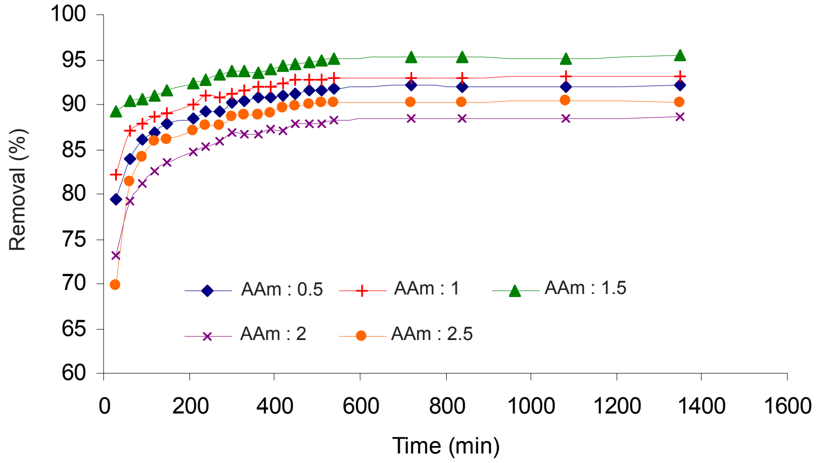


Fig. 2: Removal efficiency vs. time for different compositions (molar ratios) of acrylamide

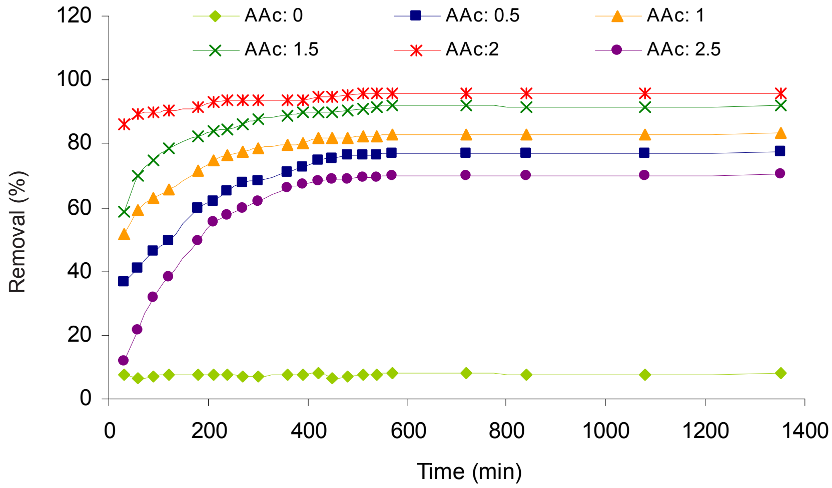


Fig. 3: Removal efficiency vs. time for different compositions (molar ratios) of potassium acrylate

due to existence of similar charges on network polymeric chain leads to less application of it to adsorption of MB. Therefore, the potassium acrylate composition of 2 percent was chosen in this step due to its maximum adsorption of MB.

Effect of polyvinyl alcohol on adsorption of methylene blue

Fig.4 shows the tendency to equilibrium adsorption of the synthesized hydrogel with various amounts of PVA. As the amount of PVA increases upto molar ratio of 2×10^{-4} , the adsorption rate decreased but the final amount of adsorption remained constant. So the best composition of PVA for adsorption of MB was determined as 2×10^{-4}.

Effect of N,N'-methylene bis acrylamide on adsorption of methylene blue

Figure.5 represents the various adsorption rate with time for different compositions of bis-acrylamide. As the amount of bis-acrylamide increased from 0.05 to 0.2, the adsorption rate decreased. However, more increase in the amount of crosslinking agent resulted in formation of more branches on the network, which decreased

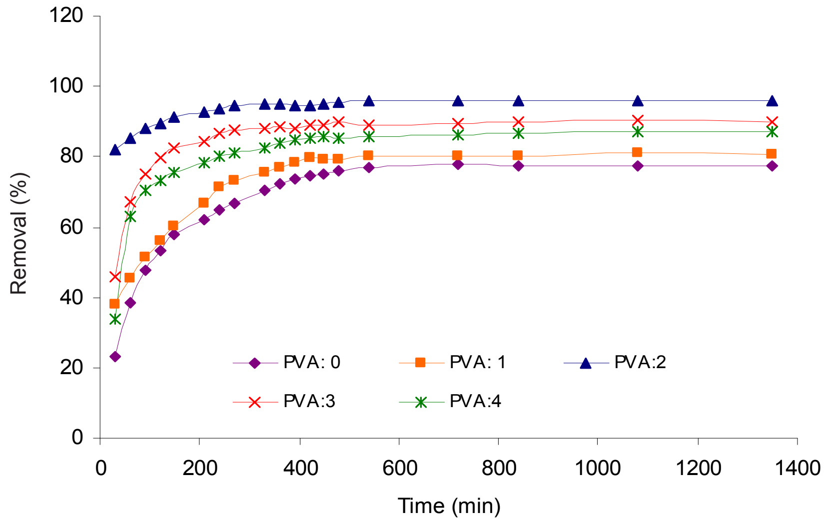


Fig. 4: Removal efficiency vs. time for different compositions (molar ratios) of PVA

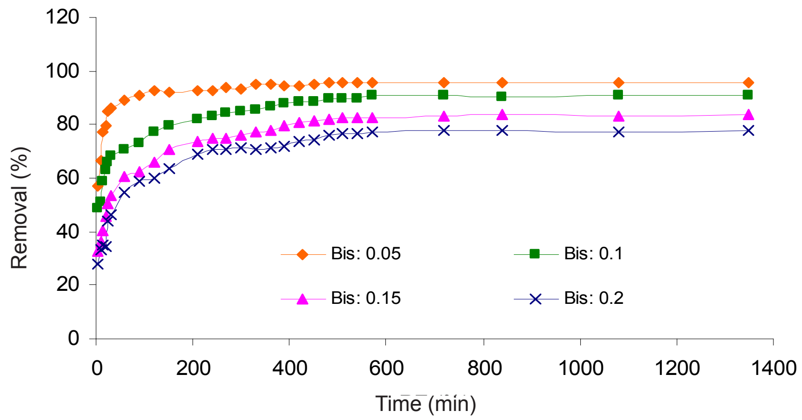


Fig. 5: Removal efficiency vs. Time for different compositions (molar ratios) of bis-acrylamide

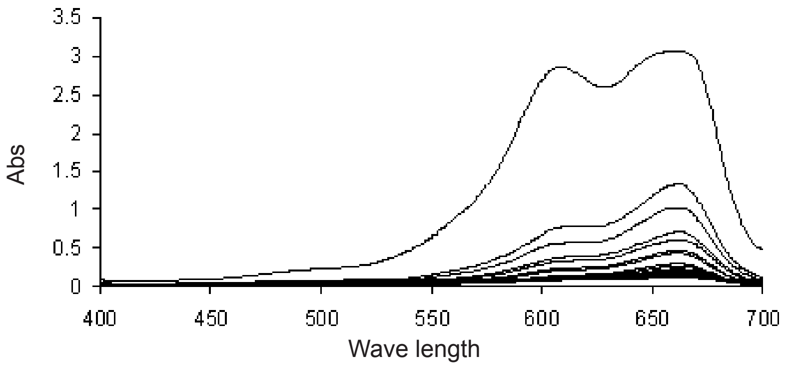


Fig. 6: Spectrum of MB in aqueous solution with synthesized sIPN

the free volume for dye diffusion. Hence, the adsorption rate decreased as well. In addition, increasing of bis-acrylamide led to a stronger but less flexible network.

DISCUSSION

sIPN hydrogels composed of poly(acrylamide-co-acrylic acid) and polyvinylalcohol were synthesized and the percent of adsorption of MB on the hydrogels was determined. Fig.6 shows the spectra of MB in aqueous solution before and after removal by sIPN. As it is demonstrated, the absorbance of MB decreased with time. It was also observed that 95% of MB was adsorbed by synthesized hydrogel. The best molar ratio for the final hydrogel were determined as 1.5 for acrylamide, 2 for acrylic acid, 2×10^{-4} for PVA and 0.05 for bis-acrylamide. This effect was attributed to the formation of ionic complex between the imine groups of MB and the ionized carboxylic groups of sIPN. In addition, no desorption was seen even after afew months.

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REFERENCES

Bell, C. L., and Peppas, N. A., (1995). Biomedical membranes from hydrogels and interpolymer complexes. *Adv. Polym*. Sci. **122**: 125.

Buchholz, F. L.,Graham, T., (1998). Modern Superadsorbent Polymer Technology. Wiley- VCH, New York, Chapter 1:4.

Crini, G., (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci*. **30**:38.

Gupta, V. K., Mittal, A., Krishnan, L., Mittal, J.,(2006). *J. Colloid Interface Sci*. **293**:16.

Han, R., Wang, Y., Zou, W., Wang, Y., Shi, J., (2007). *J. Hazard. Mater*. **145**:331.

Ho, Y. S., McKay, G., (1998). The kinetic of sorption of basic dyes from aqueous solution by sphagnum Moss peat. Can. *J. Chem. Eng*. **76**: 822.

Sannino, A., Pap pada, S., Madaghiele, M., Maffezzoli, A., Ambrosio, L., Nicolais, L., (2005). Cross-linking of Cellulose derivatives and hyaluronic acid with water-soluble carbodiimide. *Polymer*, **46**: 11206.

Stydini, M., Dimitris, I. K., Verykios, X. E., (2004). Visible light-enduced photocatalytic degradation of acid orange 7 in aqueous TiO_2 suspensions. *Appl. Catal. Environ*. **47**:189.

Walker, G. M., Hansen, L., Hanna, J. A., Allen, S. J., (2003). Kinetics of a reactive dye adsorption onto dolomitic sorbents. *Water Res*. **37**: 2081.

Yi, J., Zhang, L., (2008). Removal of methylene blue dye from aqueous solution by adsorption onto sodium humate/ polyacrylamide/clay hybrid hydrogels. *Biores. Technol*. **99**: 2182.