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Adsorption of Some Dyes on Cationic Poly(N,N-Dimethyl Amino Ethyl-methacrylate) Hydrogels

Dilek Şolpan*, Murat Şen, Zeynep Kölge, Murat Torun, Olgun Güven

Hacettepe University, Department of Chemistry, Ankara, Turkey

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Abstract

In this study, radiation synthesis of poly(N,N-dimethylamino ethylmethyacrylate) P(DMAEMA) hydrogels and their use in the adsorption of some dyes have been investigated. For the preparation of P(DMAEMA) hydrogels, the aqueous solution of N,N-dimethylaminoethyl methacrylate (DMAEMA) monomer was mixed with cross-linking agent, ethylene gylcol dimethacrylate (EGDMA) in different compositions and these mixtures were irradiated in ^{60}Co-gamma source at 3.4 kGy dose. For the determination of percentage swelling of prepared hydrogels in dye solutions, swelling experiments were followed in dye solutions at pH 4.0-7.0. Adsorption isotherms were constructed for P(DMAEMA)-dye systems.

INTRODUCTION

Water is the most important natural resource in the world since without it life can not exist and most industrial activities could not operated. Its quantity and quality are crucial. Color in wastewater may be due to presence of colored organic substances or highly colored industrial wastes. Pulp, paper and textile wastes are common as sources of coloring water. The removal of color from textile waste waters is a major environmental problem because of the difficulty of treating such waters by conventional methods. Most of the water treatment technologies practiced in both developed and developing countries look simple but attention must be given to their cast and appropriateness. Technologies such as membrane filtration are certainly very effective but at present the cost involved is prohibitive. Dye color removal by adsorption onto poly-electrolyte carriers is better option.Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole % to 100 of the repeating units. Poly-electrolytes may be anionic, cationic or amphophilic, and may be synthetic or naturally occurring [1,2]. Much attention has been directed in recent years to poly-electrolyte type hydrogels that undergo controllable volume changes in response to small variation in solution conditions. Temperature and pH have been the solution variables in typical physiological, biological and chemical systems [3].

* Correspondence to: Dilek Şolpan,

Hacettepe University, Department of Chemistry, 06800, Beytepe-Ankara, Turkey

Tel: +90312 297 7990 Fax: +90312 299 2163

E-mail: solpan@hacettepe.edu.tr

Temperature and pH sensitive gels have been suggested for use in a variety of novel applications including controlled drug delivery [4,5], immobilized enzyme systems [6] and separation processes [7,8].

Adsorptive and binding capacities of anionic polymers such as acrylamide/maleic acid and acrylamide/itaconic acid based hydrogels were utilized in the removal of some cationic dyes from aqueous solutions. While pure acrylamide hydrogels showed no adsorption towards a number of basic dyes tested, the presence of diprotic acids in these gels significantly increased their adsorptive capacities. The results of batch adsorption studies on some cationic dyes such as basic red, basic green, cresyl violet, basic blue, and basic violet from aqueous solutions onto acrylamide/maleic acid [9] and acrylamide/itaconic acid [10] hydrogels have shown the beneficial effect of diprotic acid moieties. The adsorption studies clearly showed that these superswelling hydrogels are potential adsorbents to be used for the removal cationic dyes from waste-waters and aqueous effluents.

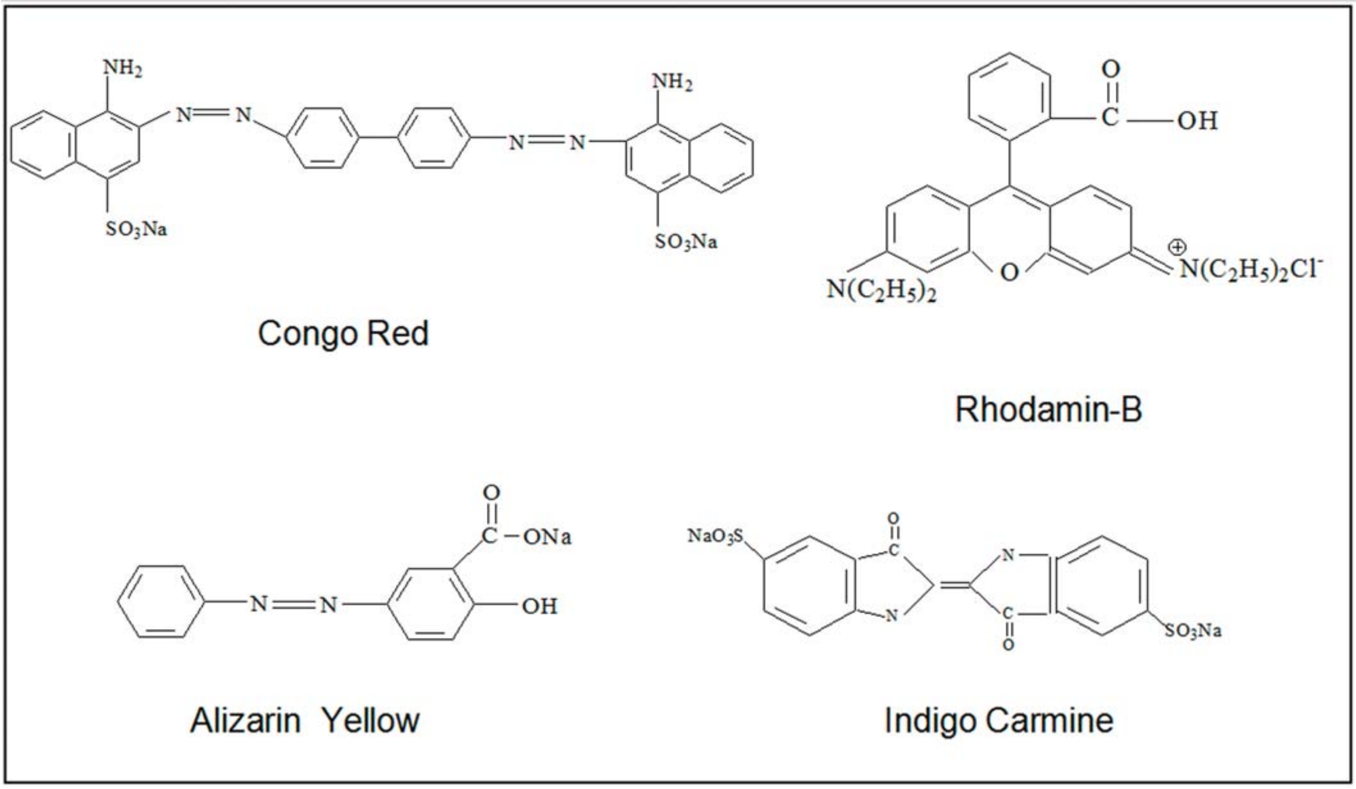
In this study, we investigated adsorption and separation of anionic dyes by using cationic P(DMAEMA) hydrogels. The effect of dye structure and adsorption conditions have also been investigated in response to changes in the pH of the adsorption media.

MATERIALS AND METHODS

The monomers used in this study, N,N-dimethyl-aminoethyl methacrylate (DMAEMA) and cross-linking agent, ethylene glycol dimethacrylate (EGDMA), were obtained from Aldrich (St. Louis, USA). Dye compounds, Alizarin Yellow (AY), Congo Red (CR), Indigocarmine (IC), and Rhodamin B (RB) were obtained from BDH (BDH Chemicals Ltd., Poole, UK). The chemical formulas of dyes are given in Scheme 1.

Preparation of Hydrogels

Three components were used in the preparation of poly(dimethylamino ethylmetacrylate) P(DMAEMA) hydrogels namely, N,N-dimethylaminoethyl



Scheme 1. The structures of dyes.

methacrylate (DMAEMA), ethylene glycol dimethacrylate (EGDMA), and water. For the preparation of monomer mixtures, firstly, 4 mL DMAEMA mixed with 11, 22, 44, and 88 mL EGDMA, then, these solutions were mixed with water. The amount of water in the final mixtures was 25% (w/w) (DMAEMA:EGDMA mol ratios; 99.72:0.28, 99.43:0.57, 98.87:1.13, 97.77:2.23). Monomer solutions, thus, prepared were placed in PVC tubes of 4 mm diameter and irradiated up to 4.0 kGy in Gammacell-220 type γ-irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogels obtained in long cylindrical shapes were cut into pieces of 3-4 mm and stored for later evaluations. Gelation (100 %) was achieved for all mixtures at 3.4 kGy irradiation. So, the initial mole percentages of DMAEMA to prepare P(DMAEMA)-1, P(DMAEMA)-2, P(DMAEMA)-3, P(DMAEMA)-4 hydrogels are 99.72, 99.43, 98.87 and 97.77, respectively.

Adsorption Studies

For the determination of dye uptake capacity of hydrogels, about 0.1 g of DMAEMA hydrogels were transferred into 50 mL of dye solution at desired pH (pH 2.0-8.0) and allowed to equilibrate for 24 hours at 25°C. These aqueous solutions were separated by decantation from the hydrogels. Concentration measurements were carried out by using Philips 8510 model UV-VIS spectrophotometer at ambient temperature. The absorbances of Alizarin Yellow (AY), Congo Red (CR), Indigo Carmine (IC), and Rhodamin-B (RB) solutions were measured at 352, 500, 610, 553 nm wavelengths, respectively.

RESULTS AND DISCUSSION

Swelling Behaviours of Hydrogels in Dye Solutions

The water intake of initially dry hydrogels in dye solutions containing in various amounts of cross-linking agent was monitored gravimetrically. The dynamic swelling curves of P(DMAEMA) hydrogels in dye solutions are given in Figures 1-4. Percentage swellings of P(DMAEMA)1-4 hydrogels were determined as 312, 307, 255, and 190% in pure water at pH 7. As can be seen from these figures, the equilibrium swelling values of hydrogels are slightly lower in dye solutions (50 ppm) than in water. This decrease was attributed to the adsorption of dye compounds in the gel system and exclusion of water molecules and increase of the ionic strength of the swelling solution. It has been determined and known that due to Donnan effect the equilibrium swelling value of P(DMAEMA) hydrogels is very sensitive to the ionic strength of the swelling solution [11].

Effect of Dye concentration on adsorption

The effect of initial concentration of dye on the adsorption capacity of P(DMAEMA) hydrogels at 25ºC and pure water solution at pH = 7.0 are given in Figures 5-8. The mass of adsorbate per unit mass of adsorbent q_e, can be calculated from the following equation [4,12]:

$$q_e = [(C_o - C_e)V]/W \quad (1)$$

q_e : the amount of dye adsorbed per unit mass of the P(DMAEMA) hydrogels (mg g^{-1})
C_o: initial concentration of dye solution (mg L^{-1})
C_e: equilibrium concentration of dye solution (mg L^{-1})
V: volume of dye solution (L)
W: the amount of dry hydrogel (g)

As can be seen from Figures 5-8, q_e values of P(DMAEMA) hdyrogels were increased with the concentration of dye solution but it is clear that q_e values decreased at all initial dye concentrations with the increasing of content of crosslinking agent, EGDMA. Figure 5 also shows that the Congo Red adsorption capacity of all hydrogel systems first increase with an increase in the initial congo red

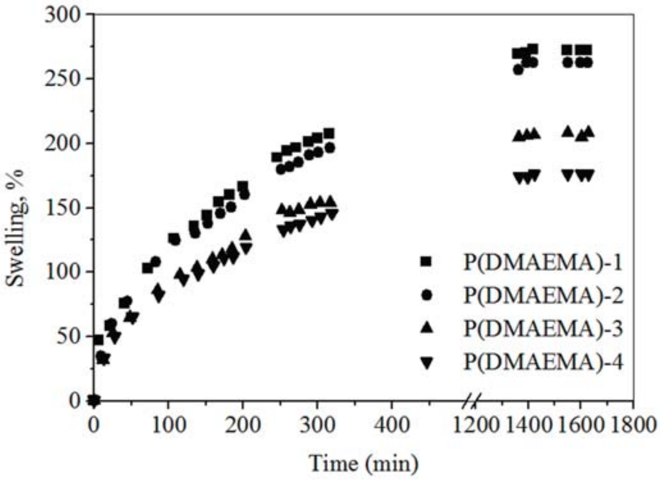


Figure 1. Swelling curves of P(DMAEMA) hydrogels in Alizarin Yellow solution.

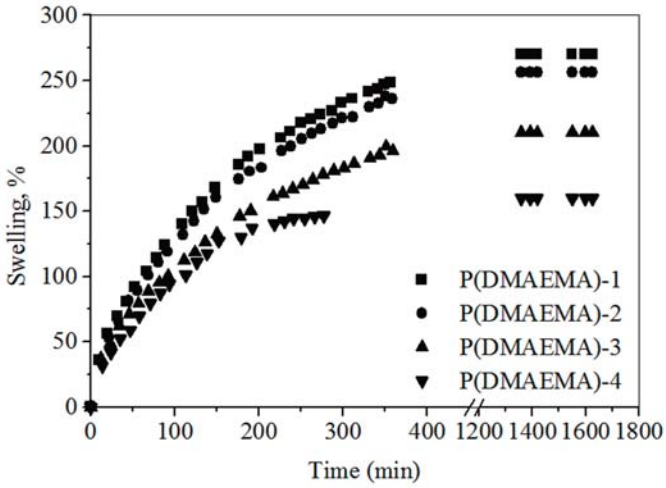


Figure 2. Swelling curves of P(DMAEMA) hydrogels in Congo Red solution.

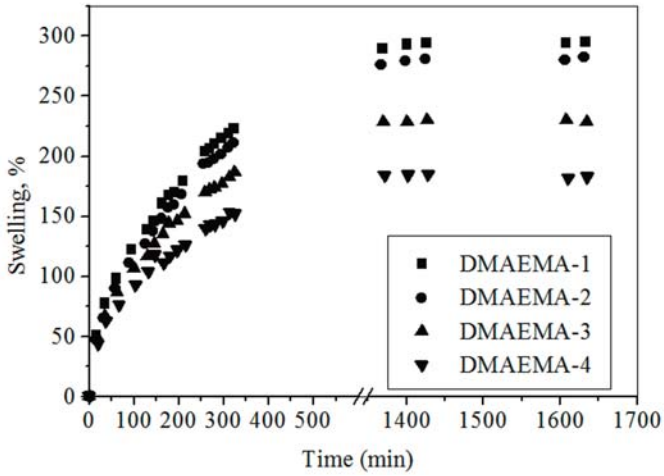


Figure 3. Swelling curves of P(DMAEMA) hydrogels in Indigo Carmine solution.

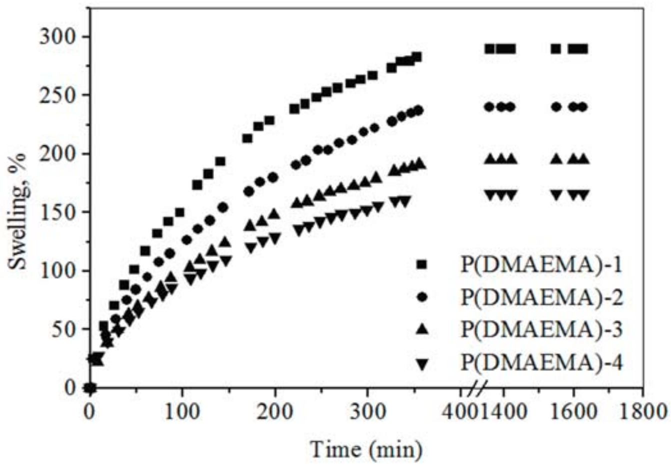


Figure 4. Swelling curves of P(DMAEMA) hydrogels in Rhodamin-B solution.

concentration and then reaches a plateau value (at about 500 ppm initial Congo Red concentration). On the otherhand, due to solubility limitations this plateau values were not observed in the other dyes.

Effect of pH on Dye Adsorption

For the investigation of the effect of external stimuli on the adsorption of dyes, initially the effect of pH was examined at pH 3.0. The extent of adsorbed dye at pH 3.0 for CR and IC are given in Figures 9 and 10. Due to precipitation of AY and RB dyes at this pH value the effect of pH on the adsorption capacities of hydrogels couldn't be investigated. As can be seen from these figures, the amount of adsorbed dye increases with decreasing pH of the solution. It has been determined that the equilibrium swelling of P(DMAEMA) hydrogels are very sensitive to pH changes of the surrounding solution, and hydrogels swell at low pH due to protonization and subsequent electrostatic repulsions of protonized groups and shrink at high pH with deprotonization. Increase in adsorption capacity of hydrogels is the result of this deionization and increasing intermolecular interactions between the positively ionized hydrogel and dye molecules.

The effect of pH on the adsorption capacity of hydrogels was also examined at basic region (pH 8.0). However, at this pH value for all hydrogel systems any adsorption was not observed. This sharply decrease in adsorption capacity of hydrogels was attributed to deprotonization of hydrogel and decrease in intermolecular interactions between the hydrogel and dye molecules.

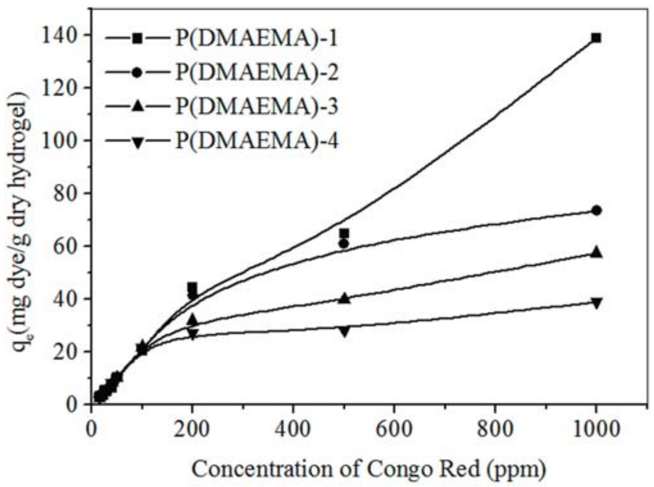


Figure 5. Effect of CR concentration on the adsorption capacity of hydrogels at pH 7.

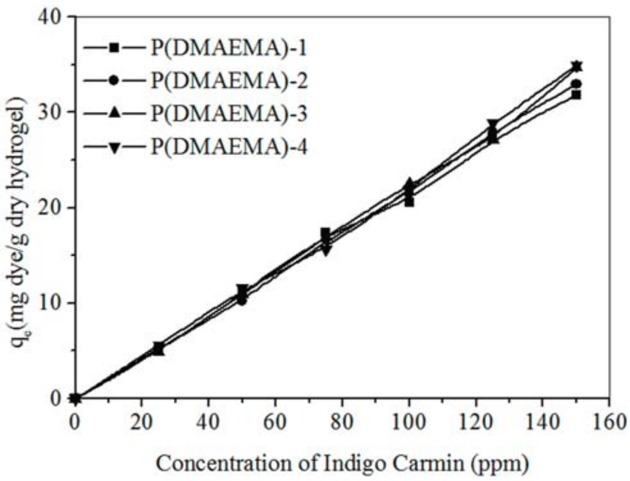


Figure 6. Effect of IC concentration on the adsorption capacity of hydrogels at pH 7.0.

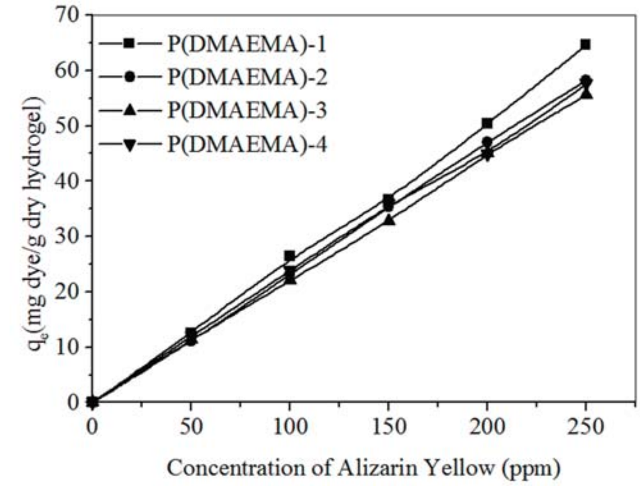


Figure 7. Effect of AY concentration on the adsorption capacity of hydrogels at pH 7.0.

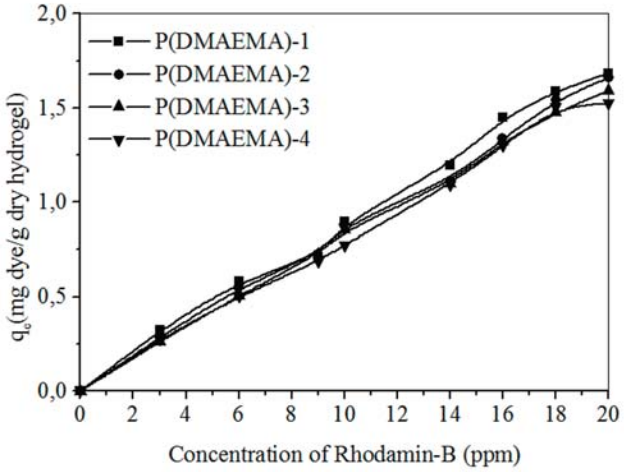


Figure 8. Effect of RB concentration on the adsorption capacity of hydrogels at pH 7.0.

Determination of Dye Adsorption Type

For the determination of dye adsorption type and the mass of dye adsorbed per unit mass of adsorbent in forming a complete monolayer on the surface q_{max} the adsorption isotherms are evaluated by Langmuir equation. The adsorption data of dyes at pH 7.0 were used for these evaluations [13,14].

$$q_e = nKC/(1 + KC) \quad (2)$$

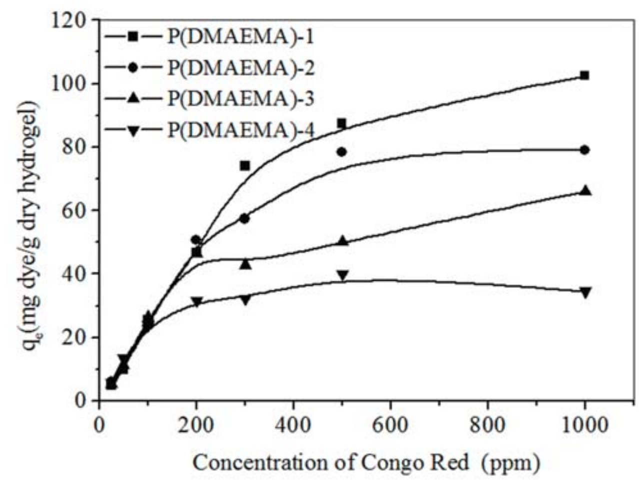


Figure 9. Effect of CR concentration on the adsorption capacity of hydrogels at pH 3.0.

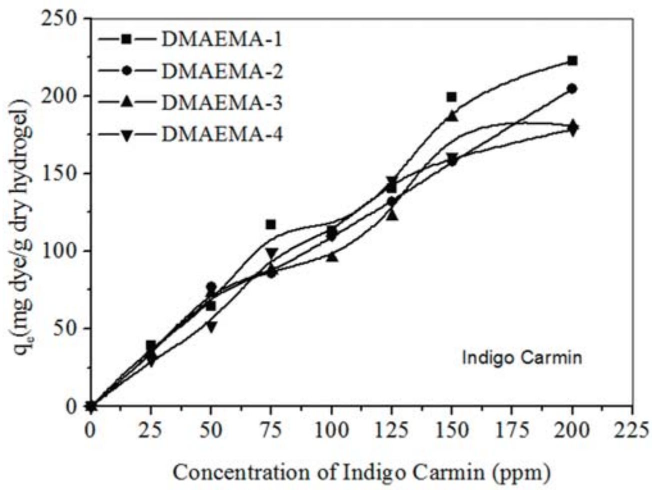


Figure 10. Effect of IC concentration on the adsorption capacity of hydrogels at pH 3.0.

Table 1. K_L, a_L and q_{max} values for the adsorption of Congo Red, Indigo Carmine and Alizarin Yellow.

Dye	P(DMAEMA)-1			P(DMAEMA)-2			P(DMAEMA)-3			P(DMAEMA)-4		
	K_L	a_L	q_{max}	K_L	a_L	q_{max}	K_L	a_L	q_{max}	K_L	a_L	q_{max}
AY	1786	20.8	85.7	1639	23.0	71.3	2174	35.7	60.8	24.4	41.7	58.5
CR	1.04	$6.6x10^{-3}$	157.5	1.25	$1.6x10^{-2}$	80.6	1.19	$2.1x10^{-2}$	57.7	0.82	$1.8x10^{-2}$	46.6
IC	8.01	0.25	32.2	4.88	0.20	24.0	7.42	0.26	28.3	13.0	0.56	23.4
CR (pH 3)	2.14	$2.1x10^{-2}$	111.4	12.9	$3.2x10^{-2}$	74.9	2.41	$3.2x10^{-2}$	74.9	33.33	94.9	35.1
IC (pH 3)	1.65	$2.6x10^{-3}$	620.2	1.46	$2.0x10^{-3}$	719.1	1.51	$3.0x10^{-3}$	497.0	1.34	$1.8x10^{-3}$	723.1

where, n is a temperature-independent constant which is supported to represent a fixed number of surface sites, K is a temperature dependent equilibrium constant and equal to a_L/K_L. The K_L/a_L ratio is defined as capacity factor(q_{max}) and the mass of dye adsorbed per unit mass of adsorbent in forming a complete monolayer on the surface. The linear form of Langmuir equation is given below.

$$C_e/q_e= [1/(K_L)] + (a_L/K_L)C_e \quad (3)$$

The linear form of the Langmuir equation was used for the determination of K_L, a_L and q_{max} values. C_e /q_e versus C_e curves of Alizarin Yellow, Congo Red, and Indigo Carmine are given in Figures 11-13.

The values calculated for these three dye are collected in Table 1. As can be seen in Table 1 where q_{max} values decreased with increasing cross-link in the gel system, they showed a variation with changing dye structure. Maximum dye adsorption on the P(DMAEMA) hydrogels at pH 7 was observed in Congo Red and at pH 3 in Indigo Carmine. However, a linear relation was not observed when Rhodamin-B adsorption analyzed by using Langmuir equation. A linear relation was obtained when the adsorption data of Rhodamin-B analyzed by Freundlich equation.

$$q = KC^{1/n} \quad (4)$$

where, K and n are empirical constants dependent on the rate of solid and adsorbate and on the temperature. C is the equilibrium concentration of the solute in the solution in mg/L. q is the amount of solute adsorbed onto the unit mass of the adsorbent for certain period of time, respectively (mg/L). According to the Freundlich equation, the amount of adsorbed increases indefinitely with increasing concentration or pressure.

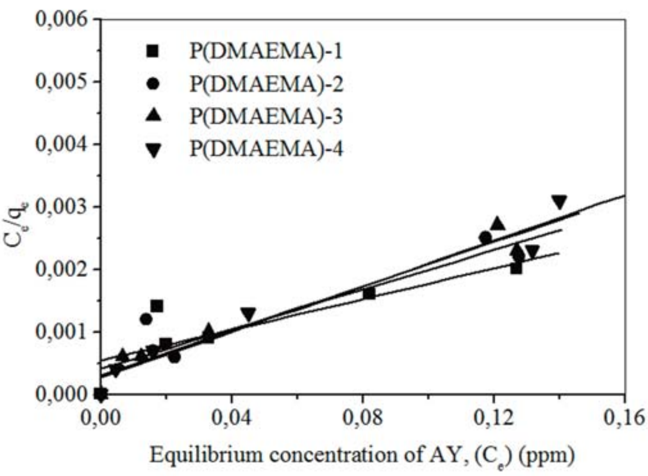


Figure 11. Langmuir isotherms of AY solution.

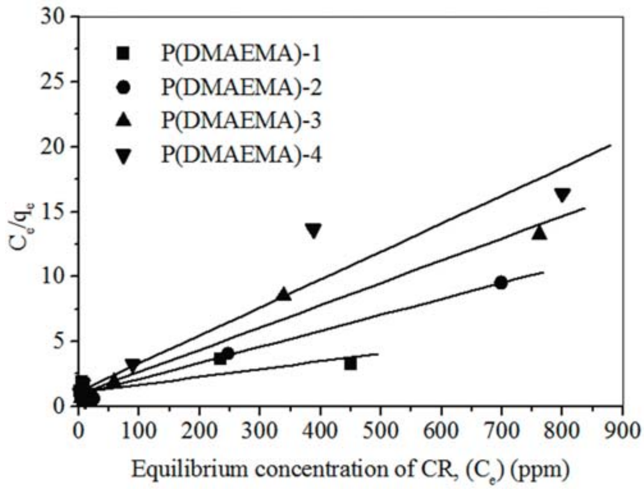


Figure 12. Langmuir isotherms of CR solution.

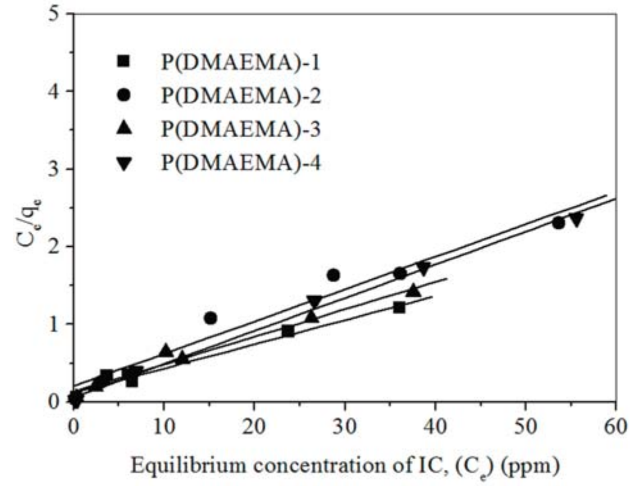


Figure 13. Langmuir isotherms of IC solution.

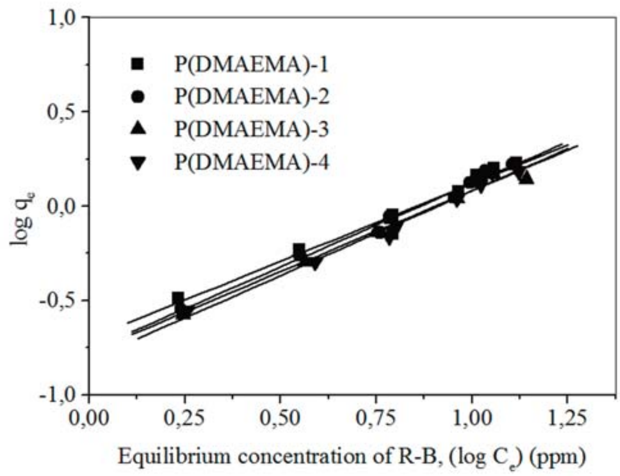


Figure 14. Freundlich isotherms of RB solution.

The variation of log q_e versus logC_e for Rhodamin-B is given in Figure 14. These results also indicate that adsorption of Rhodamin-B must be purely a physical process with no change in the configuration of the molecules in the adsorbed state.

CONCLUSION

In this study, the preparation of P(DMAEMA) hydrogels and dye adsorption behaviours have been investigated. It has been found that adsorption capacity of hydrogels decreased with increasing cross-link density of gel system. This has been explained due to decrease of dye diffusion into the hydrogel system. Adsorption studies show that one of the basic parameters affecting the dye adsorption behaviour of P(DMAEMA) hydrogels is the type of the dye. The pH of the dye solution is another important factor for the dye uptake capacity of P(DMAEMA) hydrogels. To conclude, the P(DMAEMA) hydrogels can be considered as potential adsorbing systems for the removing of some dyes from wastewaters.

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