A study on the adsorption of some cationic dyes onto acrylamide/itaconic acid hydrogels

Erdener Karadağ [1, *], **Dursun Saraydın** [1], **Olgun Güven** [2]

[1] Cumhuriyet University, Department of Chemistry, 58140 Sivas, Turkey
[2] Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey

Summary

Acrylamide/itaconic acid (AAm/IA) hydrogels prepared by irradiating with γ radiation were used in experiments on the adsorption of some cationic dyes such as basic red 9 (BR 9), basic green 4 (BG 4), cresyl violet (CV), and basic blue 20 (BB 20). Adsorption of the cationic dyes onto AAm/IA hydrogels is studied by batch adsorption technique. In the experiments of the adsorption, Langmiur type adsorption in the Giles classification system was found. Monolayer coverages for AAm/IA hydrogel-dye systems were calculated by using B point method. Adsorption studies indicated that monolayer coverages of AAm/IA hydrogel by these dyes were increased with following order; BB 20> CV > BR 9 > BG 4.

Introduction

Hydrogels are water-swellable, three-dimensional polymeric networks. The capacity of the hydrogels to absorb water is enormous and can be as much as 1000 times the mass of polymer. For this reason they are used in many fields. Some of the applications of hydrogels are in the food industry (as thickening agent, etc.), pharmaceutical (as controlled release preparations, etc.), agriculture and related fields (in controlled release of moisture, fertilizer, pesticide etc.), as technical and electronic instruments (as protector from corrosion, and short circuit etc.) biomedicine (as artificial organs etc.), bioengineering (in biomolecule immobilization), veterinary, photographic technology and adsorbent on removal of some unwanted agent in environmental applications (1, 2).

Color in drinking water may be due to presence of colored organic substances or highly colored industrial wastes, of which, pulp and paper and textile wastes are common. Highly colored, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is known. It is known that the organic coloring materials in water stimulate the growth of many aquatic micro-organisms (3,4).

---

* Corresponding author

The removal of color from textile waste waters is a major environmental problem because of the difficulty of treating such waters by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions (5,6).

In our previous works, adsorption of protein such as bovine serum albumin (7,8), uranyl ions, some heavy metal ions (9,10) and some cationic dyes (11) by acrylamide/itaconic acid and acrylamide/maleic acid hydrogels have been investigated.

The present paper is aimed to study a convenient method for removing some cationic dyes from water by adsorption on a new polymeric adsorbent such as acrylamide/itaconic acid (AAm/IA) hydrogels. Water-soluble cationic dyes, basic red 9 (BR 9), basic green 4 (BG 4), cresyl violet (CV), and basic blue 20 (BB 20) resemble the large molecular dyes found in waste waters.

Experimental

Acrylamide (AAm) and itaconic acid (IA) monomers were obtained from BDH (Poole, UK), basic red 9 (BR 9), basic green 4 (BG 4), cresyl violet (CV), and basic blue 20 (BB 20) cationic dyes were obtained from Merck (Darmstadt, Germany). Some properties of dyes are listed in Table 1.
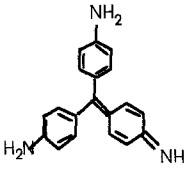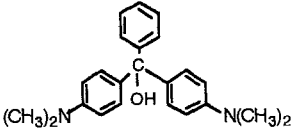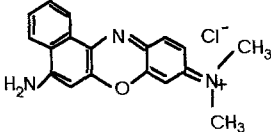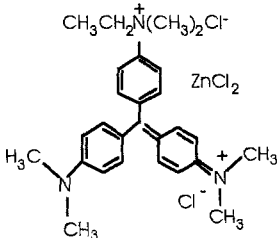
Preparation of hydrogels

Suitable quantities of itaconic acid and irradiation doses for acrylamide and itaconic acid hydrogels were selected based upon results from experiments (12). One g of acrylamide was dissolved in 1 mL of the aqueous solutions with 0, 20, 40, 60 mg of itaconic acid. These solutions were placed in PVC straws of 3 mm diameter and irradiated. Doses of 2.60, 3.73, 4.65, 5.20 and 5.71 kGy in air at ambient temperature in a Gammacell 220 type γ irradiator were applied at a fixed rate of 0.72 kGy h^{-1}. Hydrogels obtained in long cylindrical shapes were cut and dried first at air and then in a vacuum.

Adsorption of dyes

The synthetic aqueous solutions of cationic dyes were prepared in the concentration ranges; 4-20 mg L^{-1} for BR 9, BG 4 and CV, and 10-50 mg L^{-1} for BB 20. 0.1 g of AAm/IA hydrogel containing 60 mg IA and irradiated to 5.71 kGy were transferred into 50 mL of the synthetic aqueous solutions of the dyes, and allowed the equilibrate for 24 hours at 25 °C. These solutions were separated by decantation from the hydrogels. Spectrophotometric measurements were carried out using a Shimadzu 160 A model UV-VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at the wavelengths given in Table 1 (13). Distilled water was chosen as the reference. The equilibrium concentrations of dyes solutions were determined by means of precalibrated scales.

Table 1. Some properties of dyes (13)

Name	Chemical Formula	Molar Mass	C. I. Nr.	λ_{max}, /nm
Basic red 9		305.38	42 500	544
Basic green 4		346.48	42 000	617
Cresyl violet		321.34	51 180	596
Basic blue 20		458.48	42 590	630

Hydrogels separated from the dye solutions were left for 3 days in the distilled water at 25 °C to investigate their desorption.

The influences of IA content in hydrogel and irradiation doses were investigated for uptake of dyes within AAm/IA hydrogels. Hydrogel (0.1 g) prepared with different IA contents and irradiation doses were put into 50 mL of dye solutions in the suitable concentrations and left for 24 hours at 25 °C. Spectrophotometric methods were used to follow the concentrations of these dyes solutions.

Results and discussion

To observe uptake of some dyes, AAm and AAm/IA hydrogels were placed in aqueous solutions of cationic dyes such as BR 9, BG 4, CV, and BB 20, and the aqueous solutions of anionic dyes such as eosin yellowish, bromocresol purple, naftol green and evans blue, and allowed to equilibrate for 2 days. At the end of this time, AAm/IA hydrogels in the aqueous solutions of BR 9, BG 4, CV, and BB 20 showed the dark colorations of the original solutions. AAm hydrogel had not sorbed any dyes from the solutions, and AAm/IA hydrogel had not sorbed the anionic dyes. Since poly(acrylamide) is a nonionic polymer (14), ionizable groups on the polymer were increased by the addition of itaconic acid to acrylamide monomer.

Therefore these hydrogels have many carboxyl groups that can increase interaction between the cationic groups of cationic dyes and carboxyl groups of hydrogels. On the other hand, there will be anionic repulsion between anionic groups of anionic dyes and carboxyl group of IA in the hydrogels and therefore little interaction between the anionic dyes and AAm/IA hydrogels.

The other types of interaction between gel and dyes may be hydrophobic and hydrogen bond. Hydrophobic effects are specifically aqueous solutions interactions, which in the present case will involve the aromatic rings and the methyl and methine groups on the dyes molecules and the methine groups on the gel. Hydrogen bond will be expected to occur between oxygen atom on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked copolymer (15). But, electrostatic interactions between dye molecules and the hydrogel is very dominant due to hydrophobic and hydrogen bonds. As it is said before, AAm hydrogel had not sorbed any dye molecules while AAm/IA hydrogel sorbed the dyes.

These cationic dye solutions were used in the experiments of adsorption of dyes onto AAm/IA hydrogels. In a batch adsorption system at equilibrium, total solute concentration (C_I, mol L^{-1}) is

$$C_I = C_B + C \tag{1}$$

where, C_B is the equilibrium concentration of the solute on the adsorbent in mol L^{-1} (bound solute concentration) and C is the equilibrium concentration of the solute in the solution in mol L^{-1} (free solute concentration). The value of the bound concentration may be obtained by differing the use of eq. 1. For a fixed free solute concentration, C_B, is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio , r, defined by

$$r = C_B / P. \tag{2}$$

Thus with C_B in mol L^{-1} and P in base mol (moles of monomer units) L^{-1}, r then represents the average number of molecules of solute bound each monomer unit at that free solute concentration (15). Plots of the binding ratio (r) against the free concentrations of the dyes in the solutions (C, μmol dye L^{-1}) are shown in Figure 1.

Figure 1 shows that adsorptions of the dyes within AAm/IA hydrogels correspond to type L (*Langmuir type*) (BR 9, BG 4 and BB 20 correspond to the L3 type, whereas CV correspondes to the L4 type) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (16,17).

In this type of adsorption isotherm, the initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent (16,17). The types of systems which give this curve do in fact fulfil these conditions. Thus they have one of the following
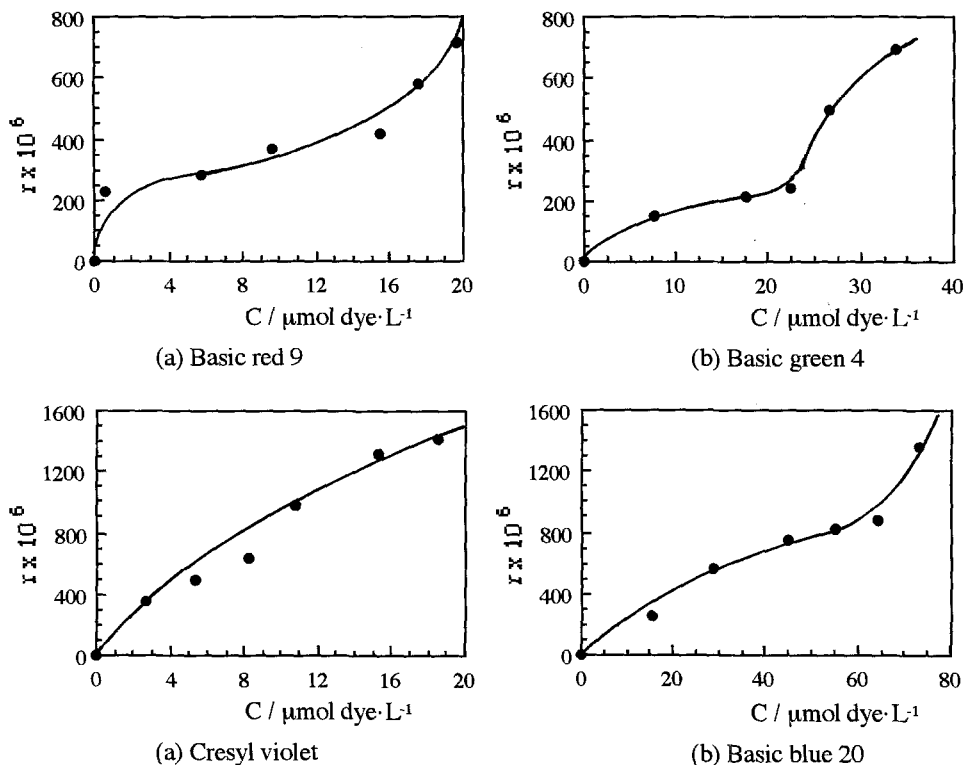
Figure 1. Binding isotherms of AAm/IA-dye systems.

characteristic: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition; examples of (ii) are (a) systems with highly polar solute and adsorbent, and a non-polar solvent, and (b) systems in which monofunctional ionic substances with very strong intermolecular attraction are adsorbed from water by ion-ion attraction. It is possible that in these cases (systems b) the adsorbed ions may have become associated into very large clusters, and just adsorption take places (16,17).

The monolayer coverages of AAm/IA for the dyes in the aqueous solutions were found by method of Point B from Figure 1. The reciprocal of n is the site-size, u, which may be taken to represent either the average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain saturates. The values of monolayer coverage and the site-size are listed Table 2.

Table 2. The values of monolayer coverage of hydrogel-dye systems

Solution	$n \times 10^6$	u
Basic green 4	100.67	9 933.4
Basic red 9	219.65	4 552.7
Cresyl violet	226.61	4 416.8
Basic blue 20	467.67	2 140.5

When Table 2 is examined, it is shown that the values of monolayer coverage of the hydrogel by the cationic dyes are increased by the following order;

$$BB\ 20 > CV > BR\ 9 > BG\ 4\,.$$

The reason of this order may be the molecular structure of the dyes (Table 1). The values of the site -size of the gel-dye systems are increased by the following order;

$$BG\ 4 > BR\ 9 > CV > BB\ 20.$$

As expected, this order is the reciprocal of n values and, the site size of BG 4 is 9933.4 mol monomeric unit of the gel per one mol dye , while it is dropped to 2140.5 mol monomeric unit of the gel per one mol of dye for BB 20.
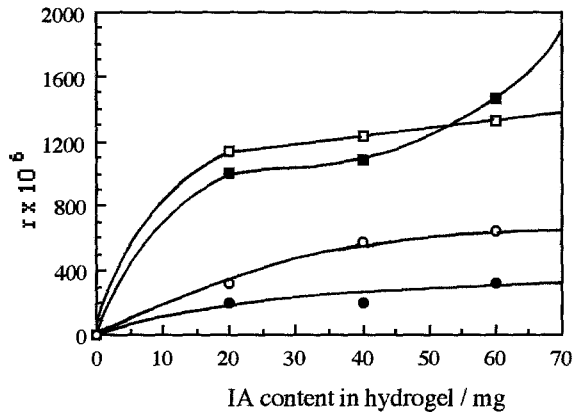
Figure 2. The variations of binding ratio of AAm/IA-dye systems with content of IA in the hydrogel. Total doses are given 5.20 kGy. (o) BR 9, (●) BG 4, (□) CV, (■) BB 20.
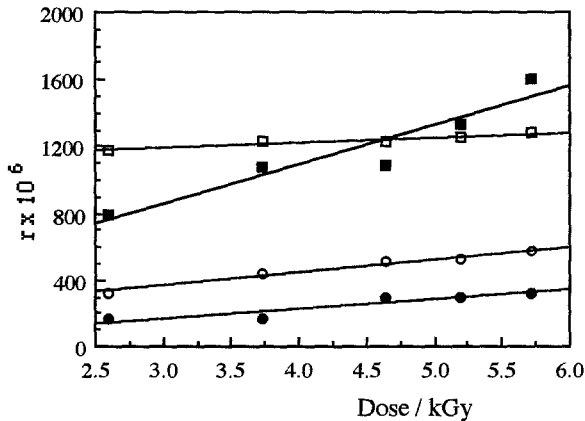
Figure 3. The variations of binding ratio of dyes-AAm/IA hydrogel containing 40 mg IA with irradiation dose. (o) BR 9, (●) BG 4, (□) CV, (■) BB 20.

Dyes were removed from hydrogels by contact with distilled water for 3 days. We have observed that desorptions of the dyes were shown by the suitable coloration in the water and also hydrogels returned to the original colors.

In later experiments, uptake of dyes to AAm/IA hydrogels were measured effects of different contents of IA and irradiated doses. The binding ratio of dye-hydrogel systems versus IA content in hydrogel and irradiation dose are plotted and shown in Figure 2 and 3.

The binding ratio of dye–hydrogel systems gradually increased with the increase of content of IA in AAm/IA hydrogels and irradiation dose. Increasing the carboxyl groups in the hydrogels with increasing the IA contents caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of IA in the hydrogels. On the other hand, the crosslinks of hydrogels increased with the increase of irradiation dose and thus reduced the size of pores. So, dye molecules in small pores of hydrogel interacted with hydrophilic groups and the amount of adsorbed dye molecules increased.

This study has shown that AAm/IA hydrogels adsorb the basic dyes such as BB 20, CV, BR 9 and BG 4, while AAm hydrogels do not. Type L adsorption isotherms in Giles classification system were found. The adsorptions of the dyes are increased with the content of IA in the hydrogels and irradiation dose.

As a result, it was shown that the AAm/IA hydrogels could be used as an adsorbent for the water pollutants such as cationic dyes, an important problem for the textile industry.

References

1. Kulicke WM, Nottelman H (1989) Polymers in Aquous Media, Performance through Association, Glass JE (ed) 223, Advanced in Chemistry Series, 15
2. Kost J, Langer R, Gombotz R (1987) Hydrogels in medicine and pharmacy, Peppas NA (ed) CRC Press, Florida (vol 3 pp 95-108).
3. Koβmehl G, Volkheimer J, Schafer H (1989) Makromol Chem 190:1253
4. Al-Issa M, Davis TP, Huglin MB, Rego JM, Rehab MMA-M, Yip DCF, Zakaria MB (1990) Makromol Chem 191:321
5. Kozuka H, Takagishi T, Yoshikawa K, Kuroki N, Mitsuishi M (1986) J Appl Polym Sci: Part A: Polym Chem 24: 2695
6. Kim WS, Seo KH, Hwang YY, and Lee JK (1988) J Polym Sci Part C: Polym Lett 26:347
7. Karadağ E, Saraydın D, Öztop HN, Güven O (1994) Polym Adv Technol 5(10):664
8. Saraydın D, Karadağ E, Öztop HN, Güven O (1994) Biomaterials 15(11):917
9. Saraydın D, Karadağ E, Güven O (1995) Sep Sci Technol 30(17):3291
10. Karadağ E, Saraydın D,Güven O (1995) Sep Sci Technol 30(20):3747
11. Saraydın D, Karadağ E, Güven O (1996) Sep Sci Technol 31(3):423 in press

12. Karadağ E (1992) Ph. D Thesis, Sivas, Turkey

13. Lurie J (1975) Handbook of chemistry, Mir Publ, Moscow

14. Weber, J W Jr. (1972) Physicochemical process for water quality control, John Wiley Sons, New York

15. Molyneux P, Vekavakayanondha S (1986) J Chem Soc Faraday Trans 1, 82:291

16. Giles C H, MacEwan T H, Nakhwa S N, Smith D (1960) J Chem Soc 3973

17. Giles C H, D'Silva A P, Easton I (1974) J Coll İnterface Sci 47:766