REMOVAL OF SOME CATIONIC DYES FROM AQUEOUS SOLUTIONS BY ACRYLAMIDE/ITACONIC ACID HYDROGELS

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Abstract. Acrylamide/itaconic acid (AAm/IA) hydrogels prepared by irradiating with γ radiating were used in experiments on the uptake of some cationic dyes such as basic red 5 (BR-5), basic violet 3 (BV-3) and brilliant cresyl blue (BCB). The removal of the cationic dyes to AAm/IA hyrogels is studied by batch adsorption technique. In the experiments of the adsorption, L3 type (Langmiur) adsorption in Giles classification system was found. Adsorption studies indicated that monolayer coverages of AAm/IA hydrogel by these dyes were increased with following order; BCB > BR-5 > BV-3.

Keywords: adsoption, cationic dyes, hydrogel, poly(acrylamide/itaconic acid), swelling

1. Introduction

Crosslinked hydrophilic polymers capable of imbibing large volumes of water (i.e. >20%) are termed hydrogels. Interest in the preparation of hydrogels with various properties has increased considerably in recent years, due to their versatile applications in biomedicine, biotechnology and in a vast field where controlled release of chemicals or drugs is required. Hydrogels have been widespread applications in the fields of bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology and others. It is used as controlled release systems of drugs, for production of contact lenses and artificial organs in biomedicine, as an adsorbent for removal of some agent in environmental applications, immobilized enzyme kinetics in bioengineering and also as a carrier of water, pesticides and fertilizer in agriculture field (Güven, 1991; Kost *et al.*, 1987; Kulicke, 1989; Al-Issa *et al.*, 1990).

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 (Kozuka, 1986; Kim *et al.*, 1988).

In our previous studies, adsorptions of some cationic dyes (Karadağ *et al.*,

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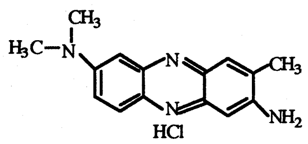
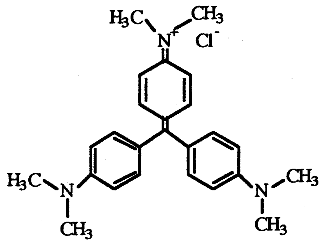
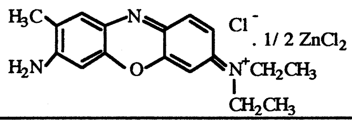
TABLE I
Some properties of dyes

Name	Chemical Formula	Molar Mass	C. I. Nr.	λ_{max}, /nm
Basic red 5		288.78	50 040	540
Basic violet 3		407.99	42 555	588
Brilliant cresyl blue		385.96	51 010	622

1996a, b; Saraydin *et al.*, 1996a, b) uranyl ions and some heavy metal ions (Karadağ *et al.*, 1995; Saraydin *et al.*, 1995), and protein such as bovine serum albumine ((Karadağ *et al.*, 1994; Saraydin *et al.*, 1994), study of biocompatibility of blood ((Karadağ *et al.*, 1996c) by acrylamide-itaconic acid ((Karadağ, 1992) and acrylamide–maleic acid hydrogels (Saraydin *et al.*, 1995) 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 as acrylamide/itaconic acid (AAm/IA) hydrogels. Water-soluble cationic dyes, basic red 5 (toluylene red, neutral red), basic violet 3 (crystall violet), and brilliant cresyl blue resemble the large molecular dyes found in waste waters.

2. Experimental

Acrylamide (AAm) and itaconic acid (IA) monomers were obtained from BDH (Poole, UK). Basic red 5 (BR-5), basic violet 3 (BV-3), and brilliant cresyl blue (BCB) cationic dyes were obtained from Merck (Darmstadt, Germany). Some properties of these dyes are listed in Table I.

3. Preparation of Hydrogels

In this study, for preparation of acrylamide and acrylamide/itaconic acid superadsorbent hydrogels, ionizing radiation processing is used (Chapiro, 1988; Zicheng *et al.*, 1987; Rosiak *et al.*, 1983). Ionizing radiation such as cobalt-60 gamma radiation is very useful in producing polymers from monomeric units and in modifying the properties of pre-existing polymers. The polymerization achieved by free radicals (occasionally ions) created in the material at the end of process.

It has been reported that gelation of polyacrylamide needs 2.00 kGy of γ-rays irradiation doses at ambient temperature (Rosiak *et al.*, 1983). So, 2.60 kGy of γ-rays irradiation doses were used for the preparation of the hydrogels. The radiation technique is a sterilization technique used in many applications. During polymerization and crosslinking reactions, all monomers reacted together by applied γ-rays irradiation. This process is used for sterilization of hydrogel systems at the same time. There is no monomer (such as toxic acrylamide) at the end of the copolymerization and crosslinking reaction between acrylamide and itaconic acid, because of 2.00 kGy is sufficient dose for 100% gelation (Rosiak *et al.*, 1983; Saraydin *et al.*, 1995b). On the other hand, some biocompatibility studies of AAm/IA hydrogels with blood ((Karadağ *et al.*, 1996c) and some biocompatibility studies of acrylamide/maleic acid hydrogels with blood (Saraydin *et al.*, 1995c) has shown that there was not important toxic effect of acrylamide monomer. For removal of toxic effect of possible residual acrylamide monomers, AAm/IA hydrogels must be washed by water before using as an adsorbent for industrial waters.

When monomers or acrylamide and itaconic acid have been irradiated with ionization rays such as γ-rays, free radicals are generated in the aqueous solutions. Random reactions of these radicals with the monomers lead to the formation of copolymers of acrylamide/itaconic acid. When irradiation dose has been increased beyond the certain value the polymer chains crosslink and then gel is obtained.

Suitable quantities of itaconic acid and irradiation doses for acrylamide and itaconic acid hydrogels were selected based upon results from experiments ((Karadağ, 1992). 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 Cammacell 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. Preparation and characterization of acrylamide (AAm) and AAm/IA hydrogels were reported in a previous study) (Karadağ *et al.*, 1996a, b; (Karadağ *et al.*, 1995; (Karadağ *et al.*, 1994; (Karadağ *et al.*, 1992).

4. Removal of the Dyes

The synthetic aqueous solutions of cationic dyes were prepared in the concentration ranges; 5–40 mg L^{-1} for BR-5, 2–10 mg L^{-1} for BV-3, and 10–50 mg L^{-1} for BCB. 0.1 g of AAm/IA hydrogel containing 60 mg IA and irradiated to 5.2 kGy were transferred into 50 mL of the synthetic aqueous solutions of the dyes, and allowed the equilibrate for 24 h 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 I (Lurie, 1975). Distilled water was chosen as the reference. The equilibrium concentrations of dyes solutions were determined by means of precalibrated scales.

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 dose were investigated for removal of dyes within AAm/IA hydrogels. Hydrogel (0.1 g) prepared with different IA contents and irradiation doses were put into 50 mL of aqueous dyes solutions of 20 mg L^{-1} of BR-5, 5 mg L^{-1} of BV-3, and 25 mg L^{-1} of BCB and left for 24 h at 25 °C. Spectrophotometric methods were used to follow the equilibrium concentrations of these dyes solutions.

5. 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-5, BV-3, and BCB, and the aqueous solutions of anionic dyes such as orange II, azo carmine B, congo red and bismark brown Y, and allowed to equilibrate for 2 days. At the end of this time, AAm/IA hydrogels in the aqueous solutions of BR-5, BV-3, and BCB 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 (Weber, 1972), 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 amine groups oxygen atom on the dye molecules and the carbonyl groups on the monomer units of crosslinked copolymer (Molyneux, 1986), 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.

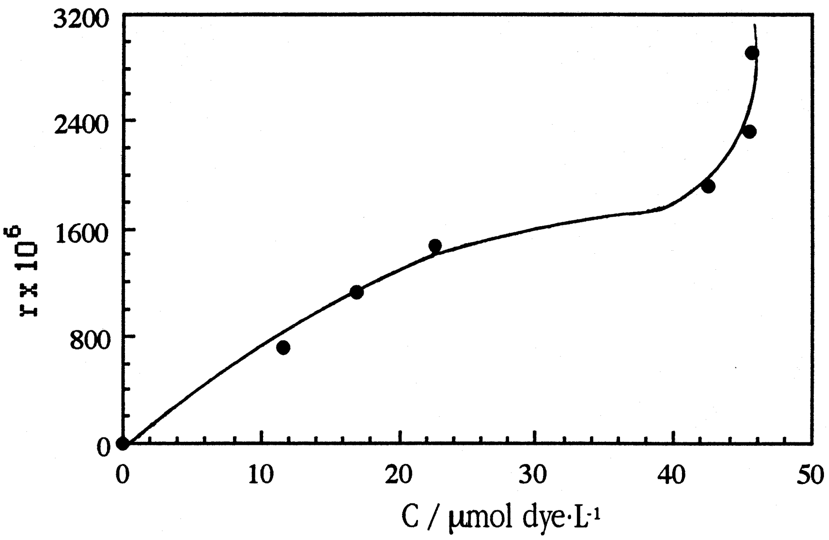


Figure 1. Binding isotherms of AAm/IA-brilliant cresyl blue system.

These cationic dye solutions were used in the experiments if uptake of dyes to 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 concentrations of the solute in the solution in mol L^{-1} (free solute concentration). The value of the bound concentration may be obtained by difference by using Equation (5). 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.

Plots of the binding ratio (*r*) against the free concentrations of the dyes in the solutions (*C*, μmol dye L^{-1}) are shown in Figures 1, 2 and 3).

Figures 1–3 show that adsorption of the dyes within AAm/IA hydrogels corresponds to type L3 (Langmiur type) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (Giles *et al*., 1960, 1974).

Langmuir type isotherms obtained experimentally display a rather long straight portion yields following an inflection point. The point at which this linear portion

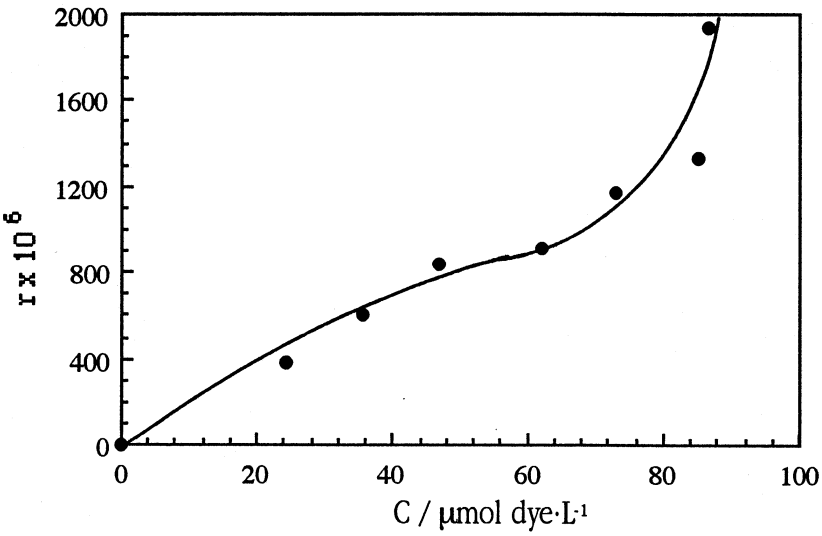


Figure 2. Binding isotherms of AAm/IA-basic red 5 system.

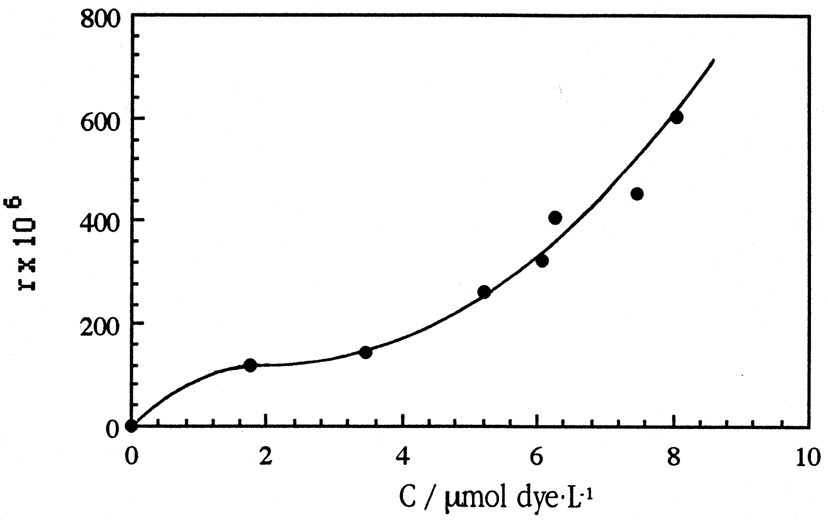


Figure 3. Binding isotherms of AAm/IA-basic violet 3 system.

begins was termed 'Point B' and was taken to indicate the completion of the monolayer, so that the adsorption at Point B, say *n*, should be equal to the monolayer covarage (Giles *et al.*, 1960). The reciprocal of *n* is the site-size, *u*, which may be taken to represent either average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain saturated. The monolayer covareges of AAm/IA for the dyes in the aqueous solutions were found by method of Point B from Figures 1–3. The values of monolayer covarage and the site-size are listed Table II.

TABLE II

The values of monolayer covarage of hydrogel-dye systems

Solution	$n \times 10^6$	u (= $1/n$)
Brilliant blue	942.0	1061.6
Basic red 5	314.1	2932.1
Basic violet 3	89.3	11203.1

If Table II is examined, it is shown that the values of monolayer coverage of the hydrogel by the cationic dyes are increased following order:

$$\mathrm{BCB} > \mathrm{BR}-5 > \mathrm{BV}-3\,.$$

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

$$\mathrm{BV}-3 > \mathrm{BR}-5 > \mathrm{BCB}\,.$$

As expected, this order is the recipocal of n values and, the size of BV-3 is 11 203.1 mol monomeric unit of the gel per one mol dye, while it is dropped to 1061.6 mol monomeric unit of the gel per one mol of dye for BCB.

Dyes were removed from hydrogels by contact with distilled water for 3 days. We have observed that desorptions of the dyes were showed by the suitable coloration in the water and hydrogels als have returned 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 Figures 4 and 5.

The binding ratio of dye-hydrogel systems gradually increased with the increase of content of IA in AAm/IA hydrogels and irradiation dose. Increasing of carboxyl groups in the hydrogels with increasing of 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 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. Swelling properties of hydrogels are decreased with the increase of irradiation dose and, increased with the increase of the itaconic acid content in the copolymers. The equilibrium swelling of acrylamide-itaconic acid hydrogels is higher than equilibrium swelling of acrylamide hydrogels. The reason of this is the hydrophilic groups on the itaconic acid. The more the hydrophilic

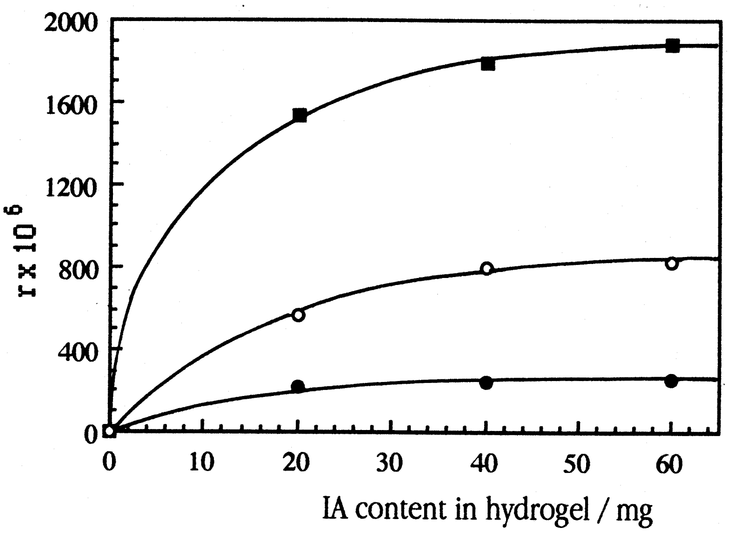


Figure 4. The variations of binding ratio of dyes-AAm/IA hydrogel system with content of IA in the hydrogel. Total dose given are 5.20 kGy. (○) Basic red 5, (●) basic violet 3, (■) brilliant blue.

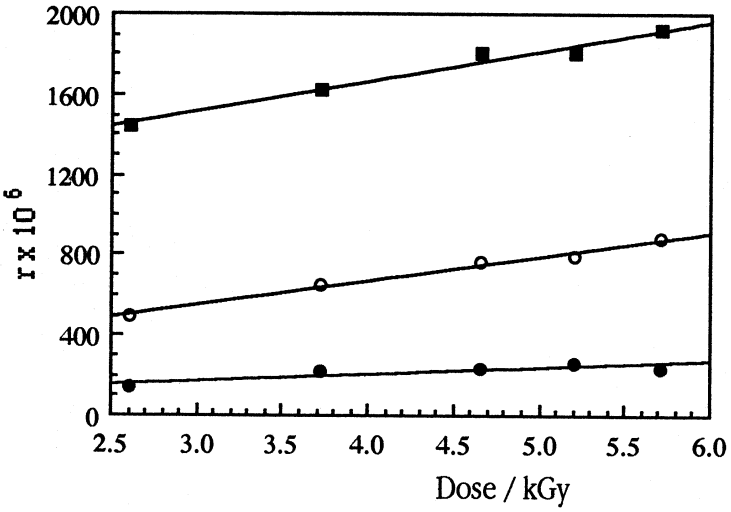


Figure 5. The variations of binding ratio of dyes-AAm/IA hydrogel (containing 20 mg IA) system with irradiation dose. (○) Basic red 5, (●) basic violet 3, (■) brilliant blue.

groups on the itaconic acid, the much swelling is on the AAm/IA hydrogels. If gamma ray dose has increased during ionizing radiation of acrylamide, itaconic acid and water ternary mixtures, the number of the small chains has increased at unit copolymerization time, and the crosslink density of the hydrogels is higher than the lower gamma ray doses, and at the same time, the number-average molar mass of the polymer between crosslinks, is smaller than the lower gamma ray doses.

6. Conclusions

This study has shown that AAm/IA hydrogels adsorb the basic dyes such as BR-5, BV-3, and BCB, while AAm hydrogels do not. Type L3 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 a sorbent for the water pollutants such as cationic dyes, an important problems for the textile industry.

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