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Sorption for removing Lauths Violets in aqueous solutions by chemically crosslinked poly(AAm-co-SA) hydrogels

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Summary

Superswelling poly(acrylamide-co-sodium acrylate) hydrogels were prepared by free radical polymerization in aqueous solution of acrylamide (AAm) with sodium acrylate (SA) as comonomer and a multifunctional crosslinker such as trimethylolpropane triacrylate (TMPTA). In the sorption studies, binding of a cationic dye such as Lauths Violet (Thionin, LV) onto chemically crosslinked poly(AAm-co-SA) hydrogels has been investigated. Sorption of LV onto poly(AAm-co-SA) hydrogels was studied by batch sorption technique at 25°C. In the experiments of the sorption, *C type sorption* in the Giles classification system was found. Some binding parameters such as initial binding constant (K_i), equilibrium constant (K), monolayer coverage (n), site-size (u), and maximum fractional occupancy ($\hat{O}$) for poly(AAm-co-SA) hydrogels-LV binding system were calculated by using Klotz and Scatchard linearization methods. Finally, the mass of sorbed LV per gram of dry hydrogel (q) was calculated to be 3,9-5,9 mg LV per gram for hydrogels.

Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but do not dissolve in water. They are three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility [1-3].

Polyacrylamide based hydrogels find many applications such as purification of wastewater and metal extraction. Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry and water purification and separation process. Due to characteristic properties such as swell ability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, environmental applications [1-3]. Recently, it was determined that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups could be used as complexing agents for removal of dyes from aqueous solutions [4-5]. Poly(AAm-co-SA) hydrogels were prepared by free radical crosslinking copolymerization [6-11]. The aim of this study is

to investigate the sorption properties of AAm hydrogels with addition of an anionic monomer such as SA.

Experimental

Poly(AAm-co-SA) hydrogels were prepared by free radical crosslinking copolymerization of AAm monomer with addition of an anionic comonomer such as SA and a multifunctional crosslinker such as trimethylolpropane triacrylate (TMPTA). The modes of purification and specifications of the sources of water, the monomers AAm and SA, crosslinker TMPTA, initiator, ammonium persulfate (APS) and activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were given in our previous study [12]. Cationic dye Lauths Violet used in sorption was purchased from Aldrich Chemical Co. (Milwaukee- US).

Solutions of the dye containing 6,9–55,7 μmol L^{-1} (2,0-16,0 mg L^{-1}) LV in distilled water were prepared. Poly(AAm-co-SA) hydrogels containing 40 mg SA was used in a known volume of dye solution until equilibrium was reached. For SA effect on the dye sorption, dye solution of concentration of 12 mgL^{-1} was used.

After sorption, dye solution was separated by decantation from the superswelling hydrogels. Spectrophotometric method was applied to dye solutions. Spectrophotometric measurements were carried out using a Shimadzu UV 1601 model UV-VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at 598 nm. Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales. The amounts of dye sorbed were determined from the initial and final concentrations of the solutions, calculated from the measured absorbances.

Results and Discussion

To observe the sorption of LV, poly(AAm-co-SA) hydrogels were placed in aqueous solutions of LV and allowed to equilibrate for four days at 25^{o}C. At the end of this period poly(AAm-co-SA) hydrogels in the LV solutions showed the dark coloration. But AAm hydrogel did not sorbed any dye from solution.

The amount of sorption per unit mass of the poly(AAm-co-SA) hydrogels were evaluated by using the following equation:

$$q = \frac{(C_o - C)V}{W} \tag{1}$$

Where q is the amount of dyes sorbed onto unit dry mass of the poly(AAm-co-SA) hydrogels (mg g^{-1}), C_o and C are the concentration of the dyes in the initial solution and the aqueous phase after treatment for a certain period time, respectively (mg L^{-1}), V is the volume of the aqueous phase (L) and w is the amount of dry poly(AAm-co-SA) hydrogels (g).

In the sorption system at equilibrium, the total solute concentration is following equation:

$$C_t = C_b + C \tag{2}$$

Where C_b is the equilibrium concentration of the solute on the sorbent per liter solution (bound solute concentration) and C is the equilibrium concentration of the

solute in the solution (free solute concentration). The value of the bound concentration may be obtained by using Eq. 2. 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

$$r = C_b / P \tag{3}$$

Thus, with in and P is base mol (moles of monomer units) per liter solute represents the average number of molecules of solute bound each monomer unit at that free solute concentration [5]. To determine the sorption kinetics of LV into poly(AAm-co-SA) hydrogels a plot of the binding ratio (r) against the free concentration of LV is shown in Fig. 1.

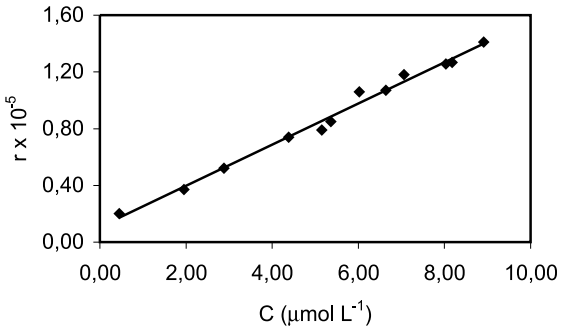

Figure 1. Binding isotherm of poly(AAm-co-SA) hydrogel-LV binding system

Fig. 1 shows that sorption of the dye with in poly(AAm-co-SA)hydrogels corresponds to *C type* (constant partitions class) sorption isotherms in the Giles classification system for sorption of a solute from its solution [13].

The linear *C* isotherm is explained by penetration of substrate micro pores by solute, with or without solvent, whereby new sorption sites are opened; the theory predicts the experimentally found sharp inflection to a plateau in the *C* curves. The number of sites remains constant [13].

The binding data was interpreted on the basis of the uniform site-binding (*u.s.b.*) model, which in statistical-thermodynamic terms corresponds to a formation of an ideal localized one-dimensional monolayer of solute on the polymer chains [14]. This leads to the hyperbolic (Langmuir) from of the binding isotherm, which applies to many polymer/solute binding system.

$$r = \frac{nKC}{1 + KC} \tag{4}$$

Where K is the binding constant, i.e. the equilibrium constant for the attachment of a molecule of dye onto a site by a specific combination of non-covalent forces. Here n is the site density (the limiting value of r) for monolayer coverage, which is therefore of density of the sites along the polymer chain. To 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, more generally the average spacing of solute molecules when the chain is saturated. The initial binding constant, K_i is the initial slope of the binding isotherm, and therefore the average binding strength of a solute molecule by a single monomer unit on an occupied chain. K_i is equal to the product $K\,n$.

To get the best values for the binding parameters from the experimental data, the linearization methods of eq. 4 have been developed by some researches as Klotz and Scatchard [14]. Klotz equation is

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK}\frac{1}{C} \tag{5}$$

Thus if this isotherm (eq. 4) holds than a plot of 1/r vs. 1/C will be straight line of slope 1/nK, ordinate intercept 1/*n*. Scatchard equation is below. A plot of *r/C* vs. *r* should be a straight line of slope *–K*, ordinate intercept *Kn*.

$$\frac{r}{C} = nK - Kr \tag{6}$$

The Klotz plot and the Scatchard plot of poly(AAm-co-SA) hydrogel-LV binding systems are shown in Fig.2 and Fig.3, respectively, and the binding parameters for poly(AAm-co-SA) hydrogel-LV binding system are calculated from the intercept and slopes of the binding isotherm methods.

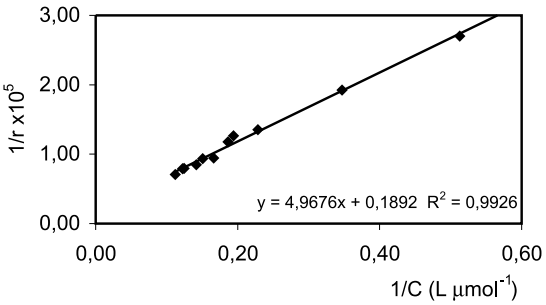

Figure 2. Klotz plot of poly(AAm-co-SA) hydrogel-LV binding system

The binding parameters K_i, *K*, *n* and *u* are listed in Table 1 for poly(AAm-co-SA) hydrogel-LV binding system. In Table 1, the final column contains the derived values of the $\hat{O}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy $\hat{O}$:

$$\hat{O} = r / n \tag{7}$$

Using the value of *r* at the maximum experimental free dye concentration and with the site-density obtained for the (*u.s.b.*) model [14].

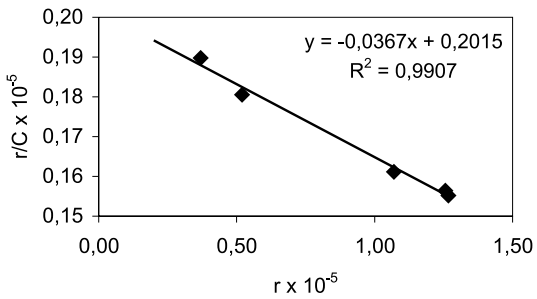

Figure 3. Scatchard plot of poly(AAm-co-SA) hydrogel-LV binding system

Table 1. Binding parameters of poly(AAm-co-SA) hydrogel-LV binding system

	K_i /L µmol^{-1}	K /L µmol^{-1}	n	u	$\hat{O}$
Klotz	0,2013	0,0381	5,2854	0,1892	0,7681
Scatchard	0,2015	0,0367	5,4904	0,1821	0,7394

In later experiments uptake of dye to was measured effects of contents of SA. The amount of dyes sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in 12 mg dye L^{-1} of aqueous solutions, and presented in Table 2. Table 2 presents that the amount of dyes sorbed onto unit dry mass of the poly(AAm-co-SA) hydrogels (mg g^{-1}) q are increased. The amount of dyes sorbed onto unit dry mass of the poly(AAm-co-SA) hydrogels gradually increased with the increase of content of SA in poly(AAm-co-SA) hydrogels. The percentage sorptions of LV onto poly(AAm-co-SA) hydrogels is changed among 65,74%-85,50%.

The ionic charge content in the polymeric structure is important. SA contains many ionic units (–COONa). The swelling degree of the hydrogels increase due to increase of the hydrophilic units on hydrogel structure. On the other hand, salts of weak acids are decomposed by water with the formation of free acid and free base, and the process of hydrolysis is reversible. The salt group is almost completely ionized, and a large number of hydrophilic groups occur [12]. Therefore poly(AAm-co-SA) hydrogels have many ionic groups that can increase interaction between the cationic dye molecules and anionic groups of hydrogels. The other types of interaction between the superswelling hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bond. Specially, hydrogen bond will be expected to occur between amine group and nitrogen atoms on the dye molecules and the amine and carbonyl group on the monomer unit of crosslinked polymer. Hydrophobic effects are specially aqueous solutions interactions, which in the present case will involve that aromatic rings and the methyl and methine groups on the dye molecules and the methine groups on the gel.

Table 2. The amount of dyes sorbed onto unit dry mass and % sorptions of the poly(AAm-co-SA) hydrogels

SA, mg	10	20	30	40	50	60	70	80
q (mg dye)	3,91	4,44	5,01	4,72	4,97	4,93	5,09	5,09
% sorption	65,75	77,42	84,50	82,25	84,33	83,00	85,42	85,50

Conclusion

This study has shown that poly(AAm-co-SA) hydrogels have sorbed the monovalent cationic dye such as Lauths Violet, while AAm do not. *Type C* sorption isotherm in Giles's classification system are found. The sorptions of the dyes are increased with the content of SA in the hydrogels. The mass of sorbed LV per gram of dry hydrogel (q) was calculated to be 3,9-5,9 mg LV per gram for hydrogels. The percentage sorptions of LV onto poly(AAm-co-SA) hydrogels is changed among 65,74%-85,50%.

The present work has given the quantitative information on the binding characteristic of LV with poly(AAm-co-SA) hydrogels. For good characterization of the binding isotherms, Klotz and Scatchard linearization methods were used. Some binding parameters were found.

At the end of this study, it is seen that chemically crosslinked poly(AAm-co-SA) hydrogels may be used a sorbent for removal of some agents and dye molecules. The utilization of these types of hydrogels, in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization and enrichment of some species makes hydrogel more popular.

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