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Swelling and dye adsorption study of novel superswelling [Acrylamide/ N-vinylpyrrolidone/ 3(2-hydroxyethyl carbamoyl) acrylic acid] hydrogels

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Summary

Super swelling acrylamide (Am)/N-vinylpyrrolidone (NVP)/3-(2-hydroxyethyl carbamoyl) acrylic acid (HECA) hydrogels were prepared by free radical polymerization of quaternary mixtures of Am, NVP, HECA and water. The hydrogels were used in experiments on swelling, diffusion and adsorption of some water-soluble monovalent cationic dyes such as Crystal Violet (CV), Malachite Green (MG) and Methylene Blue (MB). In the experiment of the adsorption of dyes from their aqueous solutions type-S adsorption isotherm were found. The diffusion of water within the hydrogel was found to have non Fickian character. The uptake of dyes within the hydrogel increased in the following order: MG>MB>CV. The binding ratio of the hydrogel/dye systems was gradually increased with the increase of HECA content in the AAm/NVP/HECA hydrogel.

Introduction

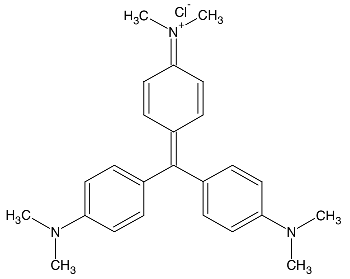
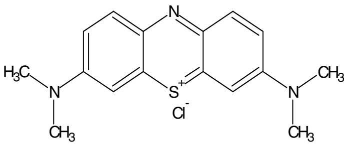
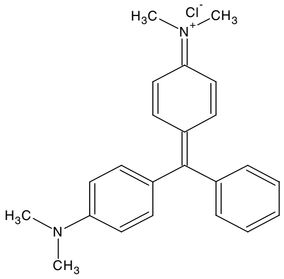
Hydrogels are three-dimensional crosslinked polymer structures which are able to swell in the aqueous environment. The capacity of Superswelling hydrogels to absorb water is enormous and can be as much as 1000 times the mass of polymer. Swelling behavior of Superswelling hydrogels may be characterized by water sorption [1-3]. Hydrogels find considerable applications and have been extensively studied because they are glassy in the dry state but swell to an elastic gel upon water penetration. These materials are of great interest due to their promising application in the field of medicine, pharmacy, biotechnology, agriculture, food industries etc. Hydrogels have been most widely used in the controlled release of drugs [4,5] .

The physical and chemical properties of hydrogels will depend upon the monomers and polymers from which they are made. They may be composed of various chemical substances. [6] Some authors have reported that poly (N-vinyl pyrrolidone) and poly (vinyl pyridine) hydrogels have been used for adsorption of cationic dyes [7,8].

Dyeing and finishing wastes in the textile industry have high color and organic content. The removal of color from textile waste water 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 used various adsorbents for the removal of acidic and basic dyes from aqueous solutions [9,10].

The aim of this study is to investigate the swelling properties and adsorption characteristics of Acrylamide (AAm) / N-vinyl pyrrolidone (NVP) hydrogels with addition of a novel anionic monomers such as 2-(hydroxyethyl carbamoyl) acrylic acid (HECA). In this work it has been aimed to study a convenient method for removing some water soluble cationic dyes from aqueous solutions by adsorption on novel polymeric adsorbent such as AAm/NVP/HECA hydrogels. Water soluble cationic dyes such as Methylene Blue, Crystal Violet and Malachite Green resemble the large molecular dyes found in waste waters.

Table 1. Properties of Water-Soluble Cationic Dyes

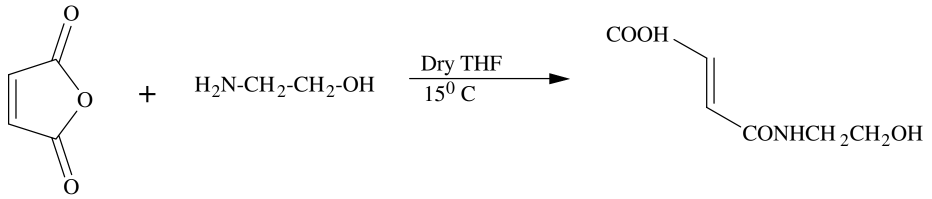
Name	Chemical Formule	Molar Mass	Colour Index Number Or CI Nr.	λ_{max}
Methylene Blue		373.90	52015	663
MalachiteGreen		366.98	42000	617
Crystal Violet		407.99	42555	585

Experimental

Materials.

The Acrylamide (AAm) and N-vinyl pyrrolidone (NVP) monomers were obtained from Aldrich. Maleic anhydride (from Lancaster) was recrystalized by chloroform before use. Ethanolamine (from Merk) was distilled under vacuum before use.

Ammonium persulphate (APS) and N, N-methylene bisacrylamide(MBAm) were obtained from Fluka and were used without further purification. Methylene Blue, Crystal Violet and Malachite Green were obtained from Merck. Some properties of these dyes were listed in Table1. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AC 300 F spectrometer in DMSO-d_6 as solvent. FT-IR spectra were taken by using Nicolet Impect 400D spectrophotometer.



Scheme 1. Preparation of HECA monomer

Synthesis of HECA monomer:-

Maleic anhydride 29.4 g (0.3mole) was dissolved in 60 ml of dry THF in a 250 ml three-necked round bottom flask fitted with a guard tube. The flask was cooled in ice-cold water at 15°C. The THF solution containing ethanolamine 18.32 g (0.3mole) was added drop wise over a period of 0.5 hr with constant stirring. The reaction mixture was then allowed to equilibrate to room temperature and continuously stirred for further 4 hr. The separated white solid was filtered, washed with hot THF

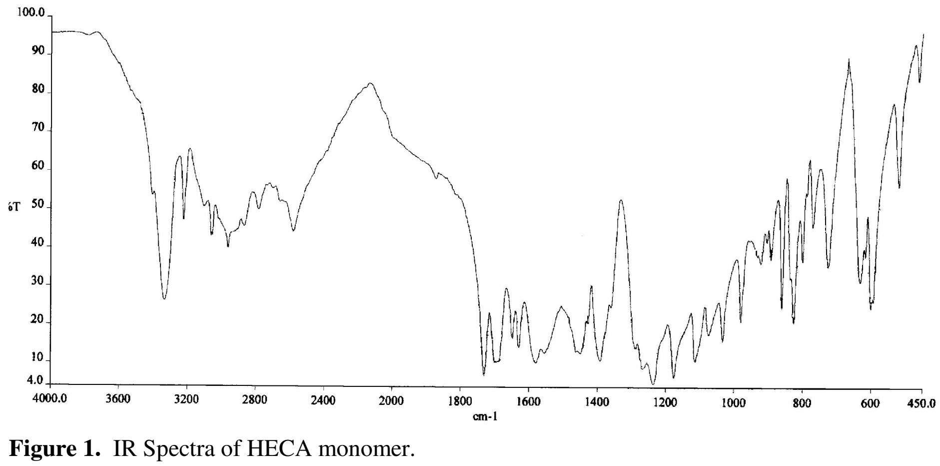


Figure 1. IR Spectra of HECA monomer.

^{1}H-NMR: 2.42 (1H, s,-OH),3.568-3.605 (2H, t, -$\underline{CH_2}$-OH), 4.269-4.306 (2H, t, -$\underline{CH_2}$-NH), 6.218-6.260 (1H, s, J=12.66, $\underline{CH}$=CH-COOH), 6.471-6.514 (1H, s, J=12.79, CH=$\underline{CH\text{-}}$CONH), 8.64 (1H, s, -NH), 11.51 (1H, s, -COOH)
^{13}C-NMR: 48.530, 62.328, 131.084, 147.561, 165.279, 172.843
Elemental analysis:
Calculated: C 45.28%, H 5.70%, N 8.80%.
Found : C 45.95%, H 5.35%, N 8.98%

and dried. The dried compound was dissolved in saturated sodium bicarbonate solution and reprecipitated using con.HCl.The solid was filtered and washed with cold water till filtrate became netural. The filtered solid was dried and recrystalised using methanol, yield 30.9 g (72%), melting point 149°C.The monomer is soluble in hot water.

Hydrogels preparation:-

Aqueous solution of monomers of 4.0 g Am, 2.0 g NVP and 0, 0.4, 0.8, 1.2 and 1.6 g HECA were prepared in 6 wt% of total wt of monomer in double distilled water. To it 0.15 mole % (of total mole) N, N-Methylene bisacrylamide (MBAm) as crosslinking agent and 0.15 mole % (of total mole) potassium persulphate as initiator were added. These mixtures were stirred to give homogeneous solutions. These solutions were poured in Petri disc and kept at 60°C for a period of 12 hr. The hydrogels were cut into the cylindrical shape and were immersed in double distilled water and kept for one day to remove unreacted monomer. The swollen gel was dried by immersion it into methanol for about 4 hr. and then after kept in an oven at 60°C to constant weight.

Swelling experiment:-

The swelling behaviors of dried hydrogels were carried out by immersion in doubly distilled water at 25°C in a water bath. The water absorbed was determined by weighing the samples after wiping at various time intervals. Swollen gels were weighed by single pan electronic balance (Dhona 100 DS, d=0.1 mg). To measure the effect of pH on swelling the hydrogel HG_5 were placed in different pH solution and similar procedure was followed as stated above.

Dye adsorption studies:-

The aqueous solutions of monovalent cationic dyes Methyline Blue, Crystal Violet and Malachite Green were prepared in the concentration ranges of 6-26 mg L^{-1}, 4-24 mg L^{-1} and 10-35 mg L^{-1} respectively. AAm/ NVP/HECA hydrogels containing 1.6 g HECA was selected for adsorption experiments. 0.1 g of dry gel were transferred in to 30 ml of the aqueous solutions of the dyes, and allowed to equilibrate for 2 days at 25°C. The influence of HECA content in the Superswelling hydrogel was investigated for adsorption of dyes on to AAm/ NVP/HECA hydrogels. Superswelling hydrogel samples prepared with 0.0, 0.4, 0.8, 1.2 and 1.6 g of HECA (Designate as HG_1, HG_2, HG_3, HG_4 and HG_5 respectively) were weighted accurately and added to 40 ml of dye solutions in the desired concentrations and left for 2 days at 25°C.

After adsorption, dye solution was separated by decantation from the Superswelling hydrogels. Spectophotometric method was applied to dye solutions. Spectophotometric measurements were carried out using a model uv-vis spectrophotometer at ambient temperature. The absorbances of these solutions were read at λ_{max} value of the dye. Distilled water was chosen as the reference. The equilibrium concentration of the dye solutions were determined by means of precalibrated scales.

Results and Discussion

Preparation of hydrogels:-

In this study, AAm/ NVP/HECA hydrogels were prepared by free radical polymerization in aqueous solutions of AAM, NVP, HECA and crosslinker such as MBAm. In the polymerization, first step is the formation of free radical from KPS by the action of heat. The formed free radical can combine with AAm, NVP and anionic monomer such as HECA or crosslinker molecule. In this process the unpaired electron is transferred to the monomeric units, so that they in turn become reactive. Another monomer or co monomers can therefore be attached and activated in the same way. The homopolymer or copolymers can continue growing indefinitely with the active center being continuously shifted to the free end of the chain. Crosslinker molecules can be incorporated into chains simultaneously and forms a permanent link between them [11-13].

Polymerization and crosslinking process take 3 hours in AAm/ NVP/HECA gelation. But the reaction conditions have been maintained for further 12 hrs to obtain good gelation. The hydrogels are colorless, soft and elastic with a slippery surface in swollen state.

Swelling and Diffusion:-

The analysis of the mechanism of diffusion in swellable polymeric systems has received considerable attention in recent years, because of important application of swellable polymers in the field of environments, biomedical, pharmaceutical and agricultural.

The swelling of the hydrogels was calculated from the following relation [2,3]:

$$\% Swelling = \frac{Wt - Wo}{Wo} \tag{1}$$

Here W_t is the mass of swollen gel at time t and W_o is the initial mass of the dry gel. The value of swelling was also called equilibrium swelling. The swelling curves of the Superswelling hydrogel in water are shown in Figure1 and are tabulated in Table 2.

Table 2. Parameters of Swelling and Diffusion of AAm/NVP/HECA hydrogels

Hydrogels	% Swelling	k x 10^2	n	D x 10^5
HG_1	1918	2.315	0.5942	3.404
HG_2	5094	2.349	0.5456	4.317
HG_3	6019	1.343	0.6564	3.129
HG_4	6225	1.670	0.6016	2.372
HG_5	6665	1.056	0.6881	3.612

From Figure 2, it can be seen that percentage swelling increases with time until a certain point, when it becomes constant. Table 2 shows that the values of equilibrium swelling of AAm/ NVP hydrogels are 1918%, but the values of equilibrium swelling of AAm/NVP/HECA hydrogels vary between 5095- 6665 %.

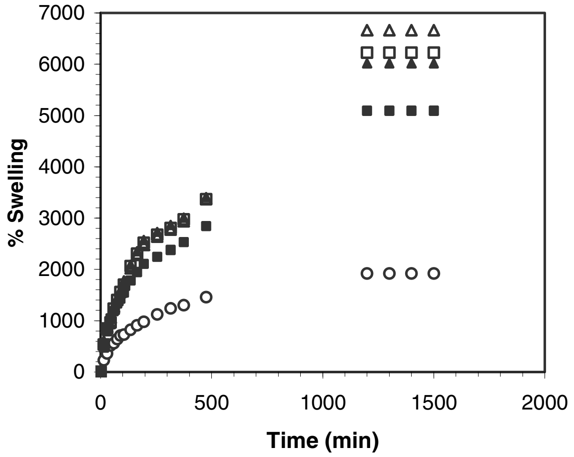


Figure 2. Swelling curves of AAm / NVP/ HECA hydrogels in double distilled water (○) HG_1, (■) HG_2, (▲) HG_3, (□) HG_4, (Δ) HG_5.

It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network [2,3]. The ionic charge content is important. HECA contains many ionic units (-COOH). As it can be seen from Table 2 the swelling increases due to an increase of the anionic units. If the content of HECA in AAm/ NVP/HECA hydrogel increased, the equilibrium swelling has increased. In a similar way as the pH of the swelling medium increase the equilibrium swelling also increases due to increase in the ionic unit (-COONa). The effect of pH on swelling of HG_5 is shown in Figure 3.

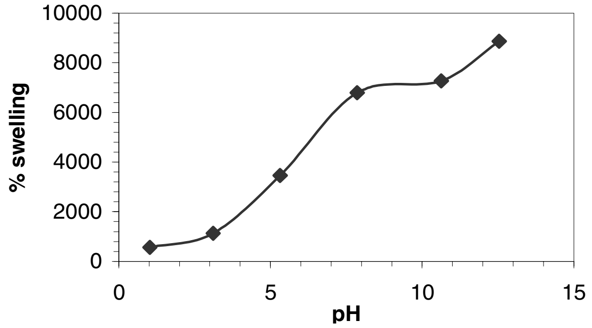


Figure 3. Variation of the % swelling with respect to the pH of swelling medium.

The following equation was used to determine the nature of the diffusion of water into the hydrogels [14-15]:

$$F = k\,t^n \qquad (2)$$

In this equation F denotes the amount of solvent fraction at time t; k is a constant incorporating the characteristic of the macromolecular network system and the penetrant; and n is the diffusion exponent, which is indicative of the transport mechanism. This equation is applied to the initial stages of swelling, and plot of lnF versus lnt are shown in Figure 4. The exponent n and k values were calculated from the slope and intercept of the lines, respectively, and are presented in Table 2.

For cylindrical shapes, n= 0.45-0.5 and corresponds to Fickian diffusion where as 0.5< n < 1.0 indicates that diffusion is non- Fickian type. In the experiment the number determining type of diffusion (n) is over 0.5, hence, the diffusion of water into the Superswelling hydrogels is found as a non–Fickian character [16]. This is generally explained as being a consequence of the slow relaxation rate of the hydrogel matrix. By comparing the values of k obtained here with the values of other hydrogels reported before [17, 18] we found that the k values is small. So the macromolecular network will have properties closer to those of the phantom network, in which the chains do not constrain the junction at all.

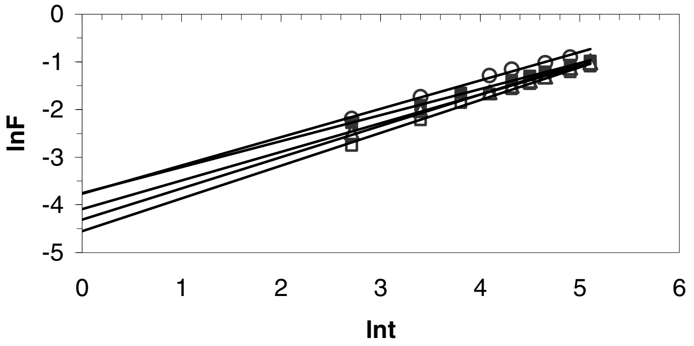


Figure 4. Plots of lnF vs. lnt for AAm/NVP/HECA hydrogels in double distilled water, HG_1 (○), HG_2 (■), HG_3 (▲), HG_4 (Δ), HG_5 (□).

The diffusion coefficient D of the penetrant was calculated from the following relations [16,19]:

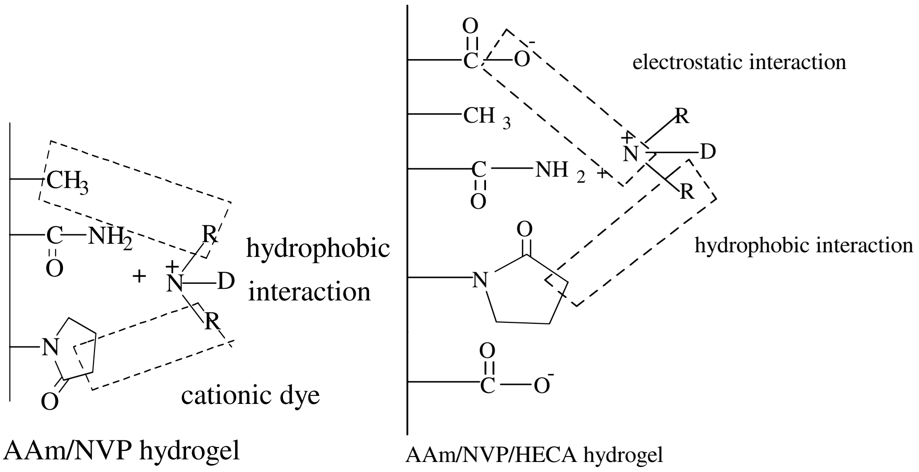
$$D^n = (k/4)(\prod r^2)^n \tag{3}$$

Where D is in cm^2s^{-1}, r is the radius of the gel. The values of the diffusion coefficient of the hydrogels are shown in table 2. If Table 2 is examined, it is shown that the values of the diffusion coefficient of the hydrogels varied from $2.372X10^{-5}$ to $4.317X10^{-5}$ cm^2 s^{-1}. Diffusion coefficients have not showed linear changing to each others. A similar trend in D values has been observed earlier [17, 18].

Adsorption of monovalent cationic dyes:-

For adsorption of cationic dyes, AAm/NVP and AAm/NVP/HECA hydrogels were placed in aqueous solutions of cationic dyes such as Crystal Violet, Methylene Blue and Malachite Green and allowed to equilibrate for two days. At the end of this time, AAm/NVP/HECA hydrogels in the aqueous solutions of Crystal Violet, Methylene Blue and Malachite Green showed the dark colorations of the original solutions and dye solutions almost became colorless. The AAm/NVP adsorb very little amount of cationic dyes. AAm/NVP hydrogel can be cationic in character on the polar lactam ring because of the resulting keto-enol tautomerism [20,21]. So cationic repulsions can occur between cationic groups of VP and cationic dyes.

While AAm/NVP/HECA hydrogels have many carboxyl groups that can increase the cationic interaction between the cationic groups of cationic dyes and carboxyl groups of hydrogels, hence dye adsorption is better. The other types of interaction between the superswelling hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bond. Hydrophobic effect are specifically aqueous solution interactions, which in the present case involves the aromatic rings and the methyl and methane groups on the dye molecule and the methane groups on the gel. Hydrogen bonding is expected to occur between the amine group and hydrogen atom on the dye molecules and the amine and carbonyl on the monomer unit of the crosslinked copolymer. But the electrostatic interaction between dye molecules and the hydrogel is very dominant because of the hydrophobic and hydrogen bonds. A possible interaction between the AAm/NVP/HECA superabsorbent hydrogel and the monovalent cationic dye molecules is presented in Scheme 2.



Scheme 2. A possible interaction between the AAm/NVP/HECA hydrogels and monovalent cationic dye molecules.

In an adsorption system at equilibrium total solute concentration (C_o gram per liter) is [22,23]:

$$C_o = C_b + C \tag{4}$$

Where C_b is the equilibrium concentration of solute on the adsorbent in g per liter (bound solute concentration) and C is the equilibrium concentrations of the solute in the solution in g per liter (free solute concentration).

The binding ratio Q can be calculated from the following equation [23]:

$$Q = \left(\frac{Co - C}{m} \right) V \tag{5}$$

Where Q is in mg adsorbate per gram dry adsorbent, V is the volume of solution of adsorbate in L, and m is mass of the dry terpolymer i.e. the hydrogels. Plot of binding ratio (Q) against the free concentrations of the cationic dyes in the aqueous solution (C g per liter) are shown in Figure 5 for Crystal Violet, Methylene Blue and Malachite Green.

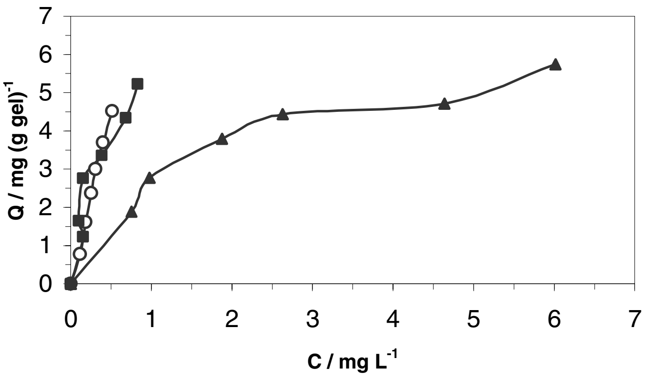


Figure 5. Binding isotherms of AAm/NVP/HECA/dye systems: CV (○), MB (■), MG (▲).

Figure 5 shows that adsorption of the dyes within AAm/NVP/HECA hydrogels corresponds to type S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution [22-24].

In the S curves in the Giles classification system, the initial direction of curvature shows that adsorption become stronger as concentration rises. In practice, the S curve usually appears when three conditions are fulfilled: the solute molecule (1) is monofunctional, (2) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (3) meets strong competition, for substrate sites, from molecules of the solvent or of another adsorbed species[22-24].

The weakness of the adsorbent-adsorbate forces will cause the uptake at low concentrations to be small, but once a molecule has become adsorbed, the adsorbate-adsorbate forces will promote the adsorption of further molecules-a cooperative process-so that the isotherm will become convex to the concentration axis.

In latter experiments, the adsorption of dyes to AAm/NVP/HECA hydrogels was measured, looking at effects of different contents of HECA monomer. The binding ratio versus HECA content in hydrogel is plotted and shown in Figure 6.

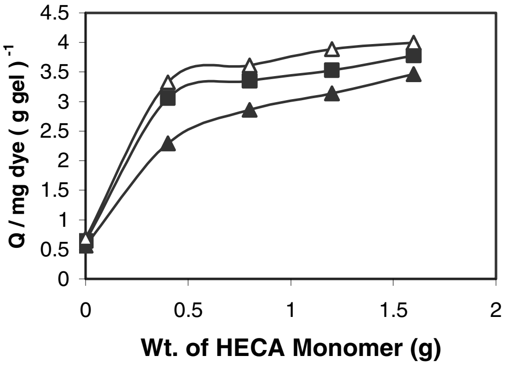


Figure 6. The variation of the binding ratios of adsorbed dyes onto AAm/NVP/HECA superswelling hydrogels with the content of HECA in the hydrogel: (Δ) MG, (■) MB, (▲) CV.

Figure 6 shows that the amount of adsorbed dyes to AAm/NVP/HECA hydrogels increased with increasing content of HECA in AAm/NVP/HECA hydrogels. Increasing carboxyl groups in the hydrogels with increasing of HECA contents caused electrostatic interactions between the cationic groups of dyes and the anionic groups of HECA in the hydrogels.

Conclusions

In this study a novel AAm/NVP/HECA Superswelling hydrogels were prepared by free radical polymerization in solution. Hydrogels were prepared in water, and swollen to equilibrium in water. Hydrogel systems swelled in the range 1915-6665%.

Some swelling parameters such as swelling exponent, swelling coefficient and diffusional behavior of water in to the hydrogel system were evaluated. The diffusion type of hydrogels was a non-Fickian diffusion character. It was seen that swelling of AAm/NVP/HECA hydrogels increased with the increasing content of HECA.

The second part of this study has shown that AAm/NVP/HECA hydrogels adsorb the monovalent cationic dyes such as Methylene Blue, Malachite Green & Crystal Violet, while AAm/NVP hydrogels do not. Type S adsorption isotherms in Giles classification system are found. The adsorption of a dye increased with the content of HECA in hydrogels.

As a result the AAm/NVP/HECA Superswelling hydrogels can be used as sorbents for water pollutants such as cationic dyes, which is an important problem for the textile industry. The highly swollen AAm/NVP/HECA hydrogels can also be used as a super water retainer for carrying of some substances in aquatic fields involving environmental, pharmaceutical, agriculture and biomedical applications.

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