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Removal of anionic dyes from aqueous solution using poly [N-vinyl pyrrolidone/2-(methacryloyloxyethyl) trimethyl ammonium chloride] superswelling hydrogels

Pratish V. Dadhaniya, Manish P. Patel, Ranjan G. Patel (✉)

Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar, Gujarat, India
E-mail: rgp.chem@spu.ernet.in

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Summary

A superswelling poly [N-vinyl pyrrolidone/2-(methacryloyloxyethyl)trimethyl ammonium chloride], poly(NVP/METAC) hydrogels were prepared by free radical polymerization using ethylene glycol dimethacrylate as crosslinker. The hydrogels were characterized by FT-IR spectroscopy and their surface morphology was determined using Scanning Electron Microscope (SEM). The influence of feed composition of both the monomers and crosslinker on equilibrium swelling and dye adsorption properties of the hydrogels were examined. The equilibrium swelling ratio and binding ratio of the hydrogel/dye systems greatly depends on the METAC and crosslinker concentration in the gels. The effects of pH of the medium and initial dye concentration on the adsorption were also studied. The binding ratio of the hydrogel/dye system increases in the following order: OR-II>RO-14>RO-13.

Introduction

Industrialization and urbanization have resulted in rapid deterioration of water quality. Increasingly stringent regulations for the quality of potable water have led to enhanced interest in the decontamination of wastewater. The type of the effluent present in industrial wastewater depends on nature of industry. However, some of the common pollutants generally present are metal ions, dyes, phenols, insecticides, pesticides and a wide spectrum of aromatics [1]. Among these, dyes are common pollutants in those wastewaters which originate from dye stuff and textile industries. The presence of dyes in wastewaters posses a severe problem as they are toxic to life as well as damaging to the aesthetic nature of the environment. Thus the removal of dyes from wastewater is important before they are mixed up with unpolluted natural water bodies.

A number of methods such as coagulation [2], filtration with coagulation [3], ozonation [4], adsorption [5], membrane process [6] and advanced oxidation processes [7,8] have been used for this purpose. Among these, the adsorption process is one of the effective techniques that have been successfully employed for the removal of dyes from wastewater. Many adsorbents such as activated carbon [9,10], peat [11,12], chitin[13,14], silica [15] and others [16-22] have been tested to reduce dye concentration from aqueous solutions. Perhaps polymeric sorbents with quaternary ammonium groups are the most efficient materials in binding of the dyes having sulfonic acid groups [23].

Hydrogels are water-swollen network (crosslinked structure) of hydrophilic homopolymer or copolymers. There has been increasing interest in the synthesis and various applications such as sensors, separation membranes and materials in medicine and pharmacy as drug delivery systems, in solving some ecological and biological problems as well as in modern technologies. Such polymeric hydrogels are promising materials as adsorbents for removal of some agents in environmental applications [24-25].

In the present work a series of co-polymeric hydrogels based on NVP and a cationic monomer METAC have been synthesized. Their swelling and dye adsorption characteristics have been investigated by varying both the monomers and crosslinker concentration. The effects of pH of the medium and initial dye concentration on the adsorption of hydrogels/dye systems were also studied.

Experimental

Materials

The monomers N-vinyl pyrrolidone (NVP) and 2-methacryloyloxyethyltrimethyl ammonium chloride (METAC) were obtained from Aldrich and were used without further purification. The crosslinker ethylene glycol dimethacrylate (EGDMA) was obtained from Fluka. Potassium persulphate (KPS) was provided by Merck. Dyes Orange-II, Reactive Orange -13 and Reactive Orange-14 were supplied by Ciba Speciality Chemicals. All other reagents used were of analytical grade. Distilled water was used to prepare all the dye solutions.

Hydrogels: synthesis and characterization

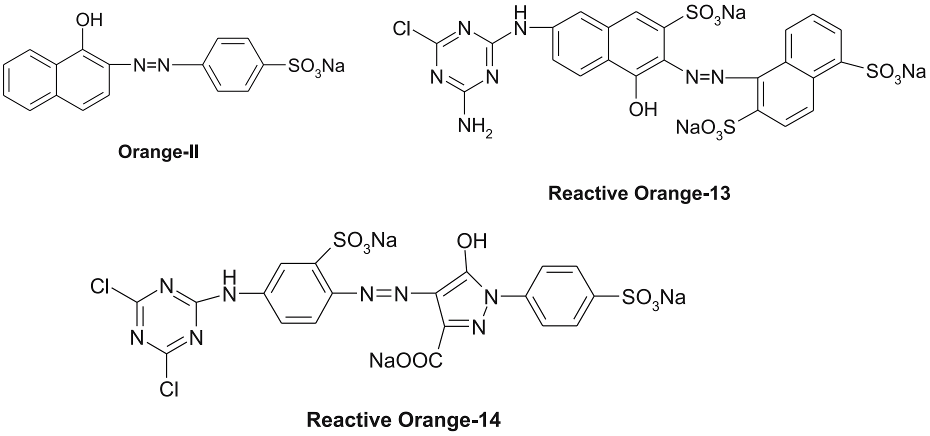
The NVP/METAC hydrogels were prepared via radical chain co-polymerization using 0.1% w/w KPS as initiator in the presence of EGDMA as a crosslinker. Monomers and crosslinker in the appropriate molar ratio were mixed together in a 100 ml beaker under magnetic stirring; an appropriate quantities of KPS dissolved in 1 ml of double distilled water was added. The mixtures were loaded in borosilicate culture test tube and heated at 60°C in a constant temperature oil bath for 6 hr even though the gels were obtained within 1 h. The polymerization reactions were carried out by varying the concentrations of NVP, METAC and crosslinker in feed. The formed hydrogels were then transferred to a 1 L beaker containing distilled water and left for 24 h by changing water at every 3 h of interval in order to remove the unreacted monomers and other reactants in the hydrogel. The swollen gels were broken into small pieces; immersed in excess of methanol and heated at 70°C for 20 minutes in order to remove the water from the gels. The gels were separated by pouring it in 200 mesh sieve and again it was immersed in fresh methanol and process was repeated until water removes completely. Finally the gels were dried in vacuum oven; grind with the help of ball mill and screened for particle size of 40 meshes. The composition details and swelling characteristics of the hydrogels has presented in table 2.

FT-IR spectroscopy (Perkin-Elmer Spectrum GX) to determine the chemical structure of hydrogels and Environmental Scanning Electron Microscope (Philips XL 30 ESEM) to observe the surface morphology of the synthesized hydrogels have been used.

Table 1 Characteristic of dyes used in this work

Name of dyes	Color Index No.	Molar Mass	Maximum adsorption Wavelength λ_{max} (nm)
Orange-II (OR-II)	15510	350.53	484
Reactive Orange-13 (RO-13)	18270	483.96	488
Reactive Orange-14 (RO-14)	19138	498.31	404

Chart 1 Structure of dyes



Orange-II

Reactive Orange-13

Reactive Orange-14

Swelling Studies

In order to determine the % equilibrium swelling (%S_{eq}) [26,27] as well as the equilibrium water content (EWC) [28,29] of the poly (NVP/METAC) hydrogels (H1-H9), the gravimetric method was employed. An accurately weighed hydrogel was put in a tea bag; immersed in a beaker containing 100 mL distilled water and allowed until it reached at equilibrium. After attaining the equilibrium, the tea bag was taken out and the excess water was removed by filter paper and then weighed accurately using an electronic balance (Citizen CX120, d=0.1 mg). Similarly the % S_{eq} of hydrogel H7 in aqueous dye solutions (50 mg L^{-1}) of OR-II, RO-13 and RO-14 was also determined. Maximum % S_{eq} in water was obtained with hydrogel H7 hence it was selected for the swelling studies for aqueous dye solutions of OR-II, RO-13 and RO-14. The % equilibrium swelling and equilibrium water content of super swelling hydrogels were calculated using the following equations 1 and 2.

$$\%Seq = \frac{W_{eq} - W_o}{W_o} X100 \tag{1}$$

$$EWC = \frac{W_{eq} - W_o}{W_{eq}} \tag{2}$$

Where W_{eq} is the weights of swollen gel at equilibrium and W_o is the weight of dry gel.

Adsorption equilibrium experimental

Bath studies were carried out in all the adsorption experiments. The adsorption equilibrium included: the effect of feed concentration of both the monomers and crosslinker, effect of pH and initial feed concentration of dyes on adsorption of dyes.

Adsorption procedures

Dried samples (0.1g each) of hydrogels were equilibriated for 24 h in 50 mL of each dye solution at 25°C. The concentrations of dyes remaining in the solution were determined by UV-Visible spectrophotometer (Shimanzu-16A) using precalibrated curves. All measurements were carried out in duplicate. The adsorption amount Q in mg g^{-1} was calculated using following equation. [30]

$$Q = \left(\frac{Co - C}{m} \right) V \tag{3}$$

Where V is the volume of solution in L, m is the weights of dry hydrogels in g and Co, C are the concentrations of dyes in solution before and after the adsorption respectively in mg L^{-1}.

Effect of feed concentrations of NVP, METAC and EGDMA on dye adsorption

Bath studies were carried out with the all prepared nine hydrogels to determine the effect of variation in feed concentrations of NVP, METAC and EGDMA on dye adsorption. Fifty mL each of OR-II, RO-13 and RO-14 dye solutions (50 mg L^{-1} concentration) were mixed with the hydrogels (0.1g) and kept at 25°C for 24 h to attain equilibrium.

Effect of initial dye concentration on adsorption

This was done by equilibrating a fixed amount of the hydrogels (0.1g) with a series of gradually increased dye concentration by keeping at 25°C for 24 h to attain the equilibrium.

Effect of pH on dye adsorption

The effect of pH on dye adsorption was measured by interacting 0.1 g of the dry hydrogel sample (H7) with 50 mL each of 50 mg L^{-1} solutions of RO-13 and RO-14. The various dye solutions were adjusted to the desired pH value by addition of 0.1N HCl or 0.1N NaOH.

Results and Discussion

Hydrogels: synthesis and characterization

In the present study, hydrogels based on N-vinylpyrrolidone and 2-(methacryloyloxyethyl) trimethyl ammonium chloride were prepared via bulk polymerization using KPS as initiator and EGDMA as crosslinker at 60°C. The polymerization process starts with the formation of free radical by decomposition of initiator. The free radical may interact with NVP, METAC and or with crosslinker, thereby initiates the polymerization, copolymerization and crosslinking process simultaneously. The synthesized hydrogels have been characterized by FT-IR and SEM.

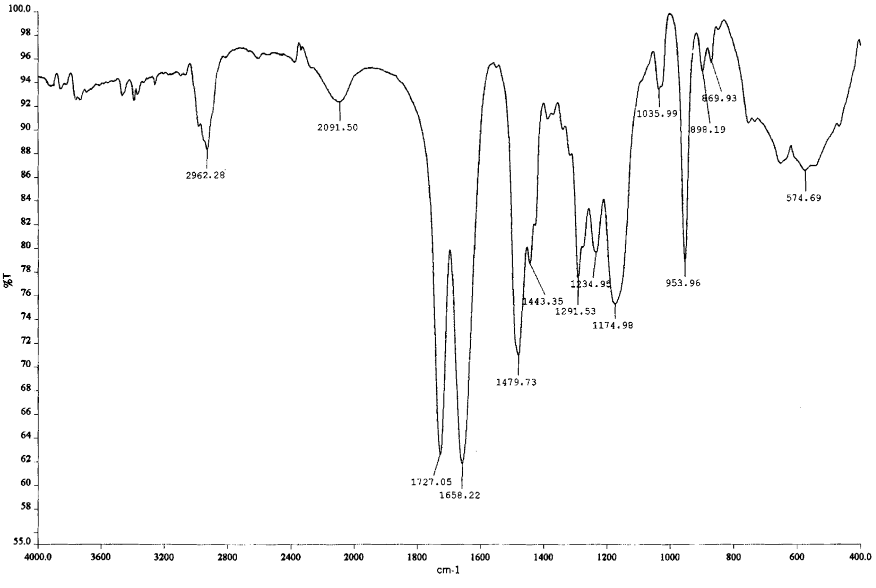


Figure 1 FT-IR spectra of poly(NVP/METAC) hydrogels

A representative IR spectrum of poly (NVP/METAC) hydrogel is presented in figure 1.The IR spectra of the hydrogel showed the presence of peaks corresponding to the functional groups of monomeric units present in the copolymeric hydrogel chain. Ester groups were identified by peaks at 1727 cm^{-1} (C=O stretching) and at 1291 cm^{-1} (C-O stretching). A strong peak appear at 1658 cm^{-1} corresponds to C=O stretching of pyrrolidone ring. The characteristic peak observed at 954 cm^{-1} is due to the quaternary nitrogen of METAC present in the hydrogels. Other peaks represent C-C and C-H vibrations of $–CH_3$ and $–CH_2$ groups. The above IR analysis indicates the presence of all monomeric units in the crosslinked hydrogel.

The surface morphology of the hydrogels was also analyzed by SEM and the representative SEM micrograph is depicted in figure 2. The SEM image of poly (NVP/METAC) hydrogels revealed the formation of pores in the hydrogels. The shape of the pores is irregular and the pore might be interconnected. The structure porosity is due to solvent drying of hydrogels.

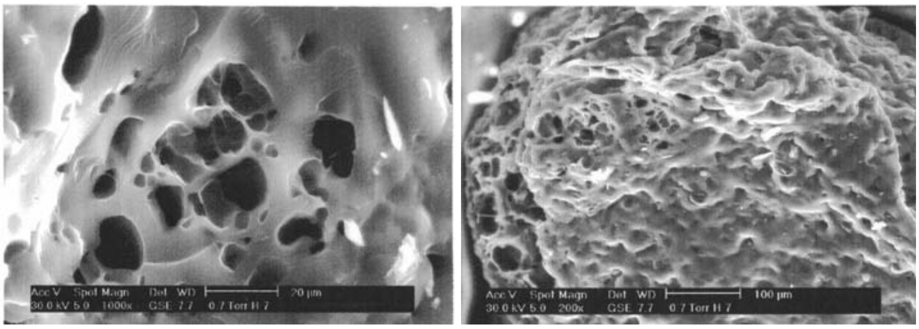


Figure 2 SEM photographs of hydrogel H7

Effect of feed concentrations of NVP, METAC and EGDMA on its swelling behavior

The effects of feed composition on the swelling of the prepared poly (NVP/METAC) hydrogels were studied and the results are presented in table 2. It can be seen from the table that the swelling behavior of the hydrogels greatly influenced by its composition.

By comparing the % S_{eq} values of H1, H2 and H3 it is clear that the % S_{eq} value increases with the increase in concentration of METAC in the hydrogels. It is well known that the swelling of hydrogel is induced by electrostatic repulsion of the ionic charge of its network [27]. Ionic charge content is important. METAC contains cationic (–NMe_3) unit. As the concentration of METAC in hydrogel increases, the cationic content in the gel increases and it will result in increase in the equilibrium swelling. In case of H4, H5 and H6 the rise in the % S_{eq} is comparatively less. Because as the content of NVP in hydrogels increases hydrophilicity of the polymer network also increases, this results in more adsorption of water.

Table 2 Composition details and swelling characteristics of hydrogels

Hydrogel Code	NVP mM	METAC mM	EGDMA mM	% S_{eq}	EWC
H1	23.4	24.0	0.1659	10653	0.9907
H2	23.4	28.0	0.1799	12728	0.9922
H3	23.4	32.0	0.1939	14778	0.9933
H4	28.1	20.0	0.1684	7436	0.9867
H5	37.4	20.0	0.2009	7803	0.9873
H6	46.8	20.0	0.2338	8330	0.9881
H7	28.1	24.0	0.1563	15459	0.9936
H8	28.1	24.0	0.2344	10346	0.9904
H9	28.1	24.0	0.3126	5884	0.9833

It is well known that the degree of crosslinking greatly depends on the concentration of crosslinker. Table 2 shows that the % S_{eq} of hydrogels H7, H8 and H9 decreases sharply i.e. the swelling of hydrogels decreases by increasing concentration of crosslinker. These results could be explained in terms of crosslinking degree. The increment in the degree of crosslinking reduces the free volume available for swelling by increasing the tightness of the network structure. A similar trend has been observed in the EWC values.

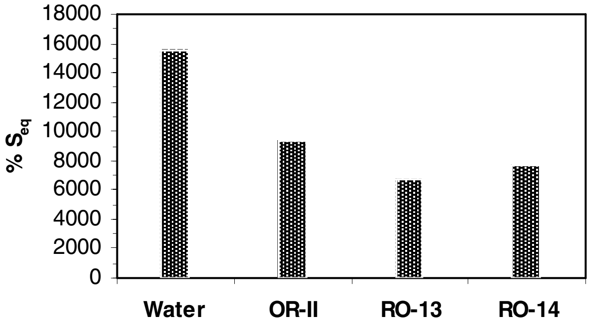


Figure 3 The % S_{eq} of hydrogel H7 in water and in 50 mg L^{-1} aqueous dye solutions

The comparison of % S_{eq} values of the hydrogel H7 in water and in aqueous dye solutions (50 mg L^{-1}) are shown in figure 3. The % S_{eq} of hydrogel H7 is between 6722 and 9367 in the aqueous solutions of the dyes but 15459 in distilled water.

The dyes contain unpaired electrons in the N and O atoms. These atoms behave like a hydrophilic group and form hydrogen bonds with water. Thus the swelling of NVP/METAC hydrogels changes as the dyes bring water into gels. At the end of this evaluation, the super swelling hydrogels in the aqueous solutions are swollen in the following order: Water>OR-II>RO-14>RO-13.

Effect of feed concentrations of NVP, METAC and EGDMA on dye adsorption

Poly(NVP/METAC) hydrogels of different compositions were investigated for the adsorption of dyes OR-II, RO-13 and RO-14 by the bath equilibrium method. The amount of dye adsorbed (in mg dye/g gel) by the different hydrogels is given in figure 4. From the figure 4(a) it is observed that the amount of adsorbed dyes i.e binding ratio increases with increase content of METAC in feed, as METAC contains cationic $-N(CH_3)_3$ group which increases the ionic interactions with the $-SO_3H$ group of the dyes. By looking at figure 4(b) we can say that the binding ratio also increases with the increase content of NVP in hydrogels, but the rise in Q is comparatively small. The possible reason for this is that, NVP can be cationic in character on the polar lactum ring because of the resulting of keto-enol tautomerism[31] . Also with the increasing content of NVP the hydrophobic interactions of the NVP ring with the dye molecule increases.

The other type of interaction between superswelling hydrogel and dyes may be:

a. Hydrophobic interaction: These are specially aqueous-solution interaction, which in the present case will involve the aromatic ring on the anionic dye molecules and the methine and methylene groups of on crosslinked polymer chain.

b. Dipole/induced-dipole interaction: These will occur between the dipolar amide and ester groups on monomer unit and polarisable aromatic groups on the dye molecules.

c. Hydrogen bonding: Bonding of this type will be expected to occur between the amine and phenolic hydroxyl groups of dye molecules with carbonyl groups of the monomer unit of the crosslinked polymer chain.

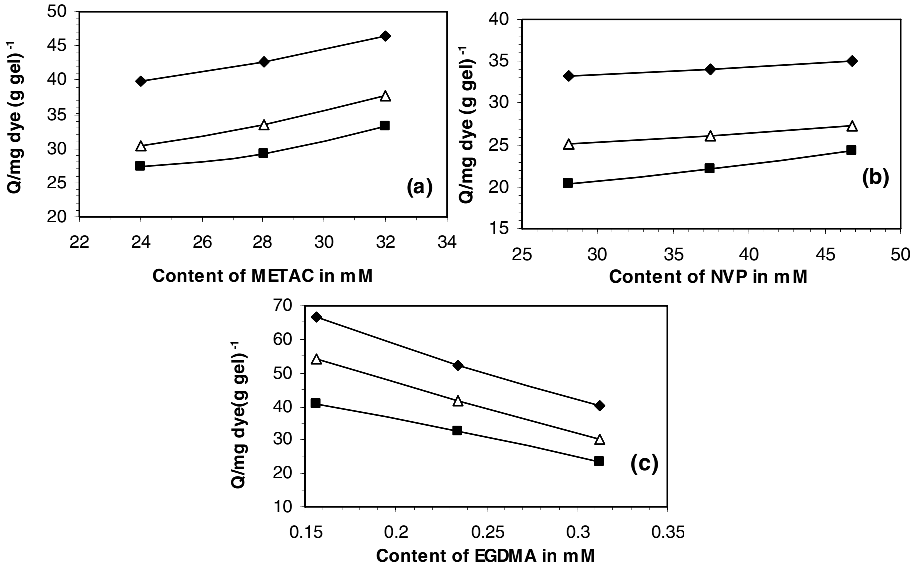


Figure 4 The variation of the binding ratios of adsorbed dyes on to NVP/METAC hydrogels in 50 mg L^{-1} dye solutions (♦) OR-II, (Δ) RO-14, (■) RO-13

Figure 4(c) indicates that the Q values decreases sharply with increase content of EGDMA. As the crosslinker content increases, crosslinking density increases. These increased crosslinking density decrease the free volume, the number of binding sites per unit volume of gels decreases hence the dye adsorption also decreases.

The binding ratio of the dyes was calculated for the uptake of dyes within the hydrogel H7 in 50 mg L^{-1} of aqueous solutions, and they are presented in Figure 5. Figure 5 shows that the binding ratio of the hydrogel/dye systems increased in the following order: OR-II>RO-14>RO-13. As expected, this result parallels the result of the equilibrium swelling.

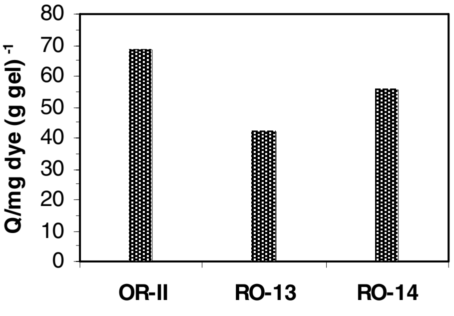


Figure 5 The binding ratios of hydrogel(H7)/dye systems in 50 mg L^{-1} of aqueous dye solutions

3.4 Effect of initial dye concentration on adsorption

To explore the applicability of the poly (NVP/METAC) hydrogels, it was informative to obtain knowledge on its sorption capacity towards OR-II, RO-13 and RO-14. This is carried out by equilibrating a fixed amount of the hydrogel H7 with a series of dye solutions of gradually increasing concentration. Figure 6 shows the uptake profile of hydrogel H7 towards OR-II, RO-13 and RO-14 with different initial feed solutions concentrations.

Figure 6 shows that the adsorption of the dyes within NVP/METAC hydrogels corresponds to type-S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution [32]. In the S curves in the Giles classification system, the initial direction of curvature shows that adsorption becomes easier as the concentration rises. In practice, the S curves usually appears when three conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in a regular array in the adsorbed layer and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another absorbed species [32].

The weakness of the adsorbent-adsorbate forces causes the uptake at low concentrations to be small; but once a molecule has become adsorbed, the adosrbate-adsorbate forces promotes the adsorption of further molecules (a cooperative process) so that the isotherm becomes convex to the concentration axis. Types-S isotherms may originate through the adsorption of either nonpolar molecules or polar molecules, always provided that the adsorbent-adsorbate force is relatively weak.

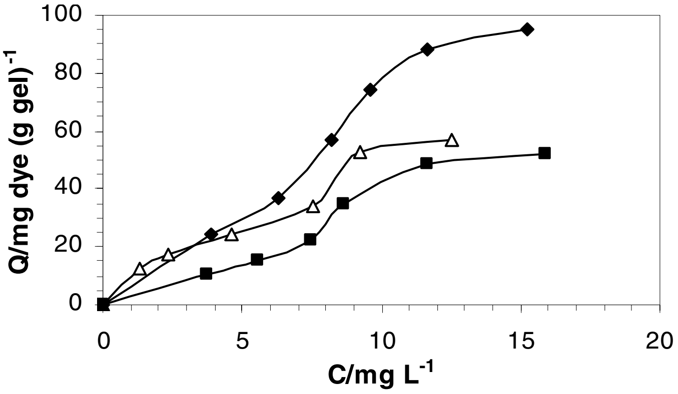


Figure 6 Binding isotherms of NVP/METAC hydrogel(H7)/dye systems. (◆) OR-II, (Δ) RO-14, (■) RO-13

3.5 Effect of pH on dye adsorption

It is well known that the pH of the medium has great influence on the performance of the hydrogels that it influences its swelling. The adsorption behavior of RO-13 and RO-14 on poly (NVP/METAC) hydrogel at various pH was investigated in the bath process and the results are presented in Figure 7.

Figure 7 shows that as pH of the medium increases the dye adsorption also increases, but the increase in Q values is small. At basic pH, dye adsorption occurs via strong ionic interaction between positive –NMe$_3$ of crosslinked hydrogel chain and negative –COONa and –SO3Na groups of the dye molecules. At acidic pH the ionic interaction

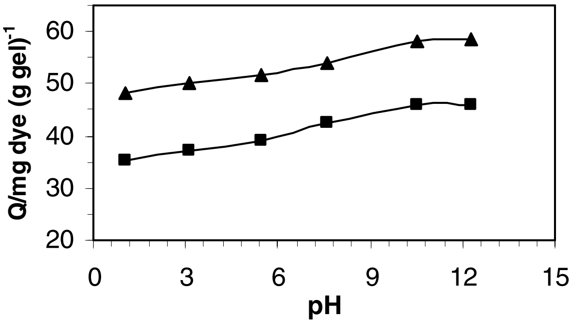


Figure 7 The variations of binding ratios of adsorbed dyes on to hydrogel H7 with respect to pH: (■) RO-13, (▲) RO-14

is comparatively weak due to partial positive charge of –COOH and –SO3H groups of dye molecules. By looking at figure 7 we can say that the pH has no profound effect on dye adsorption i.e. the poly(NVP/METAC) super swelling hydrogel can adsorb dyes over whole pH range.

Conclusions

This study showed that poly(NVP/METAC) superswelling hydrogels adsorb acid and reactive dyes such as OR-II, RO-13 and RO-14. Type-S adsorption isotherms in Giles' classification system were found. The % S_{eq} and EWC of hydrogels were increased with the content of METAC & NVP and decreased with the content of EGDMA in hydrogels. The values of EWCs were calculated in the range 0.9833-0.9936. These results showed that NVP/METAC hydrogels would be used as a new material (such as biomaterial) on some biomedical applications, because EWCs found are grater than the percent water content value of the body (about 0.6). The adsorption of the dyes was increased with the content of METAC and NVP and decreased with the content of EGDMA. The uptake of the dyes within the hydrogels increased in the following order: OR-II>RO-14>RO-13. The pH has no profound effect on dye adsorption but maximum dye adsorption was obtained at highly basic pH.

As a result NVP/METAC superswelling hydrogels can be used as sorbents for water pollutants such as acid and reactive dyes over whole pH range, which is an important problem for the textile industries.

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