Adsorption of Apollo reactive dyes on poly(\(N,N\) dimethylamino ethylmethacrylate) hydrogels

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Abstract

Poly(\(N,N\)-dimethylamino ethylmethacrylate) [P(DMAEMA)] hydrogels were prepared by irradiating the ternary mixtures of dimethylamino ethylmethacrylate (DMAEMA)/ethyleneglycol dimethacrylate (EGDMA)/water (H\(_2\)O) by \(\gamma\)-rays at ambient temperature. The swelling of four types of DMAEMA hydrogels in distilled water is higher than the swelling of these hydrogels in dye solutions. The value of equilibrium swelling of P(DMAEMA)1 hydrogel was 338% at pH 7.0 in distilled water, while it was 325% and 326% at pH 7.0 in Apollofix Red (AR) and Apollofix Yellow (AY) solutions, respectively. The adsorption capacity of P(DMAEMA)1 hydrogel was found to increase from 85 to 131 mg for AR g\(^{-1}\) dry gel and from 58 to 111 mg for AY g\(^{-1}\) dry gel with decreasing pH of the dye solutions.

Keywords: Poly(\(N,N\)-dimethylamino ethylmethacrylate) hydrogels; Adsorption of Apollo reactive dyes

1. Introduction

Polymeric hydrogels have a series of particular characteristics; they are hydrophilic, insoluble in water, soft, elastic, and swell in water keeping their shapes but increasing in volume until reaching a chemical equilibrium. Hydrogel properties depend strongly on the degree of cross-linking, the chemical composition of the polymer chains, and interactions of the network and surrounding liquid. Numerous attempts have been made to model the swelling behavior of all these ionizable gels. Much of the initial background work on charged systems has been done by some groups (Katchalsky, 1954; Katchalsky et al., 1951; Şen and Güven, 1998; Şen and Güven, 2001) who have analyzed the behavior of polyelectrolyte solutions and polyelectrolyte gels.

Crosslinked hydrogels are prepared by initiating the polymerization by ionizing radiation, by UV (with sensitizers or initiators added) or by chemical (thermal) initiators. The initiation with high-energy irradiation is generally termed a ‘‘clean technique’’, not requiring any extra chemicals and leaving no unwanted residues. It can be applied at any temperature and dose rate.

Hydrogels are used in the food industry (as thickening agent, etc.), pharmaceutical, agriculture and related fields, as technical and electronic instruments, biomedicine, bioengineering, veterinary photographic technology and adsorbent on removal of some unwanted agent in environmental applications (Kulicke and Nottelman, 1989).

Pollution caused by textile wastewater is a common problem faced by many countries. Dyeing of wastewater in textile industry is generally high in both color and organic content. Some dyes are stable to biological degradation and metal containing may be toxic (McKay and Otterburn, 1985). Some of dyes are carcinogenic and mutagenic. The removal of color from textile wastewaters is a major environmental problem because of treating such waters by conventional methods. Adsorption has evolved into one of the most effective physical processes for decoloration of textile wastewater (Yeh and Thomas, 1995). Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions (Kozuka et al., 1986).
Color in water and wastewater may be due to presence of colored organic substances or highly colored industrial wastes. Pulp, paper and textile wastes are common as sources of coloring in water. In this study, our aims are the investigation of the swelling behavior and diffusion of water and Apollo reactive dye molecules into poly(N,N-dimethylamino ethylmethacrylate) [P(DMAEMA)] hydrogels and determination of the optimum adsorption conditions like pH and dye concentration for Apollo reactive dyes.

2. Experimental

2.1. Chemicals

The monomers used in this study, N,N-dimethylamino ethylmethacrylate (DMAEMA) and cross-linking agent, ethyleneglycol dimethacrylate (EGDMA) were obtained from Aldrich. Apollofix Red (AR) and Apollofix Yellow (AY) were also obtained from Aldrich. The chemical formula of the monomers and dyes are given in Scheme 1.

2.2. Preparation of hydrogels

For the preparation of monomer mixtures, firstly, 4 ml DMAEMA was mixed with 11, 22, 44 and 88 μl EGDMA; later these solutions were mixed with water. The amount of water in the final mixtures is 25% (w/v) (DMAEMA:EGDMA mol. ratios: 99.72:0.28, 99.43:0.57, 98.87:1.13 and 97.77:2.23). Monomer solutions thus prepared were placed in PVC straws of 4 mm diameter and irradiated up to 4.0 kGy in Gammacell-220 type γ-iradiator at a fixed dose rate of 0.16 kGy h\(^{-1}\). Hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm and stored for later evaluations. Hundred percent gelation was achieved for all mixtures at 4.0 kGy irradiation. So, the mole percentages of EGDMA in DMAEMA:EGDMA mixtures to prepare P(DMAEMA)\(_1\), P(DMAEMA)\(_2\), P(DMAEMA)\(_3\) and P(DMAEMA)\(_4\) hydrogels are 0.28, 0.57, 1.13 and 2.23, respectively. The composition of the four different monomer/cross-linking agent mixtures is given in the following. The densities of DMAEMA and EGDMA are 0.933 and 1.05 g cm\(^{-3}\), respectively. Since the weight percent is not significant, we have to use the mole percents.

<table>
<thead>
<tr>
<th>Monomer mixtures</th>
<th>(v/v)</th>
<th>(w/w)</th>
<th>(n/n)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMAEMA/</td>
<td>4 ml</td>
<td>3.732 g</td>
<td>99.72/</td>
</tr>
<tr>
<td>EGDMA)1</td>
<td>88 μl</td>
<td>9.24 × 10(^{-5}) g</td>
<td>0.28/</td>
</tr>
<tr>
<td>DMAEMA/</td>
<td>4 ml</td>
<td>10.263 g</td>
<td>99.43/</td>
</tr>
<tr>
<td>EGDMA)2</td>
<td>88 μl</td>
<td>9.24 × 10(^{-5}) g</td>
<td>0.57/</td>
</tr>
<tr>
<td>DMAEMA/</td>
<td>4 ml</td>
<td>20.526 g</td>
<td>98.87/</td>
</tr>
<tr>
<td>EGDMA)3</td>
<td>88 μl</td>
<td>9.24 × 10(^{-5}) g</td>
<td>1.13/</td>
</tr>
<tr>
<td>DMAEMA/</td>
<td>4 ml</td>
<td>41.052 g</td>
<td>97.77/</td>
</tr>
<tr>
<td>EGDMA)4</td>
<td>88 μl</td>
<td>9.24 × 10(^{-5}) g</td>
<td>2.23/</td>
</tr>
</tbody>
</table>

2.3. Adsorption studies

For the determination of dye uptake capacity of hydrogels, about 0.05 g P(DMAEMA) hydrogels were transferred into 50 ml dye solution with desired pH 3.0–8.0 and allowed to equilibrate for 48 h at 25 °C. These aqueous solutions were separated by decantation from the hydrogels. Adsorption measurements were carried out by using Philip 8510 model UV–vis spectrophotometer at ambient temperature. The absorbances of AR solutions were determined at 534 and 514 nm wavelengths for pH 7.0 and 3.0, respectively. The maximum wavelength of AY solutions in pH 7.0 and 3.0 is 426 nm.

3. Results and discussion

3.1. Swelling behaviors of hydrogels in water and dye solutions

Dried hydrogels (2 mm thickness, 3 mm diameter) were left to swell in solution at pH 7.0, ionic strength \(I = 0.1\), at a temperature of 25 °C. The measurements were continued until a constant weight was reached for each hydrogel was calculated from the following relation:

\[
\%S = \left[ \frac{m_t - m_o}{m_o} \right] \times 100, \tag{1}
\]

where \(m_t\) is the mass of swollen gel at time \(t\), and \(m_o\) is the initial mass of the dry gel.

To determine water uptake of dry hydrogels, P(DMAEMA)\(_1\)–4 hydrogels were swollen in 20 ml of water, AR and AY solutions at 25 °C until equilibrium. The hydrogels were weighed after removal of excess surface water and swelling versus time was measured. The dynamic swelling curves of P(DMAEMA)\(_1\)–4 hydrogels in distilled water are given in Fig. 1. Percent swelling of P(DMAEMA)\(_1\)–4 hydrogels were close to each other and were between 195% and 326% at pH 7.0. The water uptake capacity of P(DMAEMA)\(_1\) hydrogel which contains the least amount of cross-linking agent shows the maximum equilibrium swelling than the other P(DMAEMA)\(_2\)–4 hydrogels. Since the swelling of four types of P(DMAEMA) hydrogels in distilled water is higher than the swellings of these hydrogels in dye solutions, the value of equilibrium swelling of P(DMAEMA)\(_1\) hydrogel was 338% at pH 7.0 in distilled water while it was 325% and 326% at pH 7.0 in AR and AY solutions, respectively. Since the molecular structure of water is smaller than those of dye molecules, diffusion of water molecules into P(DMAEMA)\(_1\)–4 hydrogels is performed very easily.

3.2. Effect of dye concentration on adsorption

Adsorption of the dyes from aqueous solution was investigated in continuous adsorption equilibrium.
experiments. Effects of the initial dye concentration on the adsorption rate and capacity were studied. Optimum mass of hydrogel on dye adsorption was determined. The anionic dye solutions were prepared in the concentration range of 10–250 mg l\(^{-1}\) for AR and AY. Approximately, 0.05 g of P(DMAEMA)\(\text{-}1–4\) hydrogels containing 0.28, 0.57, 1.13 and 2.23 mol of DMAEMA irradiated to 4.0 kGy were transferred into 50 ml of the dye solution at pH 7.0 and agitated magnetically at moderate rpm at room temperature and allowed to equilibrium for 48 h at 25 \(^\circ\)C.

After adsorption, the P(DMAEMA)\(\text{-}1–4\) hydrogels were removed from the adsorption medium. The concentration of the dyes in aqueous phases was measured by UV–vis spectrophotometer after the desired treatment period. The amount of adsorption per unit mass of the P(DMAEMA) hydrogels were evaluated by using the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{W},
\]

where \(q_e\) is the amount of dye adsorbed per unit mass of the P(DMAEMA) hydrogels (mg g\(^{-1}\)), \(C_0\) the initial concentration of dye solution (mg l\(^{-1}\)), \(C_e\) the equilibrium concentration of dye solution (mg l\(^{-1}\)), \(V\) the volume of dye solution (l), and \(W\) is the amount of dry hydrogel (g).

As can be seen from Figs. 2 and 3, adsorption capacities of P(DMAEMA) hydrogels were increased when the dye concentration increased. It is clear that the cross-linking agent content affected the dye adsorption of P(DMAEMA) hydrogels. The dye adsorption and diffusion into P(DMAEMA) hydrogels was the highest due to the increase of dye diffusion into hydrogel and increase specific interactions between the polymer chains and dye molecules.

3.3. Effect of pH on dye adsorption

To investigate the effect of pH on dye adsorption into P(DMAEMA)\(\text{-}1–4\) hydrogels, adsorption studies were performed at pH 3.0 for AR and AY dyes and the results were given in Figs. 2 and 3, respectively. P(DMAEMA) hydrogels showed higher adsorption at acidic medium. AR and AY contain many functional groups such as amino, azo and sulphoxide groups, which may interact with cationic groups in P(DMAEMA)\(\text{-}1–4\) hydrogels depending on the pH of the medium. It was determined that the equilibrium swelling of P(DMAEMA)\(\text{-}1–4\) hydrogels and dye adsorption into P(DMAEMA)\(\text{-}1–4\) hydrogels are very sensitive to pH changes of the solution. The intermolecular interactions between positively ionized hydrogel and dye molecules, the swelling of P(DMAEMA)\(\text{-}1–4\) hydrogels and adsorption of dye molecules into P(DMAEMA)\(\text{-}1–4\) hydrogels were the highest at low pH due to protonization and electrostatic interactions.

3.4. Determination of dye adsorption type

The capacity of P(DMAEMA)\(\text{-}1–4\) hydrogels for AR and AY dyes can be determined by measuring adsorption isotherms. The distribution of dye between P(DMAEMA)\(\text{-}1–4\) hydrogels and dye solution (Maghami and Roberts, 1988; Nassar and El-Geundi, 1991), when the system is in a state of equilibrium is important to establish to tendency of the P(DMAEMA)\(\text{-}1–4\) hydrogels for the
dyes. The adsorption isotherms are shown in Fig. 4 for the adsorption of AR dye on P(DMAEMA)1–4 hydrogels at pH 7.0 and 3.0. For the adsorption of AY on P(DMAEMA)1–4 hydrogels, the adsorption isotherms were given at pH 7.0 and 3.0 in Fig. 5. Adsorption isotherms (Duran et al., 1999) were analyzed according to the linear form of the Langmuir isotherm, as

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e,
\]

where \(C_e\) is the equilibrium concentration of adsorbate in solution, \(q_e\) represents the adsorbed dye per unit mass of P(DMAEMA)1–4 hydrogels at equilibrium and \(K_L\) and \(a_L\) are the Langmuir isotherm constants. Linearity can be obtained by plotting \(C_e/q_e\) versus \(C_e\), from the intercept \(1/K_L\) and the slope \(a_L/K_L\), are derived. The ratio \(K_L/a_L\) is defined as the capacity factor (the maximum adsorption capacity of adsorbent for a particular dye). The plots of the isotherms which are shown in Figs. 4 and 5 and are seen to be linear over the whole concentration range. The parameters \(K_L\) and \(a_L\) of the Langmuir were calculated for AR and AY. AR has an adsorption capacity of 117.04, 87.67, 107.99, 60.13 mg g\(^{-1}\) for P(DMAEMA)1–4 hydrogels at pH 7.0 and for AY 66.09, 57.80, 44.90, 36.17 mg g\(^{-1}\) for P(DMAEMA)1–4 hydrogels at pH 7.0, respectively. \(K_L\), \(a_L\) and \(q_{max}\) are given in Table 1.

Fig. 2. Effect of AR concentration on the adsorption capacity of hydrogels at pH 7.0 and 3.0.

Fig. 3. Effect of AY concentration on the adsorption capacity of hydrogels at pH 7.0 and 3.0.
Fig. 4. Langmuir isotherms of AR solution at pH 7.0 and 3.0.

Fig. 5. Langmuir isotherms of AY solution at pH 7.0 and 3.0.

Table 1

<table>
<thead>
<tr>
<th>Dye</th>
<th>P(DMAEMA)1</th>
<th>P(DMAEMA)2</th>
<th>P(DMAEMA)3</th>
<th>P(DMAEMA)4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$</td>
<td>$a_L$</td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>AR pH 7.0</td>
<td>2.22</td>
<td>0.02</td>
<td>117</td>
<td>2.45</td>
</tr>
<tr>
<td>AR pH 3.0</td>
<td>16.96</td>
<td>0.12</td>
<td>135</td>
<td>9.87</td>
</tr>
<tr>
<td>AY pH 7.0</td>
<td>1.45</td>
<td>0.02</td>
<td>66</td>
<td>1.63</td>
</tr>
<tr>
<td>AY pH 3.0</td>
<td>4.86</td>
<td>0.04</td>
<td>135</td>
<td>4.51</td>
</tr>
</tbody>
</table>

$K_L = 1 \text{ g}^{-1} \cdot \text{L} \cdot \text{g}^{-1}; a_L = \text{mg}^{-1} \cdot \text{L} \cdot \text{g}^{-1}; q_{\text{max}} = \text{mg} \cdot \text{g}^{-1}.$
4. Conclusion

P(DMAEMA) hydrogels were found to be effective in adsorption of anionic dyes, such as AR and AY. They performed high sensitivity towards pH. Adsorption capacity of the hydrogels at pH < 7.0 provides a great advantage in utilization of this hydrogel system for the removal of basic textile dyes from wastewater.

References


