Preparation of Interpenetrating Polymer Network Gel Beads for Dye Absorption

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ABSTRACT: Preparation of interpenetrating polymer network (IPN) gel beads for dye absorption was carried out by using simultaneous crosslinking method. First, sodium alginate (SA), 3-(methacrylamido) propyl trimethyl ammonium chloride (MAPTAC), and/or acrylamide (AM), $K_2S_2O_8$, and N,N′-methylenebisacrylamide (MBAM) were mixed in aqueous solution. The beads were prepared using $K_2S_2O_8$ and MBAM as the initiator and crosslinking agent, respectively. Then, the solution was dropped into $CaCl_2$ solution mixed with N,N,N′,N′-tetramethylethylenediamine (TMEDA). The former was used as the crosslinking agent of alginate and the latter was used as the accelerator for the polymerization of monomer in the alginate solution. The gel bead composed of only alginate was also prepared to compare the properties with IPN gel bead. The components in IPN gel bead were examined by FTIR analysis. The factors effecting the particle size of alginate and IPN gel beads were investigated. In alginate gel bead, the concentration of solution affected the particle size, whereas type of monomer affected the particle size of IPN gel bead. The IPN gel bead had smooth surface (from SEM results), different from the alginate bead. Alginate content caused the swelling behavior of dried IPN beads. Cationic dye was absorbed by crosslinked alginate gel bead. The absorption of reactive dye by IPN gel bead was a result of its cationic charge. The absorption density of IPN gel beads was the reciprocal of the absorbent dosage. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1585–1591, 2006

Key words: interpenetrating polymer network; gel bead; dye absorption; absorbent; cationic charge; wastewater

INTRODUCTION

Textile effluent is the polluting industrial waste. It is difficult to remove the dyes from the effluents, since most dyes are stable to light, heat and are nonbiodegradable. Absorption is one treatment technique for the removal of textile dye waste commonly containing anionic dyes such as reactive dyes. The absorption process has been considered because it has the ability to treat dye in more concentrated form.[1] Typical dye absorbents include agricultural by-products,[2,3] activated carbon,[4,5,6] and metal sludge.[7] Agriculture-based absorbents usually contain a negative charge, hence repels anionic dyes. Quaternized polysaccharide or cellulose with quaternary ammonium compound were studied.[8,9] Gangneux reported that quaternized cellulose effectively bound a variety of anionic dyes, including reactive dyes.[10] Absorbents based on synthetic polymers are commercially available and have mostly found application in areas of chromatography,[11,12] water softening, and small ionic species,[13] such as counter anion[14,15] and cations.[16] Their absorption capacity of very large molecules such as most synthetic dyes is extremely low and costly to be applied. Recently, an interpenetrating polymer network (IPN) has gained widespread acceptance in industrial application.[17] Combination of two polymers provides the possibility of effectively producing advanced multicomponent polymeric systems, with new property.[18,19]

Sodium alginate is a polysaccharide derived from sea algae. An aqueous solution of alginate is transformed into a hydrogel on addition of metallic divalent cations, such as Ca^{2+}, Cu^{2+}, and Cd^{2+}. The carboxylic groups are generally the most abundant acidic functional group in the sodium alginate. The absorption capacity of the sodium alginate is directly related to the presence of these sites on the polymer.

3-(Methacrylamido) propyl trimethyl ammonium chloride (MAPTAC) is the cationic monomer. Polymerization of MAPTAC produces the polymer PMAPTAC, which has cationically charged ——$N^+(CH_3)Cl^-$ on the polymer chain. If a polymer has charged groups on its chain, it will be more effective as an absorbent. The crosslinked polymer of quaternary ammonium compound was the fatal defect in poor wet strength attributed to the high charge density along the polymer chains.[20]

TABLE I
Experimental Conditions

Type of IPN gel bead	Conditions						Composition ratio
	SA (g)	AM (g)	MAPTAC (g)	$K_2S_2O_8$ (g)	TMEDA (g)	MBAM (g)	
SAAM	1.5	2.5	-	0.10	0.8	0.10	SA:AM, 3:5
SAM	1.5	-	2.5	0.10	0.8	0.10	SA: MAPTAC, 3:5
SAAMM1	0.5	1.66	2.5	0.17	0.8	0.17	SA:AM:MAPTAC, 1:0.33:5
SAAMM3	1.5	1.66	2.5	0.17	0.8	0.17	SA:AM:MAPTAC, 3:0.33:5

Copolymerization of acrylamide with quaternary ammonium compound such as diallydimethylammonium chloride has been studied.[21–23] The copolymer was prepared by dispersion polymerization, solution polymerization, and inverse emulsion polymerization.[24] These methods use solvents or emulsifiers for the preparation of polymer, that are difficult to remove.

The present study is carried out to prepare IPN gel beads composed of sodium alginate, acrylamide, and MAPTAC for textile dye absorption. Sodium alginate was crosslinked with $CaCl_2$, whereas acrylamide and MAPTAC were crosslinked with N,N'-methylenebisacrylamide (MBAM) using N,N,N',N'-tetramethylethylenediamine (TMEDA) as accelerator. The characteristics of gel beads were studied. Dye absorption is also presented to elucidate the dye absorption capacity of the IPN gel beads.

EXPERIMENTAL

Materials

Sodium alginate from brown algae was purchased as alginic acid sodium salt (Fluka). MAPTAC (50 wt % solution) was purchased from Aldrich. Potassium persulfate, from M and B Laboratory Chemical, was used as received. The acrylamide, MBAM, and TMEDA were purchased from Fluka. The cationic dye Taiacryl Brilliant Red 4GN (C.I. Basic Red 14) was supplied by Modern Dyestuffs and Pigment Co. The commercial reactive dye (also from Modern Dyestuffs and Pigment Co.) chosen for this study was C.I. Reactive Red 195.

Preparation of alginate gel beads

Alginate gel beads were prepared with five different percentages of alginate (2, 3, 4, 5, and 6% (w/v)). An 100 mL aliquot of the alginate solution was added dropwise into 200 mL of $0.3M$ $CaCl_2$ solution. The beads were cured in the $CaCl_2$ solution for 30 min after which the solution was decanted. They were rinsed with distilled water and then transferred into distilled water.

Preparation of IPN gel beads

The IPN gel beads were prepared as follows. First, the alginate was dissolved in distilled water at 70°C for 30 min and a 20 mL aqueous solution was made. Next, the $K_2S_2O_8$, MBAM, MAPTAC, and/or acrylamide monomer were mixed in the desired proportions. The experimental conditions and designations of the IPN gel beads are listed in Table I. The acrylamide and MAPTAC were crosslinked in the presence of alginate, using $K_2S_2O_8$ and MBAM as the initiator and crosslinking agent, respectively. The initiator and crosslinking agent were 4 wt % of monomer. Then, the viscous solution was introduced into a 25 cm³ burette and was added dropwise into 200 mL $0.3M$ $CaCl_2$ mixed with 0.8 g of TMEDA. The former was used as the crosslinking agent of alginate and the latter was used as the accelerator for the polymerization of monomer in the alginate solution. The IPN gel beads were stored at room temperature for 24 h. After that, they were washed with distilled water for 3 times and transferred into distilled water at room temperature.

Characterizations

Particle size measurement

The diameter of gel beads was measured by caliper.

FTIR measurement

FTIR spectra of IPN beads was recorded in KBr pellets by using an Omnic Nicolet Impact 400 D FTIR spectrophotometer.

Microscopic studies

The surface morphology of alginate and dried IPN beads was observed with a scanning electron microscope (SEM, XL 30 CP, Philips).

Swelling studies

Dried beads were immersed in water and in 1% NaCl solution until they swelled to equilibrium. Swollen gels were removed from the water or NaCl solution,

dried with filter paper, and weighed. The percent swelling of each gel bead was calculated from the following relation.

$$\% \, S = (W - W_o)/W_o \times 100$$

where W_o is the weight of bead in the dried state and W is the weight of bead in the swollen state.

Dye absorption characteristics

Absorption of cationic dye by alginate gel bead

Absorption of cationic dye was examined by mixing 3 g of alginate gel bead with 20 mL 100 mg/L cationic dye at room temperature for 24 h. The equilibrium concentrations of dye were measured by the Spectronic 21 UV spectrophotometer and referenced with the calibration curve.

Absorption of anionic dye by alginate and IPN gel beads

Absorption of anionic dye was observed. The gel bead (2 g) was added into the anionic dye solution at the concentration of 500 mg/L (20 mL). The absorption was examined at room temperature for 24 h. The concentration of remaining dye was measured by UV spectrophotometer at the λ_{max} of the absorbance.

Dye absorption density

Effect of absorbent dosage was studied. The dye absorption density was determined by mixing 0.3–2.14 g of IPN gel beads with 20 mL of 500 mg/L reactive dye in a 50 mL beaker at room temperature for 24 h. The equilibrium dye solution was measured by the UV spectrophotometer. The amount of absorption at equilibrium qe (mg/g) was calculated by using the following expression.

$$qe = ((C_o - C_e)V)/W$$

where C_o and C_e are the initial and equilibrium solution concentration (mg/L), respectively. V is volume of the solution (cm³), and W is the weight of gel bead used (g).

## RESULTS AND DISCUSSION

Preparation of alginate and IPN gel beads

For preparation of alginate gel bead, the alginate solutions at concentration of 2–6% were added dropwise in 0.3M CaCl$_2$ solution and crosslinked for 30 min. An alginate solution is rapidly gelled upon contact with divalent cations by the formation of junction zones
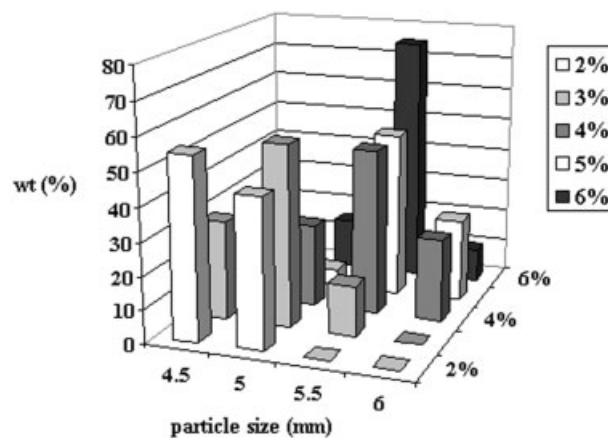
Figure 1 Particle size and distribution of alginate gel beads at different concentrations of alginate solution.

between the divalent cations and carboxyl groups of the alginate polymer chains. The particle size of freshly prepared alginate gel beads is shown in Figure 1. The particle size is found in the range of 4.5–6.0 mm. The particle size increases with the increase in alginate concentration and steady at about 4% concentration. Although the mean particle size of alginate beads at concentration of 4–6% was 5.5 mm, the weight distribution tended to shift from small particle to the large one as the concentration of alginate increased. This can be explained that the increasing of concentration of alginate increases the viscosity of the solution and leads to increase of droplet size.[25] Hence, the particle size of gel beads increased. From this result, the concentrations of alginate at 2 and 6% (w/v) were chosen for preparation of IPN gel beads (SAAMM1 and SAAMM3).

To prepare IPN gel beads composed of alginate and the other monomers, mixed aqueous solution of these components was dropped into solution of CaCl$_2$ mixed with TMEDA. The crosslinking of alginate with CaCl$_2$ and the two monomers with MBAM occurred simultaneously. Figure 2 shows the average particle size of gel beads. The particle size of the freshly prepared IPN gel beads was about 5–6.3 mm. The result shows that IPN gel bead of SAAMM3 was the highest particle size. This is due to the gel bead contained the highest polymer content. In the same way, the carboxylic acid groups of alginate formed polyelectrolyte complexes with amino groups of polyacrylamide and —N$^+$(CH$_3$)$_3$ groups of PMAPTAC. Also, particle size increased as the polymerization between acrylamide and MAPTAC proceeded. However, the particle size of SAAM was lower than that of SA. This may be due to the fact that the bead formed a compact complex structure between the carboxylic acid groups of alginate and amino groups of polyacrylamide[26] and resulted in decrease in the particle size. In SAM, the
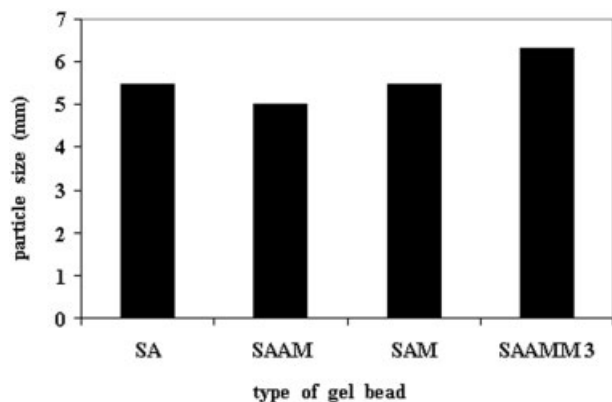
Figure 2 Average particle size of alginate gel bead at concentration of 6% and IPN gel beads.

electrostatic interactions between COO^- of the alginate and $—N^+(CH_3)_3$ group of PMAPTAC are formed. Also, the particle size produced by the hydrophilicity of SAM bead is higher than that of SAAM sample.
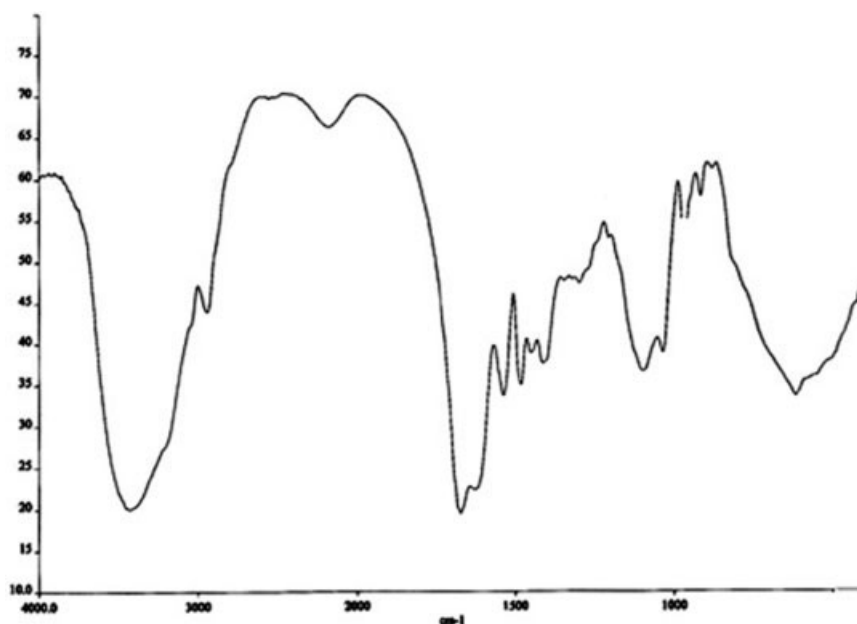
Figure 3 shows FTIR spectra of IPN bead composed of alginate, acrylamide, and PMAPTAC. It can be seen from the figure that the absorption peaks belonging to three components were confirmed: the peak at 1672 cm^{-1}, attributed to $—COO^-$ stretching of alginate; the absorption band at 3431 cm^{-1}, corresponding to the absorbance of NH functional group of polyacrylamide and PMAPTAC; the peak at 1450 cm^{-1}, attributed to $—CH_3$ stretching of PMAPTAC.

The freshly prepared alginate and IPN gel beads obtained from the preparation were found to be yel-

low-pale shaded, flexible, and of spherical shape. To the naked eye, the gel beads had a smooth surface. After the beads dried in the desiccator, the morphology of dried alginate and IPN beads was examined by using SEM analysis. The result obtained is shown in Figure 4. In alginate bead, the particle revealed by SEM image exhibits a rough-shape bead and its particle size was about 2 mm. In comparison with the dried IPN bead, the particle size was about 2.5 mm and the surface morphology was smoother than the alginate bead. This result is caused by the crosslinking of alginate, acrylamide, and MAPTAC in dried IPN bead.

Swelling behavior

The swelling property of dried beads was examined. The swelling behavior of alginate and IPN beads in water, at room temperature, is shown in Figure 5. The result shows that alginate dried bead had the lowest swelling ratio. This is due to the low hydrophilic property of SA. However, the dried IPN beads swelled rapidly because of the hydrophilic property of acrylamide and MAPTAC. As shown in Figure 5, the swelling ratio increased when dried IPN beads composed of MAPTAC. This is also due to the hydrophilicity of $—N^+(CH_3)_3Cl^-$ groups in MAPTAC. SAAMM1, containing the lowest alginate content (SA:AM:MAPTAC $= 1 : 0.33 : 5$), showed the highest swelling ratio. This resulted from the highest hydrophilicity of the bead. In comparison with SAAMM3, it contained higher alginate content (SA:AM:MAPTAC $= 3 : 0.33 : 5$) than SAAMM1. Therefore, its swelling ratio decreased. In

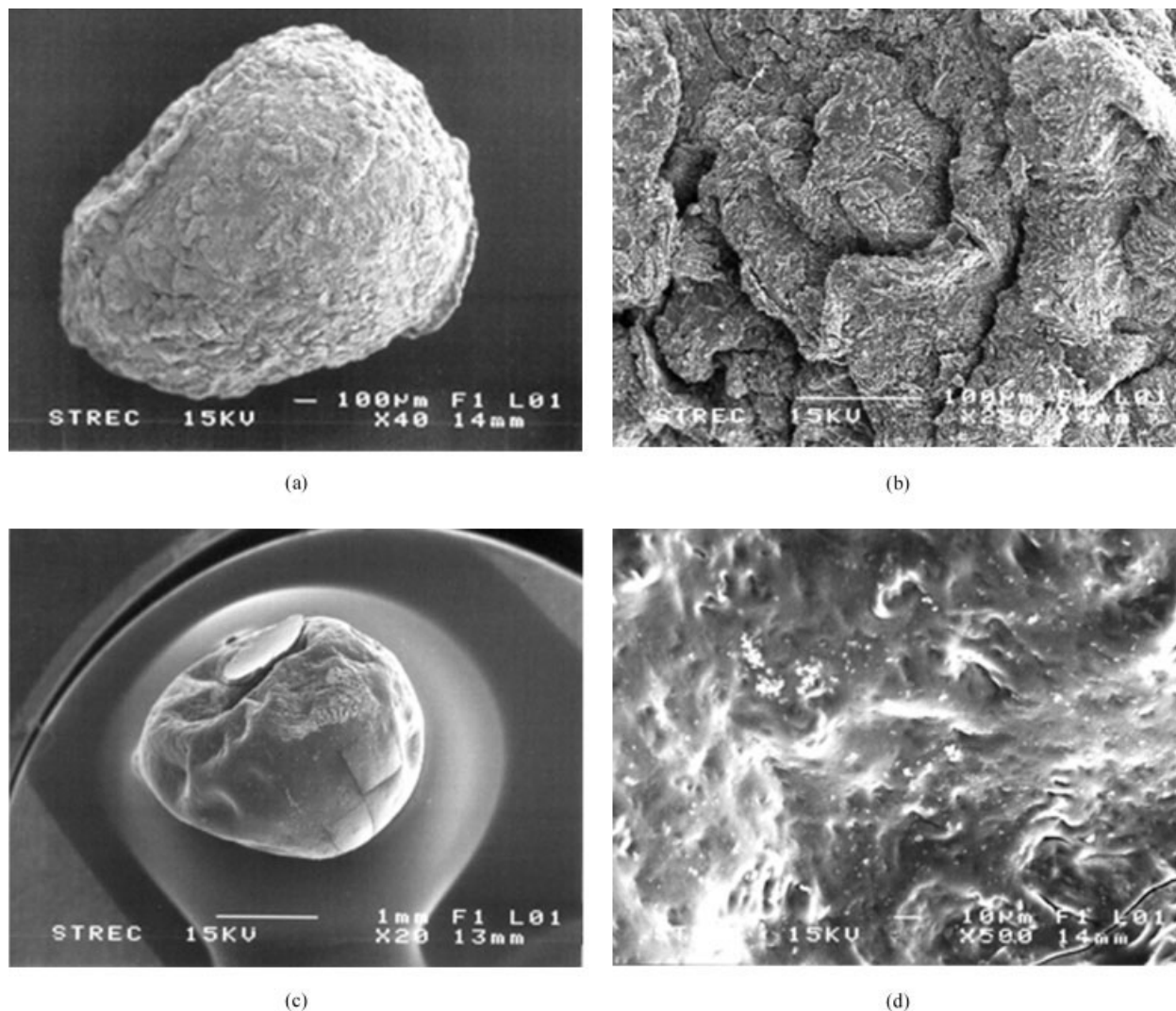**Figure 3** FTIR spectrum of IPN bead composed of alginate, acrylamide, and MAPTAC (SAAMM3).

Figure 4 SEM micrographs of dried beads: surface morphology of (a,b) alginate bead and (c,d) IPN bead (SAAMM3).

addition, decreasing the alginate ratio led to increase in the swelling ratio as a result of network expansion of acrylamide and MAPTAC in IPN beads. The similar

Figure 5 Swelling ratio of alginate and dried IPN beads.

observation was reported by Baker et al. in the study of the effect of cationic monomer content on swelling property of polymer.[27]

In NaCl solution, the swelling ratio of dried alginate bead increased (SA). As the calcium alginate contact with NaCl solution, the ion exchange between Ca^{2+} and Na^+ occurred. Because sodium alginate is water soluble, water is drawn into the bead and caused increase in the swelling ratio.[28] In contrast, the reduced swelling ratio of dried IPN beads such as SAM, SAAMM1, and SAAMM3 is the result of electrostatic screening of charged groups by NaCl.[29] The effect of NaCl on swelling property of polymer was also reported by Baker et al.[30] However, the NaCl did not affect the swelling of SAAM. This is because the SAAM was a nonionic gel bead. Therefore, the component in dried IPN bead and NaCl in aqueous solution affected its swelling property.
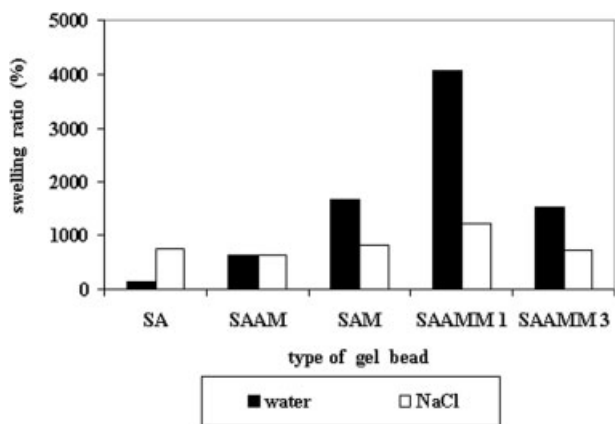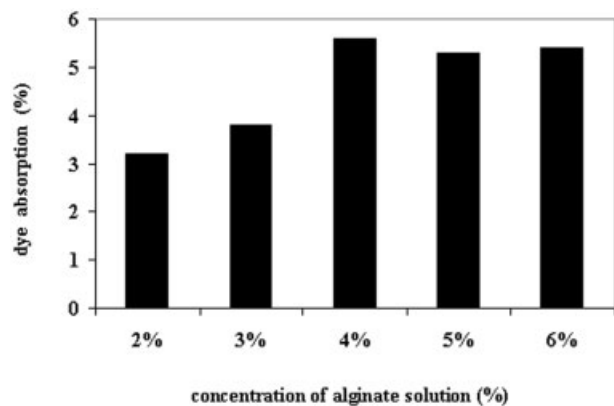
Figure 6 Absorption of cationic dye by alginate gel beads prepared from alginate solution at different concentrations.
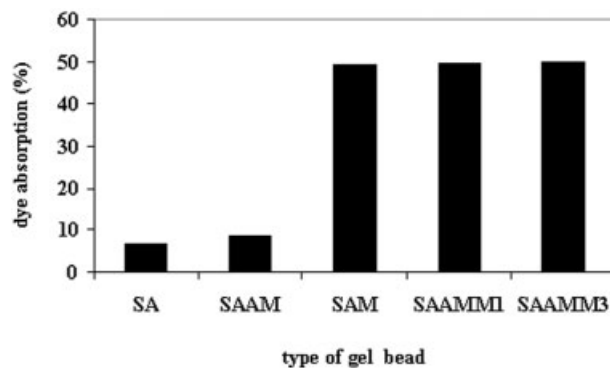
Cationic dye absorption

The absorption of cationic dye by alginate gel beads was carried out using Taiacryl Brillian Red 4GN. Figure 6 shows the effect of concentration of alginate solution for the preparation of gel bead on dye absorption. As shown in Figure 6, the dye absorption tended to increase when the concentration of alginate solution increased and leveled off about 5% concentration. The absorption of cationic dye by alginate gel beads was a result of electrostatic interactions between alginate gel beads and dye molecules. Also, the dye absorption reached equilibrium although the concentration of alginate increased. Davis et al. reported that the absorption capacity of alginate was related to the carboxylic groups.[31]

Reactive dye absorption

Effect of type of gel beads on dye absorption

The IPN gel beads were prepared from the solution of alginate, acrylamide, and MAPTAC. The absorption of reactive dye, which is an anionic dye, using alginate and IPN gel beads was studied. The gel beads were placed in the solution of reactive dye and allowed to equilibrate for 1 day. Figure 7 shows the absorption of reactive dye by using the different gel beads. The SA gel bead showed the low absorption. However, the absorption of anionic dye by alginate bead was higher than that of cationic one (see Fig. 6). It is indicated that the absorption of reactive dye by alginate was not only by electrostatic interaction but also by another type of interaction (e.g., hydrophobic interaction). In contrast, the IPN gel beads composed of MAPTAC had high absorption. PMAPTAC is the quaternary ammonium cationic polymer, thus, the negative charge in reactive dye (sulfonate group, SO_3^-) interact with cationic charge in IPN gel beads. Zemaitaitiene et al. reported that the cationic polymer tended to react with anionic

Figure 7 Absorption of reactive dye by alginate gel bead at concentration of 6% and IPN gel beads.

dyes.[29] In the sample of SAAM, the dye absorption was found to be lower than that found in other IPN gel beads. This is because polyamide is a nonionic polymer. Therefore, the absorption of reactive dye was a result of type of gel beads and PMAPTAC in IPN beads.

Effect of absorbent dosage

The absorption density of reactive dye onto the IPN gel bead (SAAMM3) for different absorbent doses (0.3–2.14 g) at room temperature was observed. The result obtained was shown in Figure 8. It is seen that the absorption density increases with decrease in the absorbent dosage. This result is caused by that the smaller amount of absorbent implies the higher amount of the dye contact with per unit weight of the absorbent. The similar observations were reported by Chiau et al.[32] and Robinson et al.[33]

CONCLUSIONS

The IPN gel beads, on the basis of SA, AM, and MAPTAC, were prepared by simultaneous crosslinking method. The particle size of the alginate gel beads depended on the concentration of solution but type of
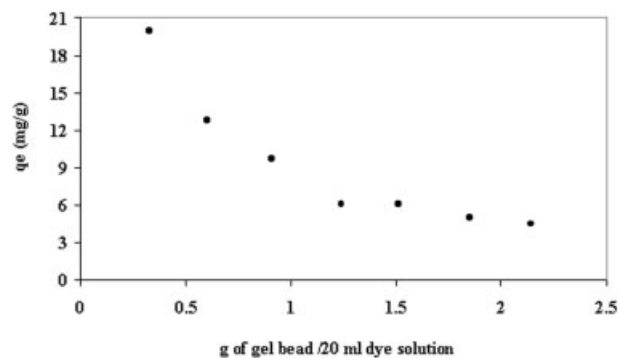
Figure 8 Absorption density of IPN gel bead (SAAMM3).

monomer affected particle size of IPN gel beads. From SEM result, it can be seen that the surface morphology of dried IPN was smoother than dried alginate bead.

The dried IPN beads exhibited high swelling ratio as the alginate content decreased. Cationic dye absorption of alginate gel bead resulted from the interaction between alginate gel bead and dye. The absorption of anionic dye, reactive dye, resulted from the cationic groups in IPN gel bead. Finally, the absorption density was investigated. The result showed that decreasing the absorbent dosage increased the absorption density. From the result, it can be concluded that IPN gel bead could be useful as dye absorbent.

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