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Poly(Acrylamide-Sepiolite) Composite Hydrogels: Preparation, Swelling and Dye Adsorption Properties

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Summary

Polymer-clay hydrogel composite was prepared on the basis of polyacrylamide (PAAm) gel containing the clay mineral sepiolite. The properties of swelling and dye adsorption of poly(acrylamide-sepiolite) (AAm/Sep) composite hydrogel were investigated. The parameters of swelling and diffusion in water and dye solutions were calculated for the AAm and AAm/Sep hydrogels. It was found that the equilibrium swelling degree of obtained composite higher than that of AAm gel. Spectroscopic analysis of composite and composite-dye systems was done with FT-IR method. Adsorption of monovalent cationic dyes such as Basic Blue 12 (BB-12) Basic Blue 9 (BB-9), and Basic Violet 1 (BV-1), was studied on the composite. In the adsorption experiments, S (*Sigmoidal*) type for composite gel adsorption isotherms in the Giles classification system was found. Adsorption studies indicated that the amounts of adsorbed dyes on the AAm/Sep composite hydrogel were increased with following order; BB-12 > BB-9 > BV-1. The composite hydrogel may be considered as good candidate for environmental application to retain more water and dyes.

Introduction

A composite is a substance composed of two or more materials with different base structures combined in such a way that the end product has different properties than either of the parent materials. Hydrogels loaded with dispersed clays are a new class of composite materials which combine elasticity and permeability of the gels with high ability of the clays to adsorb different substances [1-4]. Many hydrogel composites such as polyacrylamide with bentonites [1, 5-8] or montmorillonites [9-10], polyacrylic acid [11] or poly(N-isopropyacrylamide) [12] with montmorillonites etc. have been synthesized and studied.

Clays among the other host materials are natural, abundant and inexpensive minerals that have unique layered structure, high mechanical strength as well as high chemical resistance. It is well known that clays are good adsorbents in removing dye contaminants in waste waters of textile and dye industries. Many clay minerals are able to absorb/desorb organic molecules, and so are widely studied as carriers or support of pharmaceuticals. The clay mineral sepiolite is currently widely used as raw material due to its powerful sorbent properties [13-18].

Sepiolite has an open structure exhibiting a microfibrous morphology with a high specific surface area (around 340 m^2 g^{-1}) and a large micropore volume (around 0.44 cm^3 g^{-1}) due to the existence of intracrystalline cavities (tunnels) [14]. Sepiolite belongs to the phyllosilicate group of clay minerals with a 2:1 ribbon structure. It is composed of continuous and two-dimensional tetrahedral layers with T_2O_5 (T = Si, Al) composition and discontinuous octahedral layers. Octahedral layer discontinuity leads to the formation of internal channels in the structure, which provides high absorptive capacity. The well-known sepiolite deposit in Turkey is at Eskişehir (Anatolia) [19].

It is difficult that clays are used in free form in many studies, so clays are incorporated to a support such as a polymer to get facility in working.

The aim of this work is to provide of easily usage by adding sepiolite to poly(acrylamide) crosslinked with N,N'-methylene bisacrylamide to improve its adsorption properties of monovalent cationic dyes such as Basic Blue 12 (BB-12), Basic Blue 9 (BB-9), and Basic Violet 1 (BV-1).

Experimental

Materials

Acrylamide (AAm) (Merck, Darmstadt, Germany) as monomer, N, N'-methylenebisacryl amide (N) (Sigma, St. Louis, US) as crosslinker, ammonium persulfate (Merck, Darmstadt, Germany) as initiator, N, N, N', N'- tetramethyl-ethylene diamine (Sigma, St. Louis, US) as catalyst, Basic Blue 9 (BB-9), Basic Blue 12 (BB-12) and Basic Violet 1 (BV-1), as monovalent cationic dyes (Merck, Darmstadt, Germany) were analytical reagent-grade and used as received. Sepiolite (230 mesh) was supplied from Mihalliccik-Eskişehir, Turkey [20].

Preparation

Several samples with different amounts of sepiolite, and crosslinker, initiator, catalyst and acrylamide were prepared by free radical solution polymerization. Typical preparation conditions for samples are as follows: An aqueous solution of acrylamide containing N (95:5 in the mole ratio in 0.4 mole water) and with 0.01 mmole ammonium persulfate, 2.5 mmole N, N, N', N'-tetramethylethylene diamine and sepiolite (10, 25, 50, 75, 100 mg for 1.0 g acrylamide) were mixed and placed in PVC straws of 3 mm diameter. A gel formed 20 min of reaction. After 24 h, the hydrogel rods were cut into pieces 3-4 mm length and washed with distilled water and dried in air and vacuum, and stored. The samples synthesized were named as AAm/Sep composite.

Measurements

FTIR spectra of PAAm, AAm/Sep, and dye-loaded composites were recorded on a Mattson model a FTIR spectrophotometer. Spectra were taken with a resolution of 1 cm^{-1}. Samples were thoroughly ground with exhaustively dried KBr and discs were prepared by compression under vacuum.
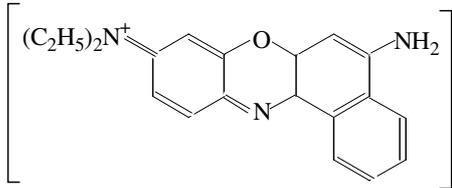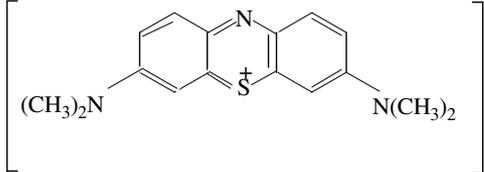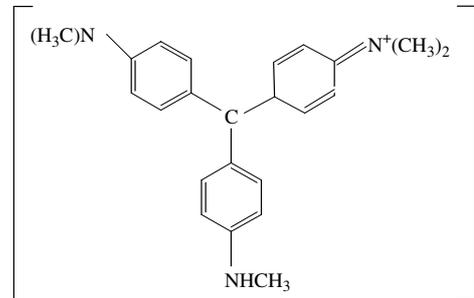
The swelling of dried gels is carried out by immersion in doubly distilled water, and in the aqueous solutions of cationic dye in the concentration of 15 mg dye L^{-1} at $25 \pm 0.1°C$

in a water bath. The solution absorbed is determined by weighing the samples, after blotting, at various time intervals.

AAm/Sep composite samples, weighing 0.110 g (containing 10.0 mg sepiolite with 100.0 mg PAAm), were transferred into 50.0 mL of the aqueous cationic dye solutions of varied initial concentrations (C_o=2.5 to 30.0 mg L^{-1}) and allowed to equilibrate for two days at 25°C in a constant water bath. After separation by decantation from the composites, the concentration of dyes in the in the aqueous phase was analyzed using a Shimadzu 160A model UV-VIS spectrophotometer at appropriate wavelengths (Table 1) at ambient temperature. Distilled water was chosen as the reference. The equilibrium concentrations of the water soluble cationic dye solutions were determined by means of precalibrated scales.

The influence of sepiolite content was investigated for binding of the dyes to AAm/Sep composite hydrogels. Composite hydrogels, weighing 0.1010g, 0.1025 g, 0.1050 g, 0.1075 g, 0.110 g (containing 10.0, 25.0, 50.0, 75.0, 100.0 mg sepiolite with 1.0 g polyacrylamide), were transferred into 50.0 mL of 15 mg L^{-1} of the aqueous cationic dye solutions. The samples left in the solution for two days at 25°C, and the absorbance of the solutions was measured spectrophotometrically.

Table 1. Some properties of cationic dye molecules used in this study

Dye	Chemical formula	Molar mass /g mol^{-1}	λ_{max}/nm
BB-12		354.0	600
BB-9		320.0	665
BV-1		394.0	560

Results and discussion

Preparation of composites AAm hydrogel and composite of AAm were polymerized by the conventional free radical polymerization. In order to prepare cylindrical composite hydrogels, AAm and N (95:5 in the mole ratio) were dissolved in 7.2 mL of distilled water. A very small amount of sepiolite (10, 25, 50, 75, 100 mg for 1.0 g acrylamide) was added to the AAm–N-water mixture. Then 0.01 mmole ammonium persulfate, 2.5 mmole N, N, N', N'-tetramethylethylene diamine (TEMED) were added to this solution, and the resulting mixture was poured into poly(vinyl chloride) straws and kept at 25°C. A gel formed 20 min of reaction. After 24 h, the resulting gels were cut into small cylindrical pieces. The rodlike gels were washed with deionized water and dried in air and vacuum, and stored. For the polymerization of AAm/Sep composite hydrogel, an illustration is presented in Fig. 1.
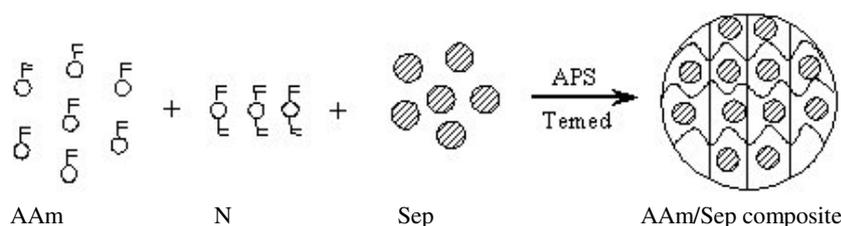

Figure 1. Schematic presentation of the preparation of AAm/Sep composite hydrogel.

Dried AAm and AAm/Sep polymers are glassy form and very hard, but swollen gels are very soft. The crosslinked polymers are obtained in the form of cylinder rods. Upon swelling, the hydrogels were strong enough to retain their shape. It was observed that sepiolite did not leave from the structure of gels during swelling.

To understand the formation of AAm/Sep composite, FTIR spectra of PAAm, sepiolite and AAm/Sep were evaluated and are presented in Fig. 2. When sepiolite is introduced into AAm gels, it was observed that peaks intensity related to AAm gels have increased and any new peak was not occurred. It can be said that sepiolite acted as active fillers.
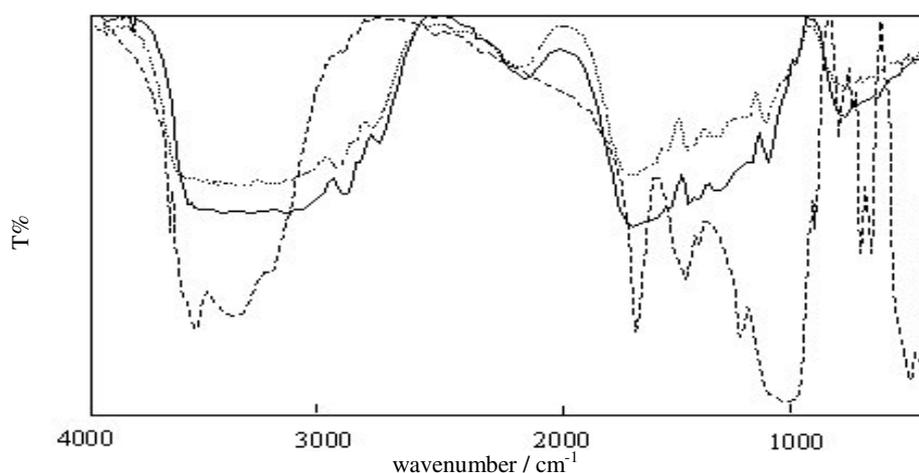

Figure 2. IR spectra of PAAm (——), Sep (----) and AAm/Sep composite hydrogel (⋯⋯).

Binding of dyes onto AAm/Sep composite hydrogel

To observe uptake of some dyes, PAAm and AAm/Sep hydrogels were placed in aqueous solutions of cationic dyes such as BB-12, BB-9, and BV-1, and the aqueous solutions of anionic dyes such as orange II, azo carmine B, congo red and bismark brown Y, and allowed to equilibrate for 2 days. At the end of this time, AAm/Sep composite hydrogels in the aqueous solutions of BB-12, BB-9, and BV-1 showed the darker colorations of the original solutions. AAm hydrogel had not sorbed any dyes from the solutions and AAm/Sep hydrogel had not sorbed the anionic dyes. Since poly(acrylamide) is a nonionic polymer [21], ionizable groups in the polymer were increased by the incorporation of sepiolite to acrylamide. Therefore composite hydrogels have many silanol groups (Si-OH) that can increase interaction between the cationic groups of cationic dyes and silanol groups of hydrogels. On the other hand, there will be anionic repulsion between anionic groups of anionic dyes and silanol group of Sep in the hydrogels and therefore little interaction between the anionic dyes and AAm/Sep composite hydrogel.
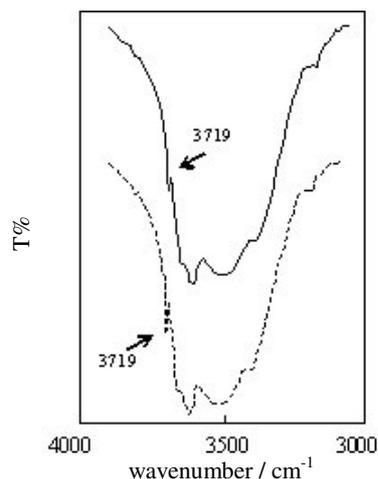

Figure 3. IR spectra of Sep (--) and BB9-adsorbed (—) Sep.

The IR spectra (Fig. 3) of sepiolite adsorbed BB-9 indicate a decrease in intensity of the band at 3719 cm^{-1} (ν_{OH} vibrations of Si-OH groups) which is perturbed due to its association with the BB-9 adsorbed species. Since the silanol groups are located at the external edges of mineral fibers, they are easily accessible and interact almost totally with the sorbate molecules [14]. Similar results were obtained for the BB-12 and BV-1 (results not shown).

Swelling studies

The swelling *S%* is calculated from the following relation:

$$S\% = \frac{m_t - m_o}{m_o} \times 100 \qquad (1)$$

where m_o is the mass of dry gel at time 0, m_t is the mass of swollen gel at time *t*.

Swelling curves of PAAm and AAm/Sep composite gels crosslinked with N in distilled water are shown in Fig 4.

The hydrogels were shown similar swelling behavior in all cases. The swelling curves are similar in shape but differ in size and position. If Fig. 4 is investigated, it is shown that swelling is increased by time, but then it levels off. This value may be named equilibrium swelling ($S_{eq}\%$). These $S_{eq}\%$ values are given Table 2.

The $S_{eq}\%$ of AAm/Sep composite hydrogel was significantly higher than that of PAAm hydrogel. This increase is related to presence of many hydrophilic groups such as silanol and hydroxyl groups in the AAm/Sep composite gels.
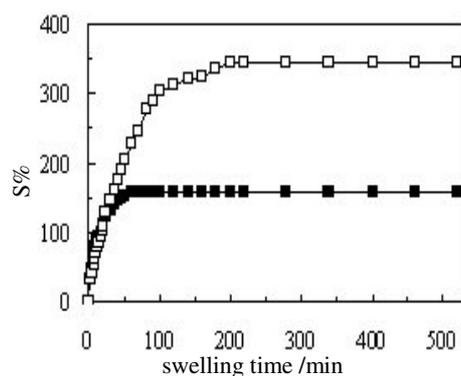

Figure 4. Time-depending swelling of the hydrogels in distilled water, ■; AAm, □; AAm/Sep.
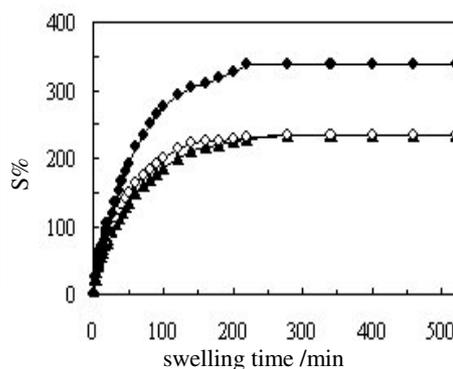
Figure 5. Time-depending swelling of AAm/Sep composite hydrogel in the cationic dye solutions, ●; BB-12, ○; BV-1, ▲; BB-9.

Table 2. Swelling and diffusion parameters of AAm and AAm/Sep composite hydrogels samples in distilled water

Polymer	S_{eq} %	n	$kx10^2$	$Dx10^6$ /cm^2 s^{-1}
PAAm	160	0.56	13.50	4.30
AAm/Sep	345	0.61	5.20	1.26

Swelling curves of AAm/Sep composite hydrogels in the dye solutions are shown Fig. 5, and the $S_{eq}\%$ values are given Table 3.

Table 3. Swelling and diffusion parameters of AAm/Sep composite hydrogel in cationic dye solutions

Dye	S_{eq} %	n	$kx10^2$	$Dx10^6$ /cm^2 s^{-1}
BB-9	235	0.56	6.70	1.15
BV-1	235	0.56	7.30	1.27
BB-12	340	0.64	4.60	1.50

The $S_{eq}\%$ values of the AAm/Sep composite hydrogels are between 230% and 340% in the aqueous solutions of the dyes, but 345% in distilled water.

The dyes contain the unpaired electrons in the N and O. These atoms behave like a hydrophilic group and form hydrogen bonds with water. Thus, the swelling of AAm/Sep composite hydrogels changes as the dyes bring water into the gels. At the end of these evaluations, the AAm/Sep composite hydrogels in the aqueous solutions are swollen in the following order: water > BB-9 > BB-12 > BV-1.

The following equation was used to determine the nature of diffusion of water into hydrogels;

$$F = kt^n \qquad (2)$$

Where F is the fractional uptake at time t. k is a constant incorporating characteristic of the macromolecular network system and the penetrant and n is the diffusional exponent, which is indicative of the transport mechanism. Equation 3 is valid for the first 60% of the fractional water uptake. Fickian diffusion and Case II transport are defined by n equal to 1/2 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected by anomalous behavior defined by values of n between 1/2 and 1 [22].

For the polymers, $\ln F$ vs. $\ln t$ graphs is plotted and representative results are shown in Fig. 6-7. n exponents and k parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 2 and 3.
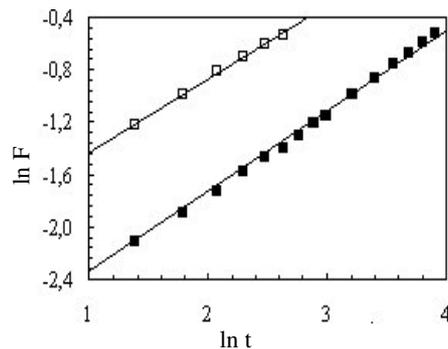

Figure 6. $\ln F$-$\ln t$ curves of the hydrogels in distilled water, ■; AAm, □; AAm/Sep.
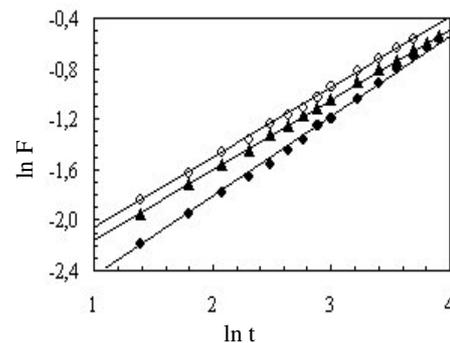
Figure 7. $\ln F$-$\ln t$ curves of AAm/Sep composite hydrogel in the cationic dye solutions, ●; BB-12, ○; BV-1, ▲; BB-9.

Table 2 and 3 show the number determining type of diffusion (n) is over 0.50. Hence the diffusions of water and aqueous solutions of the dyes into the hydrogels are generally taken as a non-Fickian character [23]. When diffusion type is anomalous behavior the relaxation and diffusion time are of the same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

$$D^n = \frac{k(\pi r^2)^n}{4} \qquad (3)$$

Where D is in $cm^2 \ s^{-1}$, n is the diffusional exponent and r is the radius of cylindrical polymer sample [24]. The diffusion coefficients were calculated from equation 3, are listed in Table 2 and 3.

The diffusion coefficient (D) values of dyes in the AAm/Sep composite hydrogels in the aqueous solutions of dyes of are in the following order: BB-9 > BB-12 > BV-1. These results are parallel to the swelling results.

Binding isotherms of dyes onto AAm/Sep composite hydrogels

In order to observe the uptake of the water-soluble cationic dyes, AAm/Sep composite hydrogels were placed in aqueous solutions of the cationic dyes and allowed to equilibrate for two days. At the end of this time, AAm/Sep composite hydrogels in the aqueous solutions of the cationic dyes displayed darker colorations of the original solutions.

Organic cations may bind to the clay by different modes. In the case of monovalent organic cations, the following three kinds of clay-organic complexes can be found [15].

A neutral complex may form by the binding of a cation to a monovalent negative site on the clay block. Such reaction is mainly electrostatic, and should be considered for both organic and inorganic cations.

A second organic cation may bind to a neutral clay-organic complex by non-coulombic inter-actions, forming a single positively charged complex with two organic cations and one charged site. This type of binding arises from hydrophobic interactions between large organic molecules, and may lead at high loads to charge reversal. The model does not consider the possibility of formation of such complexes in the adsorption of inorganic cations, and the assumption is that they occur only in organic molecules.

In sepiolite, where neutral sites occur at the external surface, a monovalently charged complex may form by the binding of one organic cation and a neutral site. Such binding was found to be responsible for the very large amount of monovalent organic cations adsorbed to sepiolite, which reached up to 400% of the cation exchange capacity (*CEC*) [15].

In a batch adsorption system at equilibrium, the total solute concentration (C_I, mol L^{-1}) is

$$C_I = C_B + C \tag{4}$$

Where C_B is the equilibrium concentration of the solute in the adsorbent in mol L^{-1} (bound solute concentration) and C is the equilibrium concentration of the solute in the solution in mol L^{-1} (free solute concentration) [25]. The value of the bound concentration may be obtained by difference with Eq. 4. For a fixed free solute concentration, C_B is the proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio, r, defined by

$$r = \frac{C_B}{P} \tag{5}$$

Thus with C_B in mol L^{-1} and P in base mol (moles of monomer units) L^{-1}, r then represents the ave-rage number of molecules of solute bound per monomer unit at that free solute concentration [25].

Plots of the binding ratio (r, μmole dye/mole monomeric unit of sepiolite) against the free concentrations of the dyes in the solutions (C, mmole dye L^{-1}) are shown in Fig. 8.

Fig. 8 shows that adsorptions of the dye within AAm/Sep composite hydrogels corresponds to type S (*Sigmoidal type*) adsorption isotherms in the Giles classifications system for adsorption of a solute from its solution. In the S curves in the Giles classifications system, initial direction of curvature shows that adsorption easier as concentration rises. In practice, the S curve usually appear when three conditions are fulled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another absorbed species [26].
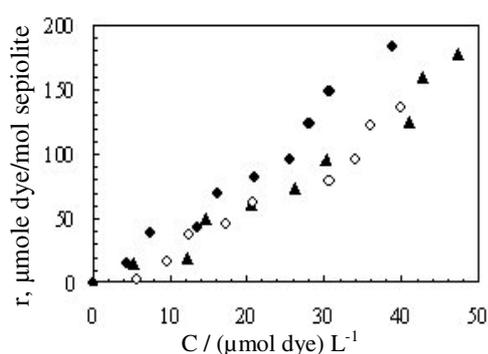

Figure 8. The binding isotherms of dye molecules on AAm/Sep composite hydrogel, ●; BB-12, ○; BV-1, ▲; BB-9.
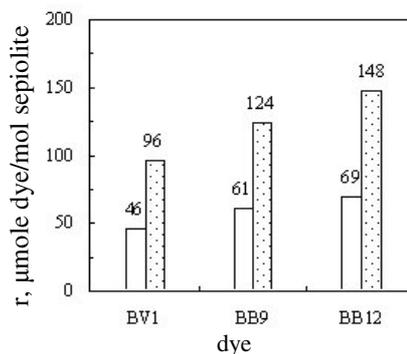
Figure 9. The removal efficiency of AAm/Sep composite hydrogel, □; 10 mg dye L^{-1}, ▦; 20 mg dye L^{-1}.

For comparation, the binding ratio of dyes solutions that have initial concentration is 10 and 20 mg dye L^{-1} on AAm/Sep composite hydrogels, Figure 9 was constructed. As can be seen from Fig. 8. and Fig. 9 the adsorption of cationic dye on the AAm/Sep composite hydrogels follows order; BB-12 > BB-9 > BV-1.

The effect of mass of adsorbent

In this part, the effect of mass of sepiolite in AAm/Sep composite hydrogels on dye adsorption was investigated. AAm/Sep composite hydrogels containing different amount of sepiolite were transferred into 50 mL of the aqueous dye solutions in constant concentrations and allowed to equilibrate for two days at 25°C in a water bath.

Removal effiency (*RE%*) of the AAm/Sep composite hydrogels was calculated by following equation:

$$RE\% = \frac{C_i - C}{C_i} \times 100 \qquad (6)$$

C_i and C; are the initial and equilibrium concentrations of dye solutions in mg L^{-1}, respectively. Plots of *RE%* values against the mass of sepiolite in AAm/Sep composite hydrogels are shown in Fig. 10.

Fig. 10 shows that the percentage of dye removed from solutions increased with the increase of the mass of sepiolite clay in AAm/Sep composite hydrogels.
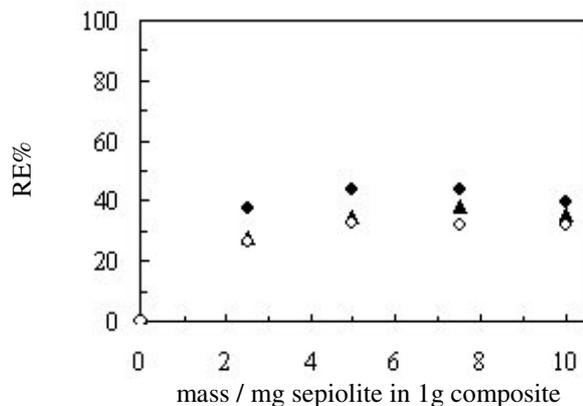
Figure 10. The variation of removal efficiency by mass of Sep in AAm/Sep composite hydrogel, ●; BB-12, ○; BV-1, ▲; BB-9.

Conclusions

Sepiolite was incorporated to poly(acrylamide) crosslinked with N,N'-methylene bisacrylamide during polymerization and AAm/Sep composite hydrogels were synthesized. It was observed that sepiolite didn't leave from the structure of hydrogels during swelling and adsorption experiments.

The swelling degree of AAm/Sep composite hydrogels was found higher than that of poly(acrylamide) gels due to presence a lot of hydrophilic groups in AAm/Sep composite hydrogels. From FTIR spectra of dye adsorbed AAm/Sep gels, it was observed that monovalent organic cations may bind to silanol groups of sepiolite clay.

The adsorption of the dye within AAm/Sep composite hydrogels corresponds to Type S (*Sigmoidal)* type adsorption isotherms in the Giles classification system for adsorption of a solute from its solution.

The values of equilibrium swelling degree ($S_{eq}\%$), diffusional exponent (n), diffusion coefficient (D), binding ratio (r) and removal efficiency ($RE\%$) were found by the following order for AAm/Sep composite hydrogels: BB-12 > BB-9 ≥ BV-1.

The AAm/Sep composite hydrogel may be considered as good candidate for environmental application to retain more water and dyes.

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