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ORIGINAL PAPER

Hydrogel nanocomposite sorbents for removal of basic dyes

Mahir Kaplan · Hasine Kasgoz

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Abstract Hydrogel nanocomposites having high amount of functional group, enhanced swelling ability, and improved mechanical properties were prepared for removal of basic dyes from aqueous solutions. Acrylamide (AAM) and itaconic acid sodium salt (IANa) were polymerized using polyethyleneglycol (400) diacrylate as crosslinker in the presence of montmorillonite (MMT). The products were characterized by swelling degree, total basic group content, XRD analysis, and FTIR spectroscopy. It was observed that MMT addition increased the itaconic acid gelation. The incorporation of low amount of MMT into the hydrogel structure increased also swelling degree. The products were used as adsorbent for removal of brilliant cresyl blue (BCB) from aqueous solutions. It was observed that the adsorption of BCB onto the nanocomposite completed in 30 min. It was found that the adsorption kinetics followed a pseudo-second-order kinetic model. Equilibrium isotherm of nanocomposite was analyzed using Freundlich and Langmuir isotherms. It was seen that the Langmuir isotherm model fit the adsorption data. These hydrogel nanocomposites have been shown to have the potential to be used as novel, fast-responsive and high capacity adsorbent materials for the removal of cationic dyes which is a serious problem, especially in textile industry.

Keywords Hydrogels · Nanocomposites · Clay · Adsorption

Introduction

Many industries (plastics, paper, textile, and cosmetics) use dyes to color their products. The release of toxic and hazardous dyes from these industries has created

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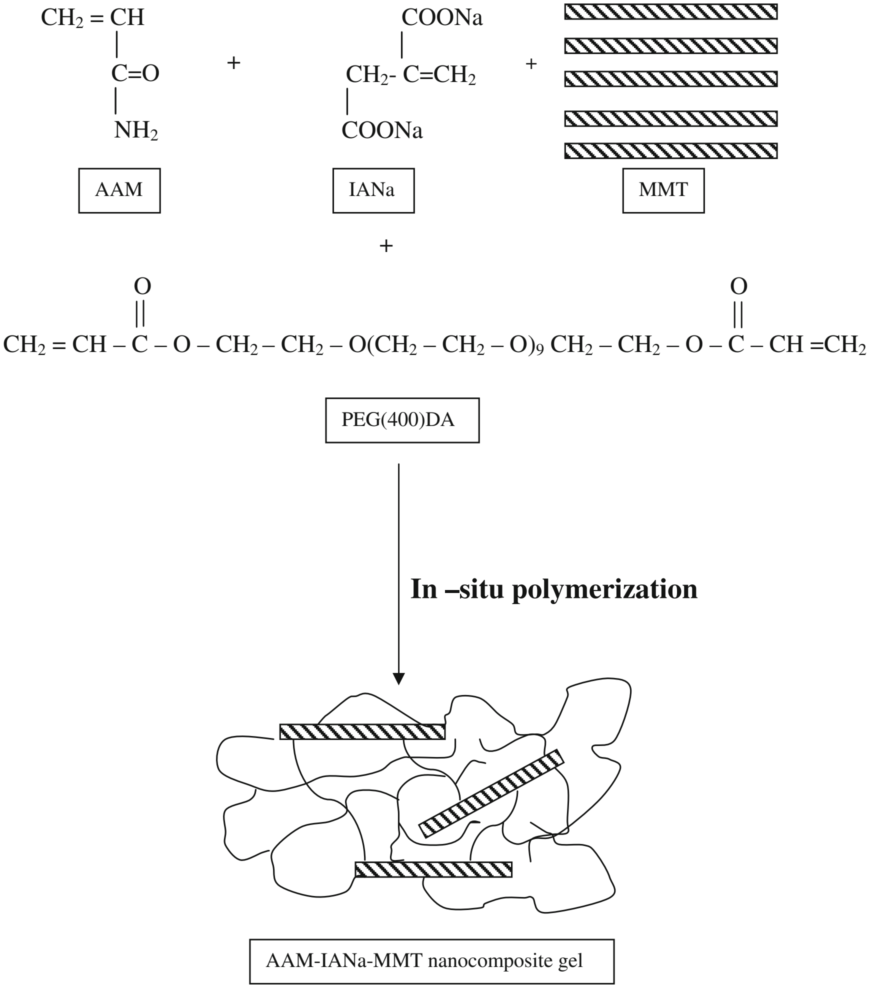
M. Kaplan · H. Kasgoz (✉)
Faculty of Engineering, Department of Chemical Engineering, Avcilar Campus,
University of Istanbul, 34320 Avcilar, Istanbul, Turkey
e-mail: hasineka@istanbul.edu.tr

a global concern due to their immense toxicity toward mankind. Dyes impart undesirable color to water and are lethal for aquatic life. The toxic and hazardous substances created by these dyes after undergoing oxidation and reduction in water further increase the need for their removal from wastewater. For removal of dyes from wastewater, adsorption process appears to offer the best prospects over other treatment technologies (chemical coagulation-flocculation, biological process, different type oxidation processes, etc.) due to high efficiency, easy handling and availability of different adsorbents [1].

Nowadays, the use of several polymers having different functional groups in adsorption process has gained great importance for wastewater treatment due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes [2, 3]. Hydrogels possessing different functional groups have also been investigated in the preceding literature [4, 5]. They can be defined as water-swollen, three-dimensional networks, and also show stimuli-responsive properties to the various external parameters such as temperature, pH, solvent, and salt composition leading them to be used in a variety of application areas. But the use of hydrogels in some applications is limited as they typically exhibit low gel strength and poor stability. In recent years, hydrogel/clay nanocomposites have attracted much attention due to their improved mechanical, thermal and swelling properties, dimensional stability compared to the pure hydrogels [6–10]. Synthesis of hydrogel composites and nanocomposites through in situ polymerization of monomers using micronized inorganic materials such as montmorillonite [6], kaolin [11], attapulgite [12], and mica [7] has been recently investigated.

Polyacrylamide-based hydrogels have also received considerable attention in many fields due to their ability of copolymerizing with different functional monomers and reactivity of amide group for the modification reactions. Itaconic acid is a water soluble monomer having two carboxylic acid groups (Fig. 1). Due to its double functionality, itaconic acid polymers offer interesting possibilities as functional polymers for wastewater treatment. However, literature on the homopolymerization of IA is limited [13] and it is stated that it was a non-polymerizable monomer [13, 14]. The majority of the studies on the itaconic acid hydrogels have focused on the copolymerization with different monomers, especially with acrylamide monomer [15–19]. Furthermore, in previous literature it is stated that the copolymer starts to be formed and crosslinked only when the concentration of AAM monomer exceeds 60% [16] and some small gelation content data, belongs to the IA including hydrogels, are also present being smaller than 30% [20].

The aim of this study is to synthesize and characterize the novel AAM-IA-MMT hydrogel nanocomposite with high IA amounts and to investigate their uses as adsorbent for removal of basic dyes from aqueous solutions. In this study, polyethyleneglycol (400) dimethacrylate was used as crosslinker in the preparation of acrylamide–itaconic acid hydrogels (Fig. 1), for the first time. The hydrogel nanocomposites were characterized by FTIR, XRD, swelling degree, and total basic group content analysis. Also, their adsorption properties were investigated and the effects of the adsorption parameters like adsorption time, initial dye concentration, and pH were exhibited.



$CH_2=CH-C(=O)-NH_2$ + $CH_2=C(COONa)-CH_2-COONa$ + MMT + $CH_2=CH-C(=O)-O-CH_2-CH_2-O(CH_2-CH_2-O)_9CH_2-CH_2-O-C(=O)-CH=CH_2$

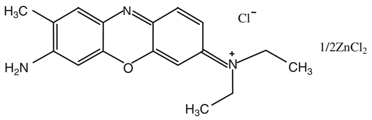
Fig. 1 Schematic illustration of the formation of nanocomposite hydrogels

Experimental

Materials and instruments

Acrylamide (AAm) and itaconic acid (IA) monomers were obtained from Merck and they were used without a further purification in polymerization reactions. Amoniumpersulfate and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were also purchased from Merck and were used as received. Polyethyleneglycol (400) diacrylate (PEG(400)DA) was kindly received from Sartomer and used without further purification. Clay mineral used in this study is a montmorillonite (Cloisite-Na) which was supplied from Southern Clay. The cation exchange capacity of the

Table 1 The chemical structure and some properties of BCB

Name	Chemical structure	Molar mass (g/mol)	Color index number	λ_{max} (nm)
Brilliant Cresyl blue		385.96	51010	622

clay was 92 meq/100 g and the mean size of the particles was less than 13 μm. Brilliant cresyl blue ($C_{17}H_{20}N_3OCl.1/2ZnCl_2$, BCB) was obtained from Merck. The molecular structure and identification information of BCB are depicted in Table 1. All the other reagents used throughout this study were extra pure chemicals.

FTIR spectra of the samples were recorded with a Digilab Spectrometer, Excalibur-FTS 3000MX model (Digilab, USA) in the range from 4000 to 400 cm^{-1} using KBr pellets. Spectra were taken with a resolution of 2 cm^{-1}. XRD analyses were performed with a Rigaku D/Max-2200/PC model (Rigaku, Japan) wide angle X-ray diffractometer (XRD) with Cu anode, running at 40 kV and 40 mA, scanning from 2° to 15° at 0.05°/min. The dye concentration determinations were performed using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer.

Preparation of hydrogel nanocomposites

Acrylamide (AAM) and itaconic acid (IA) were polymerized with 60:40 AAM/IA mass ratios in aqueous solution. MMT content was also varied as 0, 3, 5, 7, and 10% (w) in total monomer mixture. IA monomer was neutralized by equivalent NaOH before polymerization. PEG (400) DA was used as 1% mole of the total monomers. The schematic illustration of the formation of nanocomposites is given in Fig. 1. Polymerization reaction was initiated by adding ammonium persulfate and TEMED as the initiator and activator, respectively. In hydrogel nanocomposite preparation, firstly, MMT were dispersed in water by ultrasonic probe, then added into the monomer solution and stirred at ambient temperature for 3 h. Reactions were carried out in sealed petri dishes at 25 °C for 24 h after bubbling dried nitrogen into the mixture. Gel samples were purified by disintegrating in methanol/isopropyl alcohol mixture followed by filtering and washing with the excess of water and then with methanol. After that, these gel samples were dried at 50 °C under vacuum to obtain powder samples.

Characterization

Determination of total basic group (TBG) content

Total basic group (TBG) content is considered as the sum of basic groups from sodium itaconate and MMT (0.06 mmol/g). For determination, samples were equilibrated with the HCl solution (20 mL, 0.1 N) by stirring 24 h in a sealed flask, followed by filtration and the residue was washed with distilled water to remove unreacted HCl. The filtrate was titrated with 0.1 N NaOH solution in the presence of phenolphthalein indicator. The gelation amount of IA was also calculated by the ratio of the amount of IANa groups determined to the theoretically IA amount in polymer and was defined as gelation % of IA.

Determination of swelling degree

Swelling degrees of the samples were gravimetrically determined by the tea-bag method. The tea-bag was made of nylon screen. The tea-bag containing 0.1 g of sample was entirely immersed in distilled water. It was taken out of the water at regular time intervals, wiped superficially with a filter paper, weighed and replaced in the same water to ensure a state of equilibrium swelling. Swelling degree was calculated from the following equation:

$$S\ (\mathrm{g/g}) = (W_\mathrm{s} - W_\mathrm{d})/W_\mathrm{d} \tag{1}$$

where W_s and W_d are the weights of swollen and dry sample, respectively. Swelling degree of the sample in equilibrium state was named as equilibrium degree of swelling (EDS).

Adsorption studies

Adsorption experiments were carried out at 25 °C, in magnetically stirred (160 rpm) thermostated cylindrical glass vessels, in batch conditions. The polymers (50 mg) were added into brilliant cresyl blue (BCB) solution (50 mL) with the concentration of 500 mg/L for the determination of adsorption capacity. The amount of residual dye in the solution was determined spectrophotometrically after 24 h. Dependence of the adsorption capacities on time was determined and adsorption kinetics was investigated in detail. Furthermore, adsorption isotherm was obtained by stirring 60-40-c3 product in the dye solutions with various initial concentrations for a period of time equal to the respective equilibrium times. Adsorption capacity of 60-40-c3 product was also determined in the pH range of 3.0–8.0. The pH of the initial solutions was adjusted using dilute HCl or NaOH. The residual concentrations of dye were determined as described above. All the experiments were carried out triplicate. The adsorption capacity, Q (mg dye per g polymer), of polymers was calculated using the following expression:

$$Q\ (\mathrm{mg/g}) = (C_\mathrm{i} - C_\mathrm{e})\ \mathrm{V/m} \tag{2}$$

where C_i and C_e are the initial and equilibrium concentrations of dye (mg/l), respectively, V is the volume of the solution added (l), and m is the amount of polymer (g).

Results and discussion

FTIR characterization

Absorption peaks originated from the C=O group at 1666–1669 cm^{-1} and NH$_2$ groups at 1615–1617 cm^{-1} of the AAM unit were seen in the spectrum of AAM-IANa hydrogel (60-40-c0) (Fig. 2). The peaks originating from the sodium itaconate at 1561 and 1398 cm^{-1} were also observed. Furthermore, the asymmetric stretching vibration of the C–O–C bond of the PEG (400) DA crosslinking agent at 1183–1191 cm^{-1} was observed. It was concluded that the crosslinker participated into the polymer matrix and crosslinking reaction between PEG (400) DA and the monomers occurred. In spectrum of montmorillonite, the absorption peaks indicating OH stretching of water molecules in the clay structure and also OH groups between octahedral and tetrahedral sheets were observed at 3451 and 3628 cm^{-1}, respectively [21]. Other characteristic peaks originating from the H–O–H bending at 1638 cm^{-1} and Si–O stretching at 1044 cm^{-1} were also observed. In spectrum of the hydrogel nanocomposite (60-40-c10), all the characteristic peaks of montmorillonite and AAm-IANa hydrogel were observed. These confirm that the montmorillonite participated to the polymer structure. On the other hand, disappearing of the absorption peak at 3628 cm^{-1} which corresponds to the OH groups in clay structure supposed that the grafting mechanism was occurred on the clay mineral layers [22, 23].

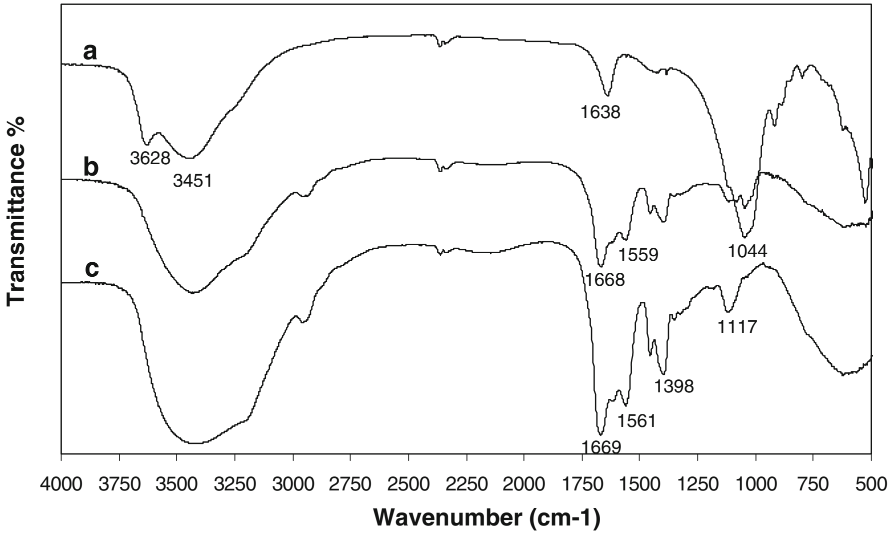


Fig. 2 The FTIR spectra of MMT (*a*), AAM–IANa–MMT nanocomposite (*b*), and AAM–IANa hydrogel (*c*)

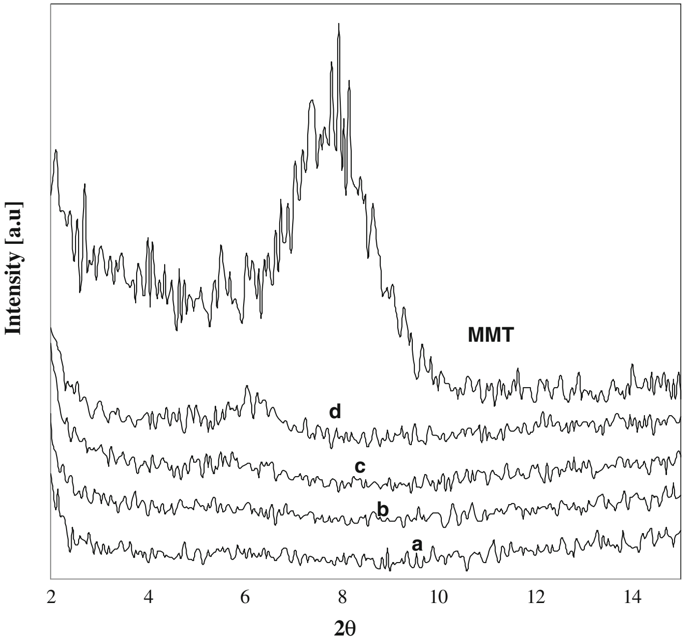


Fig. 3 XRD patterns of the MMT and AAM–IANa–MMT hydrogel nanocomposites. (*a* 60-40-c3, *b* 60-40-c5, *c* 60-40-c7, *d* 60-40-c10)

XRD analysis

The main reflection which could be attributed to the specific d_{001} basal spacing of montmorillonite (2:1) was seen at $2\theta = 7.84°$ in the XRD pattern of Cloisite-Na (Fig. 3) and d_{001} basal spacing of montmorillonite was calculated as 11.3 Å by the Bragg equation. But, no reflection corresponding to the d_{001} basal spacing of montmorillonite layers was observed for hydrogel nanocomposites. The absence of this reflection indicated that the montmorillonite layers were exfoliated. Only for 60-40-c10 product, this reflection shifted to the lower diffraction angle ($2\theta = 6.12°$) and the d_{001} basal spacing of montmorillonite layers expanded (14.5 Å). This confirmed the existence of the intercalated clay structure together with the exfoliated one.

Properties of hydrogel and hydrogel nanocomposites

Total basic group (TBG) content, gelation % of IA and equilibrium degree of swelling (EDS) of products are given in Table 2. MMT addition increased the TBG value and also gelation of IA. For instance, the TBG value of hydrogel increased from 2.85 to 3.29 mmol/g by addition of low amount of MMT (3%) and the gelation of IA increased from 62.9 to 70.6%. It was supposed that MMT acted as crosslinker and increased the IA gelation. It is known that increasing the amount of IA in monomer composition decreases the gel formation and effective crosslinking

Table 2 Preparation conditions and properties of AAM–IANa hydrogel nanocomposites

Polymer[a]	Clay ratio[b] in total monomer (w%)	TBG content (mmol/g)	Gelation % of IA	EDS[c] (%)	*Q* (mg/g)
60-40-c0	–	2.85	62.9	300.3	419.7
60-40-c3	3	3.29	70.6	339.7	457.4
60-40-c5	5	3.08	64.9	286.7	436.5
60-40-c7	7	3.28	65.8	256.9	405.4
60-40-c10	10	3.17	63.9	219.5	386.9

EDS equilibrium degree of swelling, *TBG* total basic group

[a] Samples were prepared with 60:40 AAM:IA (w) ratio. PEG(400)DA/total monomer mole ratio was 1/100 and $(NH_4)_2S_2O_8$: 150 mg, TEMED: 1 mL (25% aqueous solution), water: 40 mL were used per 4 g total monomer

[b] Clay ratio was presented in feed

[c] EDS was determined in distilled water

densities of polymer networks [15, 24]. Likewise, in this study, disk shape gel with high IA ratio could be obtained by addition of MMT (Fig. 4).

The AAM–IANa hydrogel has quite high EDS values (300.3 g water/g) as seen in Table 2. It is supposed that the PEG(400)DA structure would be also effective on

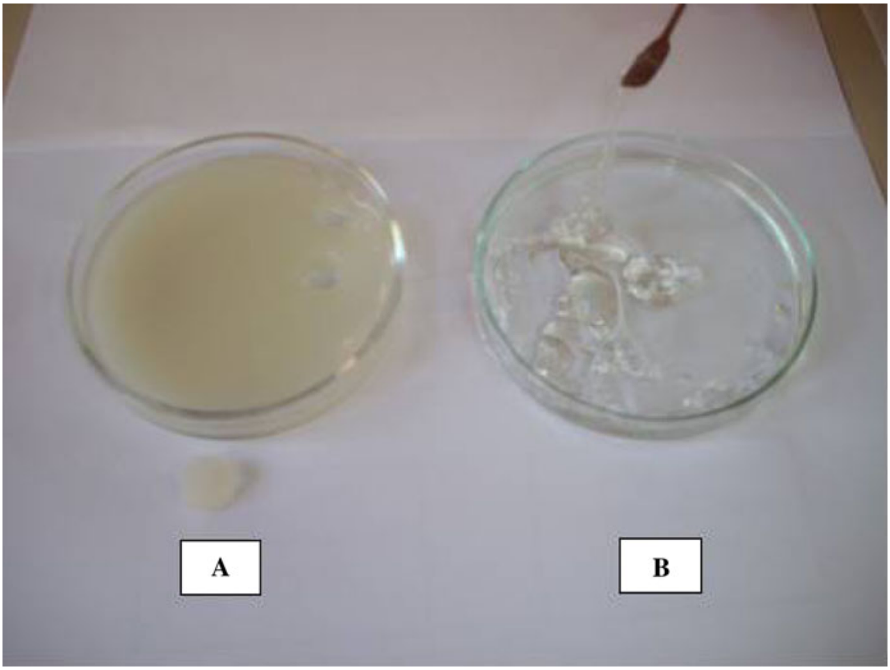


Fig. 4 The photographs of AAM–IANa–MMT nanocomposite (**a**) and AAM–IANa hydrogel (**b**) after polymerization

the swelling degree. In literature, higher swellable hydrogels were obtained using PEG (400) DA instead of *N*,*N*-methylenebisacrylamide (NMBA). PEG (400) DA has a longer and more flexible chain structure than that of NMBA [25]. Its longer chain length provides a larger space among the acrylamide chains (Fig. 1). As a result; water diffuses into the gel structure more easily and provides higher EDS value. In nanocomposite hydrogels, addition of low amount of MMT into the polymeric structure increased the EDS values (60-40-c3 product) (Table 2). It is supposed that the increasing in the gelation of IA by the addition of MMT increased the EDS value. Furthermore, it is stated in literature that the addition of low amount clay into the hydrogel increased the swelling ability due to the hydrophilic structure of montmorillonite [26, 27]. According to the Flory's theory, swelling degree of a gel depends on the ionic osmotic pressure, crosslinking density, and the affinity of the gel for the liquid. As the cations present in MMT are easily ionized, MMT is dispersed into the polymer. Higher hydration and distention of MMT could enhance the hydrophilicity of the nanocomposite and hence it swells more. But high clay content decreases the swelling ability since the clay layers act as a crosslinking agent. So, additional crosslinking points between polymer and clay layers are generated in the polymeric network, which increases crosslink density of the hydrogel and then the elasticity of polymeric chains decreases [6, 22, 28]. Likewise in this study, all nanocomposites have higher TBG values and IA amounts than the hydrogel (60-40-c0), but they have lower EDS values except for the 60-40-c3 product.

In addition to the increase of the swelling capacity, swelling rate also increased with the MMT addition due to its higher hydration and distention ability [26, 27] (Fig. 5). Another interesting point is that no visible MMT loss was observed from the sample structure during the swelling and purification process. The photographs of hydrogel nanocomposites in different stages (just after preparation, dried and swollen) during this process are shown in Fig. 6. Hydrogel nanocomposite is transparent and keeps its original shape without changing at the swollen state.

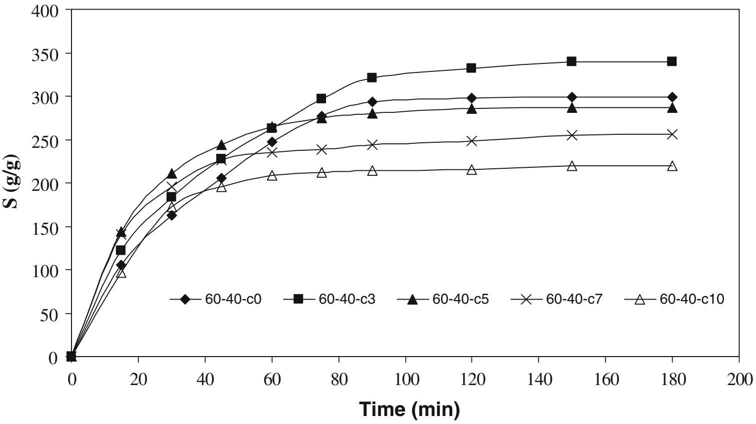


Fig. 5 Swelling isotherms of the AAM–IANa hydrogel and hydrogel nanocomposites in distilled water at 25 °C

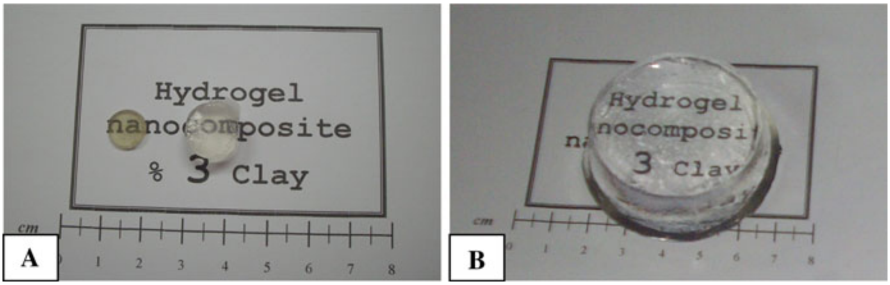


Fig. 6 The photographs of AAM–IANa–MMT hydrogel nanocomposite. **a** Dried (on the *left*) and removed from mold after polymerization (on the *right*). **b** Swollen (the sample was prepared in disk shape to compare the size and transparency of the hydrogel nanocomposite)

Adsorption studies

The brilliant cresyl blue (BCB) was selected as model compound to investigate the uses of the AAM–IANa hydrogel and hydrogel–MMT nanocomposite for the removal of basic dyes from aqueous solutions. Adsorption properties of the products were evaluated by depending on adsorption time, initial dye concentration, and also product properties. All samples have quite high BCB adsorption capacities (Table 2). Carboxylate groups on the polymer structure have the ability to create interactions with the amino groups of dye. Furthermore, the hydrophobic interactions between the aromatic rings of the dye and the hydrophobic groups on the polymer may be present. Adsorption capacity of the products varied by depending on their TBG and EDS values. This value increased up to 3% MMT content and decreased later. The BCB adsorption capacity of hydrogel (60-40-c0) increased from the value of 419.7 to the value of 457.4 mg/L by the addition of low amount of MMT into the polymer structure. This increase may also be attributed to the high TBG and EDS values of the 60-40-c3 product. Also, strong interactions between the clay mineral layers and polymer matrix will be affecting the adsorption capacity. Clay mineral layers may easily adsorb organic cations. In adsorption experiments, the adsorption capacity of the Cloisite-Na was found to be 387.3 mg/g. Furthermore, the EDS value of products became effective on their dye adsorption capacity. The 60-40-c5 product has lower TBG content (3.08 mmol/g) than the 60-40-c7 product (3.28 mmol/g), but it exhibits higher dye adsorption capacity (Table 2). This increase may also be attributed to the high EDS value of the 60-40-c5.

The AAM–IANa hydrogel (60-40-c0) and hydrogel nanocomposite (60-40-c3) were left in dye solution and their capacities were determined at specified time intervals to investigate the time dependency of the adsorption capacity (Fig. 7). The saturation was observed approximately within 60 min in case of 60-40-c0. In case of 60-40-c3 nanocomposite, high adsorption rates were observed at the beginning (approximately within 15 min) and then plateau values were gradually reached within 30 min. This high initial rate suggests that the adsorption occurs mainly on the polymer surface. The adsorption behavior of dyes is directly related to some

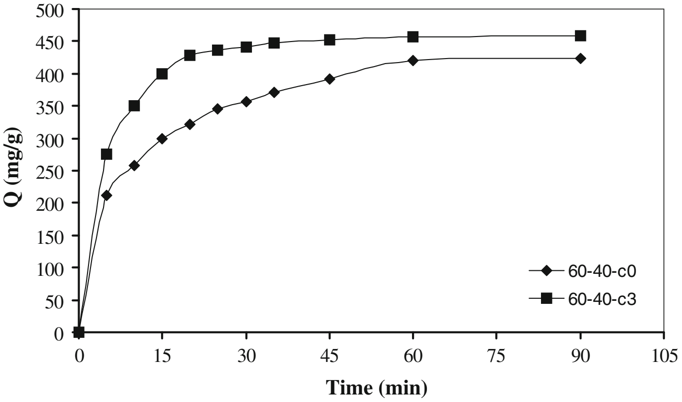


Fig. 7 Plots of the adsorbed BCB dye amounts by the AAM–IANa hydrogel and hydrogel nanocomposite versus time. Adsorption conditions: 500 mg/L initial dye concentration, 25 °C, 160 rpm

experimental factors such as pH of the solution, characteristics of the adsorbent, dimensions of the dye molecule. It was reported that the equilibrium time changed between 12 h and 2 days for the various adsorbents used for removal of BCB [29–31]. The quite high adsorption capacities and higher adsorption rates of hydrogel nanocomposites will provide an important advantage for using of these materials in basic dye solutions.

In order to express the mechanism of the adsorption process onto 60-40-c0 and 60-40-c3, kinetic data were analyzed by a pseudo-first-order [32] and a pseudo-second-order [33] equations. The linearized equation of the pseudo-first-order kinetic model is:

$$\log(Q_\mathrm{e} - Q_t) = \log Q_\mathrm{e} - k_1 t/2.303 \tag{3}$$

where Q_e and Q_t refer to the amount of dye adsorbed (mg/g) at equilibrium and a given time (t, min), respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The values k_1 and Q_e can be determined from the slope and intercept of the straight-line plots of log (Q_e − Q_t) against t.

On the other hand, the linearized equation of a pseudo-second-order equation is expressed as the following form:

$$t/Q_t = 1/\left(k_2 Q_\mathrm{e}^2\right) + (1/Q_\mathrm{e})t \tag{4}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min^{-1}). The values of k_2, Q_e and the initial adsorption rate ($r_i = k_2 Q_\mathrm{e}^2$, mg/g min) can be obtained from the slope and intercept of the plot of t/Q_t against t.

The validity of these two models can be checked by analyzing the linearized plots (Fig. 8). It is revealed that the pseudo-second-order kinetic model fitted better than the first-order model as the correlation coefficients (r_2^2) are closer to 1 than those of the first-order kinetics (r_1^2) (Table 3). Moreover, the Q_e values for the second-order kinetic model is close to the Q_e values obtained experimentally (experimental Q_e values are 419.7 and 457.4 mg/g of 60-40-c0 and 60-40-c3 products, respectively).

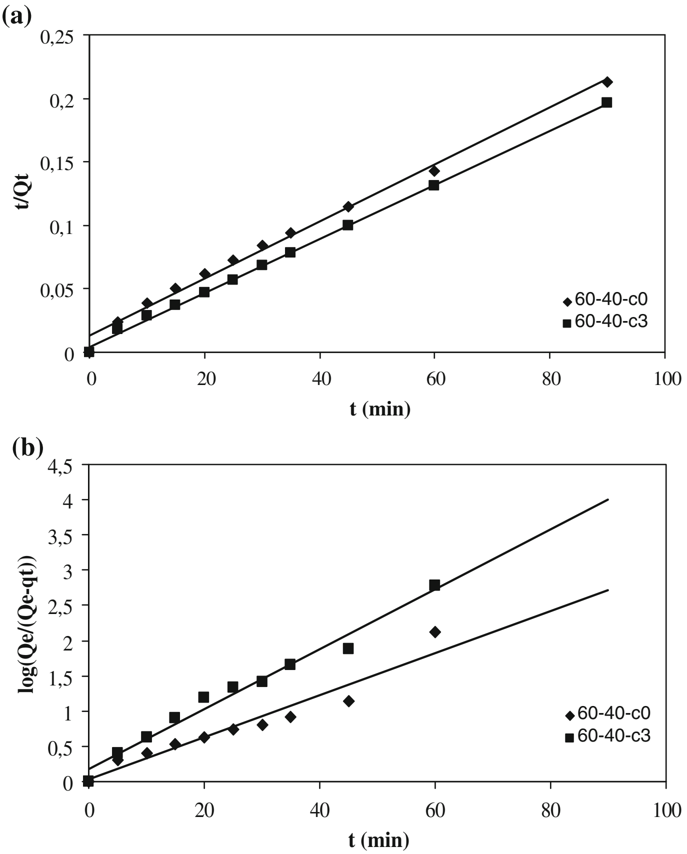


Fig. 8 Adsorption kinetics of the BCB onto the AAM–IANa hydrogel and AAM–IANa–MMT hydrogel nanocomposite according to pseudo-second-order model (**a**) and pseudo-first-order model (**b**)

Table 3 The pseudo-first and pseudo-second rate constant for BCB onto hydrogel (60-40-c0) and hydrogel nanocomposite (60-40-c3)

Polymer	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
	Q_e (mg/g)	k_1 (min^{-1})	r_1^2	Q_e (mg/g)	k_2 (g/mg min)	r_i (mg/g min)	r_2^2
60-40-c0	13.468	6.86 × 10-2	0.9289	454.5	3.66 × 10-4	75.62	0.9924
60-40-c3	11.955	9.76 × 10-2	0.9784	476.2	9.80 × 10-4	222.23	0.9987

The effect of the initial dye concentration on the adsorption capacity was investigated by the experiments carried out at various initial dye concentrations (40–500 ppm). Dye adsorption capacity of 60-40-c3 product increased with the increasing initial dye concentration until saturation (Fig. 9). Results obtained from the adsorption isotherm were evaluated by means of Langmuir and Freundlich adsorption models.

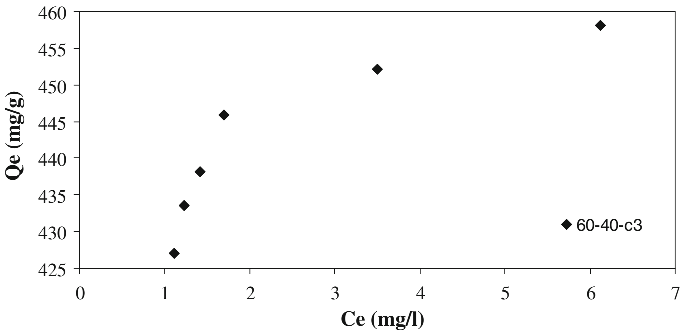


Fig. 9 Equilibrium adsorption values of the BCB onto the AAM–IANa–MMT hydrogel nanocomposite. Adsorption conditions: 50 mg polymer, 25 °C, 160 rpm

Basic assumption of the Langmuir adsorption model is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm is represented by the following equation:

$$C_e/Q_e = 1/(bQ_{\max}) + C_e/Q_{\max} \tag{5}$$

where Q_e (mg/g) is the amount of the adsorbed dye per unit mass of adsorbent at the final equilibrium concentration of the dye solution (C_e, mg/L). The $Q_{\max}$ signifies the maximum adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The essential characteristic of the Langmuir equation can be expressed in terms of the dimensionless separation factor R_L, which is defined by

$$R_L = 1/(1 + bC_0)) \tag{6}$$

where C_0 is the highest initial dye concentration (mg/L) and b is the Langmuir constant. The value of R_L indicates the type of the isotherm either to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The isotherm data were applied to Langmuir and Freundlich isotherm model for the hydrogel nanocomposite. Langmuir model fitted the adsorption isotherms better than the Freundlich model. The correlation coefficient was found as 0.9997 for Langmuir isotherm model and the low value of R_L indicates a favorable adsorption (Table 4).

To evaluate the influence of the pH on the adsorption of BCB, the 60-40-c3 product was left in dye solutions having different pH values between 3 and 8, and the adsorption capacities were determined (Fig. 10). The adsorption capacity increased with increasing pH of the initial solutions. It is supposed that the ionization of carboxylate groups in the itaconic acid unit was effective on

Table 4 Langmuir constants for the BCB adsorption onto 60-40-c3 hydrogel nanocomposite

Polymer	Langmuir constants			
	$Q_{\max}$ (mg/g)	b (L/mg)	R_L	r_L^2
60-40-c3	500	6.67	0.0003	0.9997

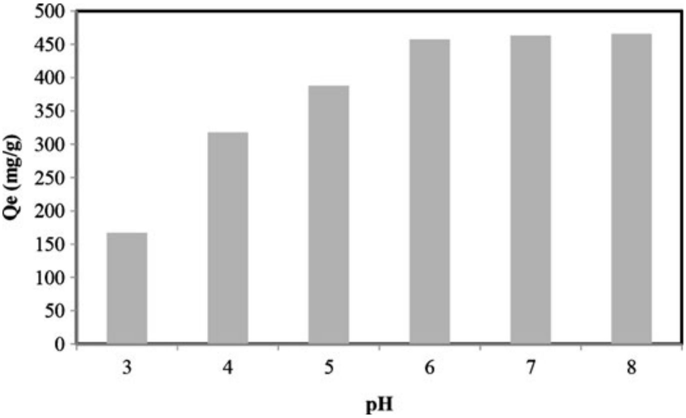


Fig. 10 Effect of pH on the adsorption capacity of BCB by 60-40-c3 (initial dye concentration = 500 mg/L, 50 mg polymer, 25 °C, 160 rpm, 24 h)

adsorption at higher pH values. At low pH, the carboxylic acid groups are present in non-ionized form and probability of interactions between carboxylic acid groups and dye molecules are low [34]. At high pH values, the concentration of anionic groups (carboxylate anions) in the polymer network increases. The other effect of the increasing pH value is on the EDS value, increasing in ionization degree of carboxylic acid group will increase the repulsion of polymer chain resulted in easily expansion of polymer network, it means increasing of EDS value. The pKa_1 and pKa_2 values of itaconic acid are 3.85 and 5.45, respectively. It is seen from the Fig. 10 that the adsorption capacity increased up to pH value of 6 and then no increase was observed at higher pH values because of completion of ionization of the carboxylate groups. Also, the adsorption of charged dye molecules onto clay substance is primarily influenced by the surface charge depending on the solution pH. At low pH, the clay had net positive charge and would be prone to electrostatically repel cations [35].

Conclusion

New hydrogel nanocomposites were prepared by in situ copolymerization of AAm and IANa monomers in the presence of montmorillonite by using PEG (400) DA as crosslinker. MMT incorporation into the copolymer structure enhanced the itaconic acid gelation and swelling properties of hydrogel. FTIR analysis showed that the hydrogel/MMT nanocomposites were successfully obtained. Furthermore, XRD analysis of the samples showed that clay mineral layers were exfoliated in the hydrogel with low clay loading (3–7%) and exfoliated/intercalated clay dispersion was observed when the clay loading is higher (10%). Products were also used in adsorption of the BCB dye from aqueous solutions. It was found that the hydrogel nanocomposite has quite high adsorption rate (equilibrium time is approximately

30 min) and adsorption capacity (458.1 mg/g). Kinetic and equilibrium studies showed that the AAm–IANa–MMT hydrogel nanocomposites can be used as novel, fast-responsive and high capacity adsorbent materials for the removal of cationic dyes.

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