ORIGINAL PAPER

Removal of acidic dye from aqueous solutions using poly(DMAEMA–AMPS–HEMA) terpolymer/MMT nanocomposite hydrogels

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Abstract In this study, poly(DMAEMA–AMPS–HEMA) terpolymer/montmorillonite nanocomposite hydrogels were prepared by in situ polymerization technique using 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA), 2-acrylamido-2-methlypropane sulfonic acid (AMPS), 2-hydroxyethyl methacrylate (HEMA) monomers in clay suspension media. N,N-methylenebisacrylamide (NMBA) was used as crosslinker and potassium persulfate/potassium bisulfide were used as initiator and accelerator pair. The water absorption capacities and acidic dye (indigo carmine) adsorption properties of the nanocomposite hydrogels were investigated. Adsorption properties of the hydrogels were investigated at different conditions such as different initial dye concentration and contact time. The concentrations of the dyes were determined using UV/Vis Spectrophotometer at wavelength 610 nm. Langmuir and Freundlich isotherm models were used to describe adsorption data and the results clarified that these models were the best-fit for the adsorption of indigo carmine.

Keywords Hydrogel · 2-Acrylamido-2-methlypropane sulfonic acid ·
2-Hydroxyethyl methacrylate · 2-(N,N-dimethylamino)ethyl methacrylate ·
Indigo carmine · Clay · Nanocomposite hydrogel

Introduction

Superabsorbent hydrogels are loosely crosslinked hydrophilic polymers that can absorb, swell and retain aqueous solutions up to hundreds of times their own weight [1]. Hydrogels have received increasing attention of researchers due to their wide

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applications such as drug delivery systems, immobilization of enzymes, dewatering of protein solutions, solute separation, baby diapers, feminine napkins, soil for agriculture and horticulture, water-blocking tapes, absorbent pads, etc. [2, 3]. There are some hydrogels that sometimes undergo a volume change in response to a change in surrounding conditions such as temperature, pH and solvent composition [4]. Temperature and pH responsive hydrogels are more favorable ones because both of them are important environmental factors in biomedical and other systems [5].

In recent years, the study of organic–inorganic nanocomposites has become a very important field [6]. Many layered, inorganic mineral micropowders such as mica, attapulgite, and kaolinite have been used in the preparation of polymers to achieve lower production costs and higher properties [7]. The poor mechanical properties of the hydrogels restrict their applications widely. To improve these properties of hydrogels, many layered clays were used by many researchers. Using this method, different nanocomposite hydrogels such as poly(sodium acrylate)/ sepiolite [3], poly(acrylic acid)/montmorillonite (MMT) [7], poly (N-isopropylacrylamide)/MMT [8] and poly(acrylic acid)/mica [9] were prepared. Clays have sandwich-type structures with one octahedral Al sheet and two tetrahedral Si sheets. Because of their hydrophilic nature, clays are suitable for use in water absorbents as additives [6]. MMT is main natural mineral clay widely used to prepare composite hydrogels, due to their good water absorption, extensive swelling in water and cation exchange capacity [10]. MMT is a kind of loose-layer, hydrophilic, swollen natural clay.

Colored organic effluent is produced in the textile, paper, plastic, leather, food and mineral processing industries [11]. The main pollution source of textile effluent emerges from the dyeing process. Dyeing and finishing wastes in the textile industry have high color and organic content. Synthetic organic dyes present certain hazards and environmental problems. Effluents discharged from dyeing industries are highly colored with low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD) [12]. Disposal of these effluents into water can be toxic to aquatic life [13]. The dyes upset the biological activities in water bodies. They cause a health problem because they may be mutagenic and carcinogenic [14] and can cause severe damage to human beings such as in the liver and the central nervous system [12, 15]. Methods and effluent treatment for dyes may be divided into three main categories physical, chemical and biological. Among them adsorption technology is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent [16]. Dyes can be effectively removed by adsorption process. Activated carbon [12, 17], natural clays [18], modified clays [19, 20], some industrial wastes and by-products [17] have been used as adsorbents for removal of organic compounds from wastewater. In recent years polymeric adsorbents have been increasingly used to remove and recover organic pollutants from waste waters [21–24].

In this study, nanocomposite hydrogels were prepared using 2-acrylamido-2-methlypropane sulfonic acid (AMPS), 2-hydroxyethyl methacrylate (HEMA), 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) monomers and MMT. The effect of MMT content in nanocomposite hydrogels on the swelling behavior was

examined. Also, the removal of indigo carmine from aqueous solutions using nanocomposite hydrogels and effects of various parameters such as treatment time, initial dye concentration and MMT content on the adsorption were investigated. Adsorption isotherms were described using Freundlich and Langmuir models.

Experimental

Materials

The monomers, AMPS, HEMA, DMAEMA, the crosslinking agent, N,N-methyl-enebisacrylamide (NMBA), the water soluble initiator and accelerator pair; potassium persulfate (PPS), and potassium bisulfide (PBS) were all purchased from Merck AG (Darmstadt, Germany). Acidic dye indigo carmine (5,5′-indigodisulfonic acid disodium salt) was also obtained from Merck AG and its chemical structure is shown in Fig. 1. MMT was kindly provided by Kenan Çinku from the Mining Engineering Department of Istanbul University.

Other reagents were chemically pure grade and all solutions were prepared with distilled water.

Instruments

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max Ultima+ X-ray diffractometer equipped with CuK α radiation ($\lambda = 1.5405$).

The clay was suspended by using Bandelin UW 2200 model ultrasonic irradiation equipment.

Spectrophotometric measurements were carried out using Pharmacia Novaspec II model UV/Vis spectrophotometer.

FTIR spectra of samples were taken as KBr pellets using Digilab Excalibur-FTS 3000MX model FTIR Spectrophotometer.

Preparation of hydrogels

The nanocomposite hydrogels (DMAEMA-AMPS-HEMA terpolymers/MMT) were prepared by free radical chain polymerization in clay suspension. Firstly, the clay was suspended in water thoroughly under ultrasonic irradiation. The monomers (DMAEMA, AMPS, and HEMA) and the crosslinking agent (NMBA) were dissolved in suspended clay and taken in 12-cm long glass tubes of 2 cm diameter. After sealing the tubes with rubber caps, oxygen-free nitrogen gas was purged in the

Fig. 1 Chemical structure of Indigo Carmine
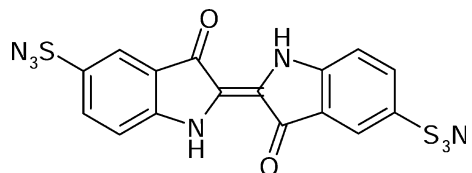
solution for 20 min and the tubes were placed in a water bath at 70 °C. Then, PPS and PBS at the same concentration (4.5 g/100 mL water) were added to the solutions in the tubes. The polymerization reactions were carried out for 2 h at 70 °C. In all experiments, the initiator (PPS) and NMBA concentrations were 1% (mole) and 0.25% (mole) of the total amount of monomers, respectively. The amount of accelerator (PBS) was equal to the PPS in weight, and the amount of the MMT was used as 1, 4 and 6% (wt.) of the total amount of monomers. At the end of the polymerization, the glass tubes were carefully broken. Hydrogel products were taken and cut into discs in 5-mm length and put in distilled water. The discs were held in water at room temperature for 4 days and in order to remove unreacted monomers, the water was replaced with fresh water twice in a day. After the hydrogels were dried under vacuum at 40 °C, they were used for the water absorption (swelling) and dye adsorption experiments. The compositions of hydrogels were listed in Table 1.

Determination of water absorption capacities

A gravimetric procedure, tea-bag method was adopted to monitor the progress of the swelling process. The tea bag was made of 250-mesh nylon screen; it contains a weighted amount of dried hydrogel sample and was fully immersed in distilled water. In order to obtain equilibrium swelling degree (Q_e), it was kept there for reaching to the constant weight, then hung up for 1 min to drain the excess solution and weighed. The water absorbency of the nanocomposite hydrogels was calculated using the following equation.

$$Q_e = (W_{wet} - W_{dry})/W_{dry} \tag{1}$$

where Q_e is the water absorbency as grams of water per gram of sample, W_{wet} and W_{dry} are the weights of the swollen sample and the dry sample as gram, respectively. The swelling experiments were repeated three times and the averages of the results were reported.

Dye adsorption studies

Indigo carmine solutions with different concentrations were prepared by dissolving dye in distilled water. The nanocomposite hydrogels (0.2 g) were added into indigo

Table 1 The feed compositions of the hydrogels

Symbols of the hydrogels	Monomers DMAEMA-HEMA-AMPS (mole %)	MMT (wt%)	NMBA (mole %)
H-0.25-0	40-40-30	0	0.25
H-0.25-1	40-40-30	1	0.25
H-0.25-4	40-40-30	4	0.25
H-0.25-6	40-40-30	6	0.25

carmine solutions (50 mL). Initial concentrations of dye solutions were 500 mg/L. The amount of residual dye in aqueous solution was followed by UV/Vis Spectrophotometer up to 120 h. In experiments of equilibrium adsorption isotherm, a fixed amount of 0.2 g adsorbents were contacted with 50 ml of aqueous solutions indigo carmine with different concentrations (100–500 mg/L). The amount of residual dye in aqueous solution was determined by UV/Vis Spectrophotometer after 48 h. The equilibrium adsorption capacity, q_e (mg/g), was calculated from the following equation:

$$q_e = \frac{(C_o - C_e) \cdot V}{W} \tag{2}$$

where C_o is the initial concentration (mg/L), C_e is the residual concentration at equilibrium (mg/L), V is the volume of solution (L), W is the weight of the sample (g).

Results and discussion

X-ray diffraction analysis

Figure 2 illustrates the XRD of MMT and nanocomposite hydrogels. There is intense diffraction for MMT ($2\theta = 7.4°$), while no diffraction peak appears for nanocomposite hydrogel samples H-0.25-1 (1 wt% MMT) and H-0.25-6; (6 wt% MMT), it was attributed that clay sheets are exfoliated and uniformly dispersed in organic network.

FT-IR analysis

Since all three monomers are acrylic base monomers, they have similar characteristic peaks. But because of their different functional groups (amino group for DMAEMA, sulfonic acid group for AMPS and free –OH group for HEMA) the
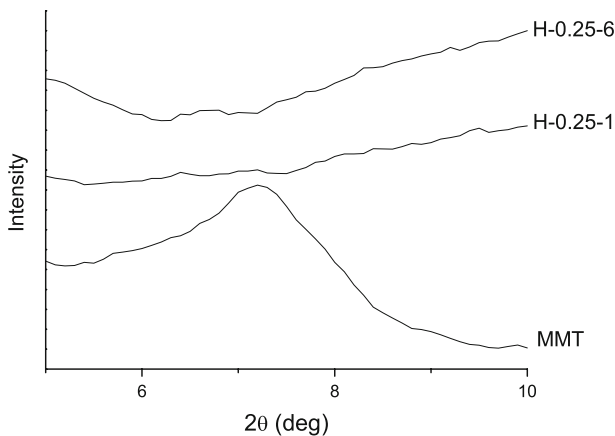

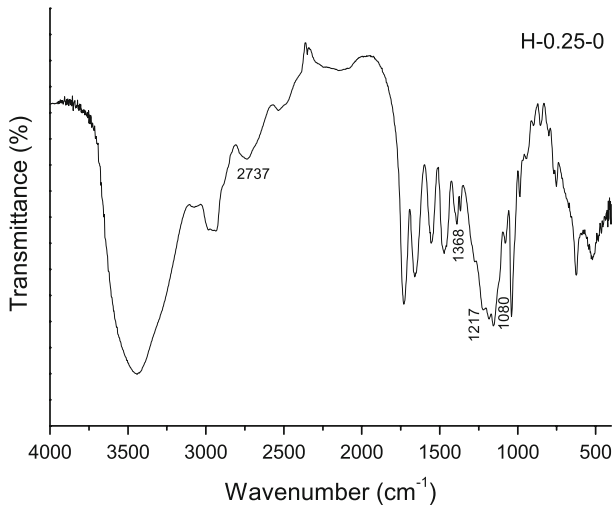**Fig. 2** XRD spectra of MMT and nanocomposite hydrogels

Fig. 3 FTIR spectra of the terpolymer

FT-IR spectra of the hydrogels could be able to give some information about the chemical structure of the hydrogels. It was observed that absorption peaks (sharp and small peaks or shoulders) at 2,737 cm^{-1} due to the $(CH_3)_2N$ groups, at 1,217 and 1,080 cm^{-1} due to the symmetric stretching vibration of $-SO_3H$ groups and at 1,368 cm^{-1} due to the free $-OH$ groups stretching in the monomers (Fig. 3) [25].

Swelling behavior of the nanocomposite hydrogels

Figure 4 shows the effect of the content of MMT on the water absorbency of nanocomposite hydrogels. Increasing the MMT weight ratio up to 4% causes an increment in water absorbency, which indicates that MMT can improve the water absorbency of the samples but further increase of MMT causes a decrease in water absorbency. When the concentration of the clay is too high, the neighboring clay–clay interparticle distance will be too small. This causes small size polymeric networks which decrease the water absorption amount [26]. Moreover, MMT acts as co-crosslinking points of the terpolymer chains; this causes the overall decrease on the swelling behavior of the nanocomposite hydrogels [10].

Dye adsorption studies

Adsorption properties of the nanocomposite hydrogels were evaluated by depending on different adsorption conditions such as different initial dye concentration and contact time. The concentrations of the indigo carmine solutions were determined using UV/Vis Spectrophotometer at wavelength 610 nm.

Figure 5 illustrate the effect of adsorption time on the dye adsorption efficiency. The amount of dye adsorbed increases with adsorption time until it reaches to the equilibrium value. Compared with pure hydrogel, the hydrogel nanocomposites
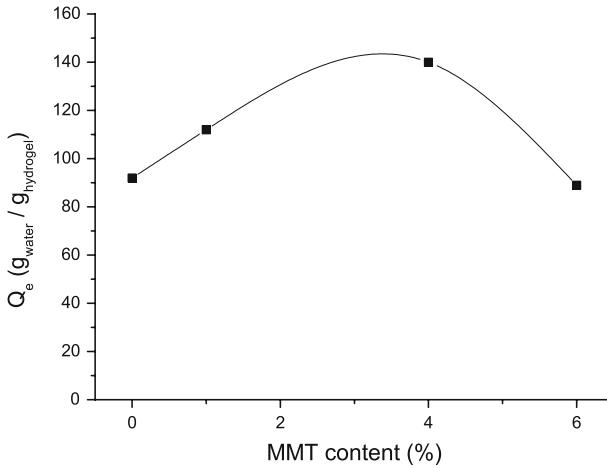
Fig. 4 The effect of the content of MMT on the water absorbency of nanocomposite hydrogels
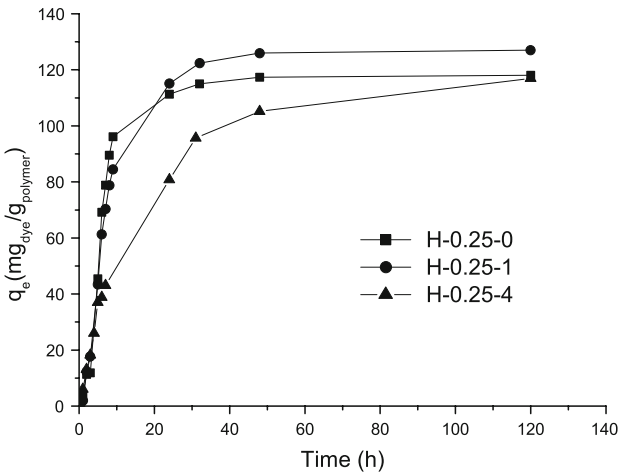

Fig. 5 The effect of adsorption time on the dye adsorption efficiency of nanocomposite hydrogels

H-0.25-1 and H-0.25-4 have higher equilibrium swelling degree as indicated in Fig. 4. In case of adsorption of acidic dye, pure and H-0.25-1 hydrogels reach adsorption equilibrium in 24 h, H-0.25-4 hydrogel continues to adsorb dye and reaches 105, 117 mg/g hydrogel in 48 and 120 h, respectively. The pure and H-0.25-4 nanocomposite hydrogels adsorb almost same amounts of acidic dye in 120 h. Increasing the MMT weight ratio up to 1% causes an increment in dye adsorption capacity but further increase of MMT causes a decrease in dye adsorption rate. This may be attributed to the fact that the MMT reacts with the monomers (for example hydroxyl groups on the surface of MMT would react with the –OH and –SO$_3$H groups of the HEMA and AMPS, respectively) and acts as crosslinking agent. So, more crosslink points are generated in the polymeric network, which increases
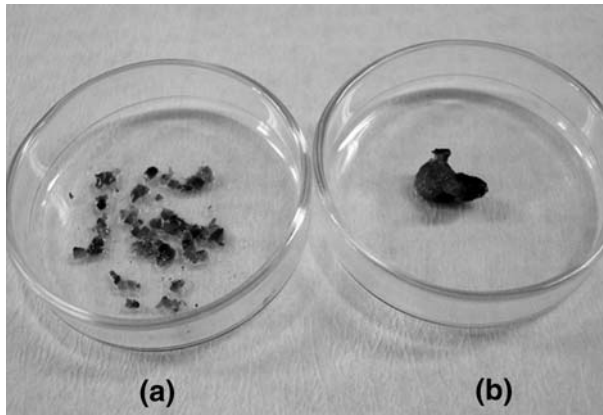
Fig. 6 The appearance of the hydrogels after adsorption of basic dye. **a** 0% MMT, **b** 4% MMT

crosslink density of the nanocomposite hydrogel and then the elasticity of the polymer chains decreases [1, 27, 28]. Figure 6 shows the physical views of pure and composite hydrogel after the adsorption studies. While the pure hydrogel dissipates in the dye solution, the nanocomposite hydrogels protect their physical forms. This property makes possible to remove used hydrogel from the solution easily. Removal of used hydrogels from the media is an important case due to environmental aspects, thus improved mechanical properties of these hydrogels make them considerable.

Adsorption isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Equations often used to describe the experimental isotherm data are those developed by Freundlich, by Langmuir. The Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbent used in water and wastewater.

In the experiments of equilibrium adsorption isotherm, a fixed amount of 0.2 g adsorbents were contacted with 50 mL of aqueous solutions indigo carmine have different concentrations (100–500 mg/L).

Freundlich isotherm

The Freundlich equations were used to fit the equilibrium isotherms. The Freundlich equation [29] is the earliest known relationship describing the adsorption equation.

Table 2 Freundlich constants of adsorption isotherms for indigo carmine onto hydrogels

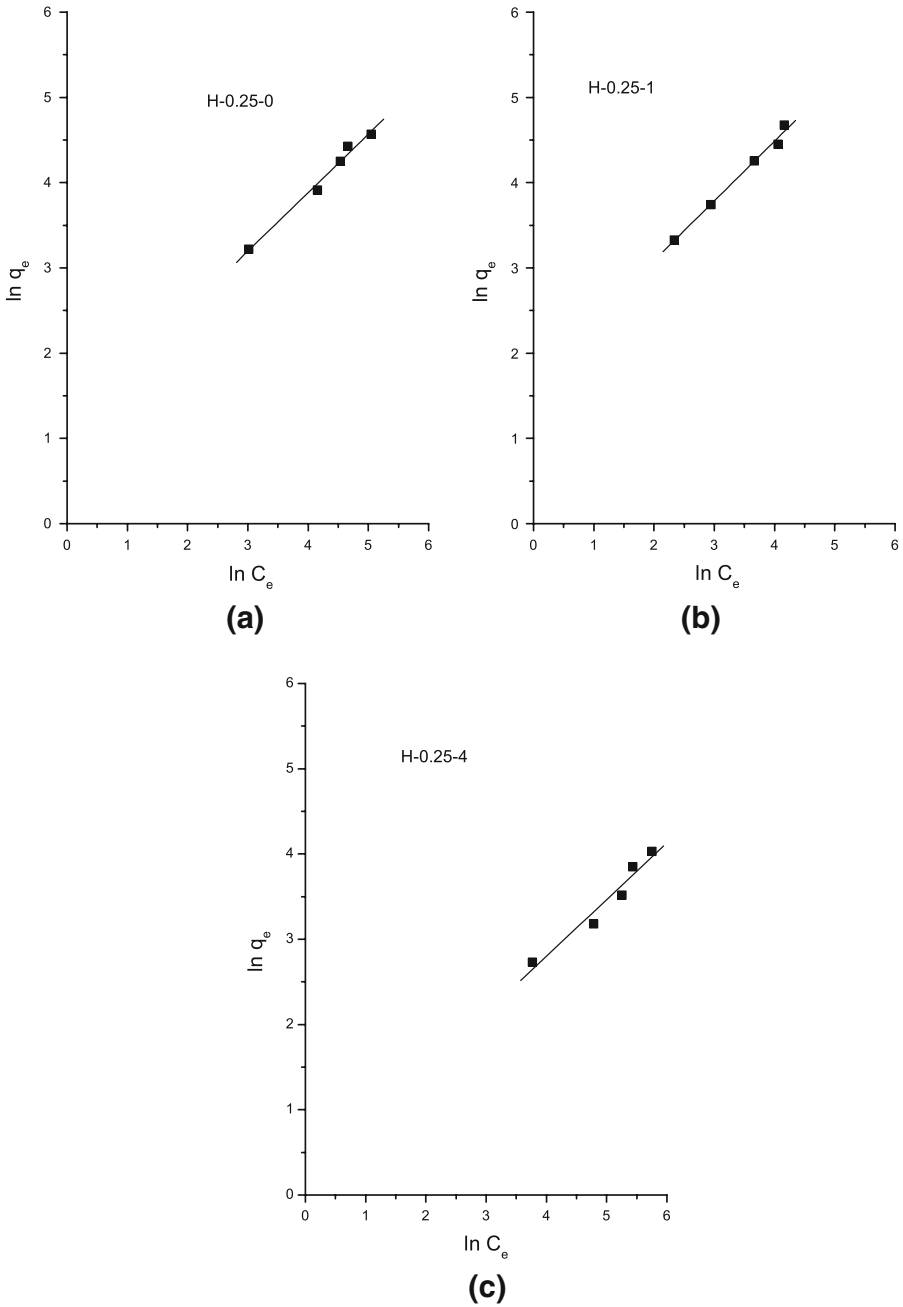| Hydrogels	K_f	n	R^2
H-0.25-0	1.1331	1.4548	0.9932
H-0.25-1	1.6849	1.4276	0.9952
H-0.25-4	0.1483	1.5080	0.9751

(a)

(b)

(c)

Fig. 7 Freundlich isotherms of the hydrogels. **a** 0% MMT, **b** 1% MMT, **c** 4% MMT

Table 3 Langmuir constants of adsorption isotherms for indigo carmine onto hydrogels

Hydrogels	q_o	b	R_L	R^2
H-0.25-0	168.07	0.010	0.17	0.9883
H-0.25-1	173.61	0.018	0.10	0.9957
H-0.25-4	74.13	0.006	0.25	0.9874

Freundlich isotherms were obtained by different initial dye concentrations (100–500 mg/L) and 0.2 g sample for a constant time of 48 h. The adsorption isotherms data were correlated with the Freundlich equations and the Freundlich constants K_f (mg/g) and n (intensity of adsorption) were calculated from the following equations:

$$q_e = K_f \times C_e^{1/n} \tag{3}$$

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{4}$$

where q_e is the amount of dye adsorbed (mg/g) onto hydrogel. The parameters of Freundlich isotherm, K_f and n as well as the regression coefficients R^2 are given in Table 2. Linear plots of $\ln q_e$ versus $\ln C_e$ for the different initial dye concentrations illustrated that the adsorption follows the Freundlich isotherm (Fig. 7). It can be seen from Table 2, the regression coefficients R^2 were found to be as 0.975–0.995, so the Freundlich adsorption law is applicable to be adsorption of indigo carmine onto nanocomposite hydrogel. The n values between 1 and 10 indicate beneficial adsorption [29]. For the adsorption of indigo carmine onto nanocomposite hydrogels, the n values were in a range of 1.4276–1.5080 which indicate beneficial adsorption ($n > 1$).

Langmuir isotherm

The Langmuir model is probably the best known and most widely applied sorption isotherm. It may be represented as follows:

$$q_e = q_o b C_e/(1 + b C_e) \tag{5}$$

$$1/q_e = 1/q_o + 1/q_o b C_e \tag{6}$$

The Langmuir constants q_o and b are related to the adsorption capacity and the energy of adsorption, respectively. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter:

$$R_L = 1/(1 + b C_o) \tag{7}$$

where b is the Langmuir constant and C_o is the highest initial dye concentration (mg/L). 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 ($R_L = 0$) [19]. The parameters of Langmuir isotherm, q_o, b and R_L as well as the regression coefficients R^2 are given in Table 3. The R_L values calculated from above expression, lies in the range of 0–1, indicates favorable adsorption of indigo carmine on nanocomposite hydrogels (Table 3; Fig. 8).
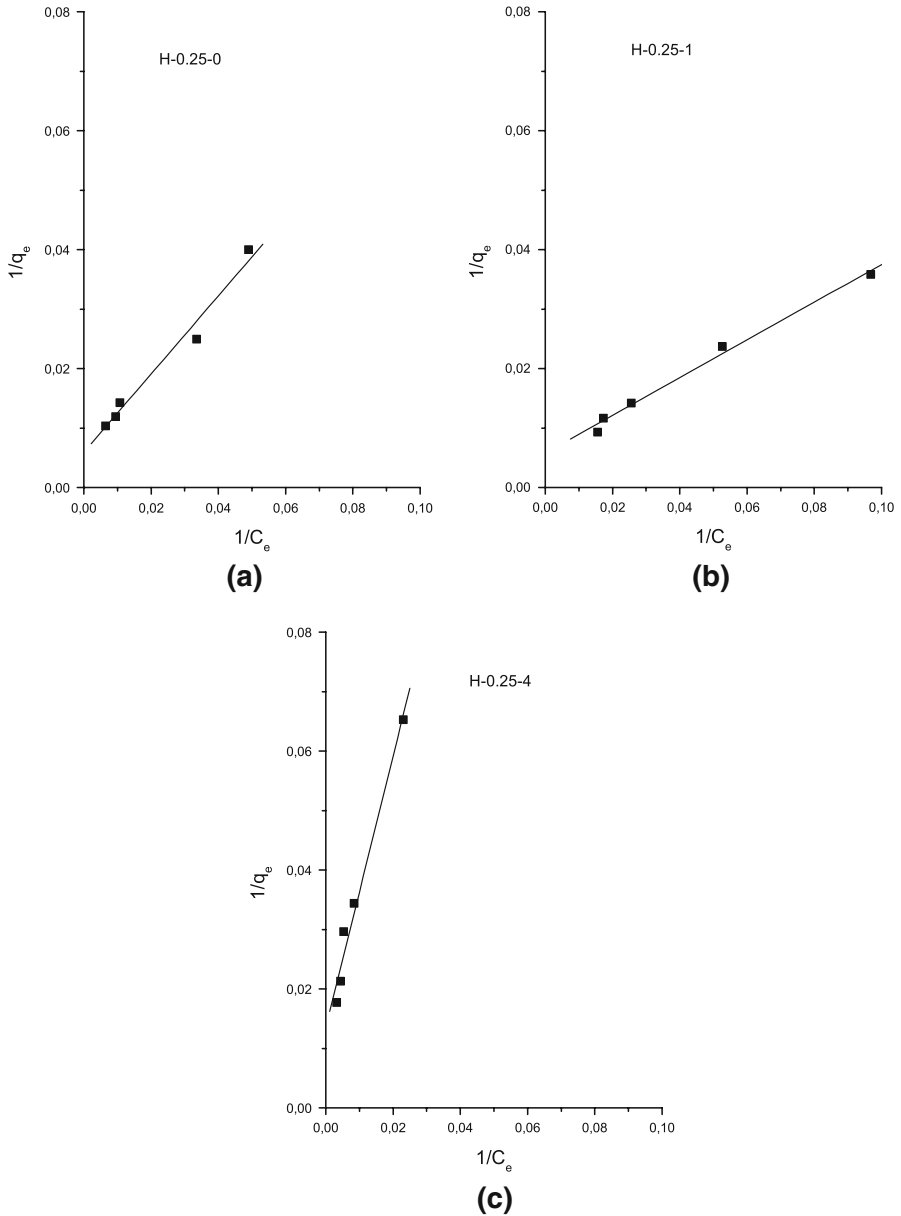
Fig. 8 Langmuir isotherms of the hydrogels. **a** 0% MMT, **b** 1% MMT, **c** 4% MMT

Conclusion

The main purpose of this work is investigation of removal of the acidic dyes from aqueous solutions using nanocomposite hydrogels. For this purpose nanocomposite hydrogels were obtained by free radical polymerization in clay suspension and used

as new adsorbents for the removal of indigo carmine from aqueous solution. The isotherm data were fitted with Freundlich and Langmuir isotherms. Their swelling properties were also investigated. The following conclusions can be drawn:

- Increasing the MMT weight ratio up to 4% causes an increment in water absorbency, which indicates that MMT can improve the ability of water absorbency but further increase of MMT causes a decrease in water absorbency.
- Increasing the MMT weight ratio up to 1% causes an increment in dye adsorption capacity but further increase of MMT causes a decrease in dye adsorption speed.
- Langmuir and Freundlich isotherm models were used to describe adsorption data. The result revealed that the adsorption of acidic dyes onto hydrogels was the best-fit both Langmuir and Freundlich isotherms.

References

1. Santiago F, Mucientes AE, Osorio M, Rivera C (2007) Preparation of composites and naocomposites based on bentonite and poly(sodium acrylate). Effect of amount of bentonite on the swelling behaviour. Eur Polym J 43:1–9
2. Ni C, Zhu XX (2004) Synthesis and swelling behavior of thermosensitive hydrogels based on N-substituted acrylamides and sodium acrylate. Eur Polym J 40:1075–1080
3. Santiago F, Mucientes AE, Osorio M, Poblete JP (2006) Synthesis and swelling behaviour (sodium acrylate)/sepiolite superabsorbent composites and nanocomposites. Polym Int 55:1–9
4. Lee WF, Jou LL (2004) Effect of the intercalation agent content of montmorillonite on the swelling behavior and drug release behavior of nanocomposite hydrogels. J Appl Polym Sci 94:74–82
5. Ma J, Xu Y, Fan B, Liang B (2007) Preparation and characterization of sodium carboxymethylcellulose/poly(N-isopropylacrylamide)/clay semi-IPN nanocomposite hydrogels. Eur Polym J 43:2221–2228
6. Lee WF, Chen YC (2005) Preparation of reactive mineral powders used for poly(sodium acrylate) composite superabsorbents. J Appl Polym Sci 97:855–861
7. Liu PS, Li L, Zhou NL, Zhang J, Wei SH, Shen J (2006) Synthesis and properties of a poly(acrylic acid)/montmorillonite superabsorbent nanocomposite. J Appl Polym Sci 102:5725–5730
8. Xia X, Yih J, D'Souza NA, Hu Z (2003) Swelling and mechanical behavior of poly(N-isopropylacrylamide)/Na-montmorillonite layered silicates composite gels. Polymer 44:3389–3393
9. Lin J, Wu J, Yang Z, Pu M (2001) Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. Macromol Rapid Commun 22:422–424
10. Paranhos CM, Soares BG, Oliveira RN, Pessan LA (2007) Poly(vinyl alcohol)/clay-based nanocomposite hydrogels: swelling behavior and characterization. Macromol Mater Eng 292:620–626
11. Orthman J, Zhu HY, Lu GQ (2003) Use of anion clay hydrotalcite to remove colored organics from aqueous solutions. Sep Purif Technol 31:53–59
12. Nasr MF, Abo El-Ola SM, Ramadan A, Hashem A (2006) A comparative study between the adsorption behavior of activated carbon fiber and modified alginate I. Basic dyes adsorption. Polym Plast Technol 45:335–340
13. Kadirvelu K, Brasquet C, Cloiree P (2000) Removal of Cu(II), Pb(II) and Ni(II) by adsorption on to activated carbon cloths. Langmuir 16:8404–8409
14. Rajeswari S, Namasivayam C, Kadirvelu K (2001) Orange peel as an adsorbent in the removal of acide violet 17(acid dye) from aqueous solution. Waste Manage 21:105–110

15. Kadirvelu K, Palanivel M, Kalpana R, Rajeswari S (2000) Activated carbon prepared from agricultural by-product for the treatment of dyeing wastewater. Bioresour Technol 74:263–265

16. Tsai WT, Chang CY, Ing CH, Chang CFJ (2004) Adsorption of acid dyes from aqueous solution on activated bleaching earth. Colloid Interf Sci 275:72–78

17. Dhodapkar R, Rao NN, Pande SP, Kaul SN (2006) Removal of basic dyes from aqueous medium using a novel polymer: Jalshakti. Bioresour Technol 97:877–885

18. Tahir SS, Rauf N (2006) Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. Chemosphere 63:1842–1848

19. Baskaralingam P, Pulikesi M, Ramamurthi V, Sivanesan S (2006) Equilibrium studies for the adsorption of acid dye onto modified hectorite. J Hazard Mater B 136:989–992

20. Bouberka Z, Kacha S, Kameche M, Elmaleh S, Derriche Z (2005) Sorption study of an acid dye from an aqueous solutions using modified clays. J Hazard Mater B 119:117–124

21. Chao L, Zhaoyang L, Aimin L, Wei L, Zhenmao J, Jinlong C, Quanxing Z (2005) Adsorption of reactive dyes onto polymeric adsorbents: effect of pore structure and surface chemistry group of adsorbent on adsorptive properties. Sep Purif Technol 44:91–96

22. Güçlü G, Keleş S (2007) Competitive removal of nickel (II), cobalt (II), and zinc (II) ions from aqueous solutions by starch-graft-acrylic acid copolymers. J Appl Polym Sci 106:2422–2426

23. Al E, Güçlü G, İyim TB, Emik S, Özgümüş S (2008) Synthesis and properties of starch-graft-acrylic acid/Na-montmorillonite superabsorbent nanocomposite hydrogels. J Appl Polym Sci 109:16–22

24. İyim TB, Acar I, Özgümüş S (2008) Removal of basic dyes from aqueous solutions with sulfonated phenol-formaldehyde resin. J Appl Polym Sci 109:2774–2780

25. Bellamy LJ (1975) The infra-red spectra of complex molecules. Chapman and Hall, London

26. Luo W, Zhang W, Chen P, Fang Y (2005) Synthesis and properties of starch grafted poly[acrylamide-co-(acrylic acid)]/montmorillonite nanosuperabsorbent via γ-ray irridation technique. J Appl Polym Sci 96:1341–1346

27. Zhang J, Wang A (2007) Study on superabsorbent composites. IX: synthesis, characterization and swelling behaviors of polyacrylamide/clay composites based on various clays. React Funct Polym 67:737–745

28. Zhang FQ, Guo ZJ, Gao H, Li YC, Ren L, Shi L, Wang LX (2005) Synthesis and properties of sepiolite/poly (acrylic acid-co-acrylamide) nanocomposites. Polym Bull 55:419–428

29. Baskaralingam P, Pulikesi M, Elango D, Ramamurthi V, Sivanesan S (2006) Adsorption of acid dye onto organobentonite. J Hazard Mater 128:138