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Synthesis and Characterization of Poly (HEMA-co-AAc)/Diatomite Hydrogel Composites: Their Application for Heavy Metal Removal from The Aqueous Solution

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ABSTRACT

Poly (2-hydroxyethyl methacrylate-co-acrylic acid)/diatomite hydrogel composite (DHC) materials were synthesized using in situ free radical addition polymerization technique. The effects of particle size and amount of diatomite were investigated on swelling properties such as the swelling degree (SD), equilibrium swelling degree (ESD) and water retention (WR) of DHC. The particle size and amount of diatomite were not affected clearly in the swelling properties. The synthesized DHC with the particle size of -45μm and the amount of 5 wt % of diatomite showed the highest swelling properties. The SD (g/g), WR (%) and ESD (%) values of hydrogel were increased up to 29.2, 45.5 and 96.7 from 1.1, 41.3 and 89.3 by adding diatomite into the structure of hydrogel, respectively. The hydrogel and DHC were characterized using Fourier transform infrared spectrometer (FTIR) and an optical microscope. Also, their thermal behavior was analyzed by differential scanning calorimeter (DSC). The FTIR spectrums showed that diatomite incorporated into the hydrogel matrix at the high amount of diatomite. The DSC results indicated that the glass transition temperature (Tg) and melting temperature (Tm) of hydrogel increased with the addition of 2 wt % diatomite. The adsorption studies were performed using the hydrogel composite including 5 wt % of diatomite.

Key Words:
Hydrogel Composite; Swelling Properties; Adsorption; Heavy Metal

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INTRODUCTION

Heavy metal pollution is a serious environmental problem and it threats human health and ecosystem due to toxic and carcinogenic effects even at low concentrations. Many methods have been employed for the removal of heavy metals from water such as chemical precipitation, ion change, membrane separation and adsorption. Among the methods, adsorption is regarded as the most reliable choice due to technically and economically applicability [1- 4].

The hydrogels having three-dimensional networks of polymer chains have attracted great interests due to their high absorb, swell and water uptake capacities [5-8]. Many polymers such as polyacrylic acid (PAAc), poly (2-hydroxyethyl methacrylate, PHEMA), polyvinyl alcohol (PVA) are used in the synthesis of hydrogels. The hydrogels based on PHEMA and PAAc have been widely investigated because of their unique properties (synthetic and biocompatible) and pH and temperature sensitivities, respectively [9-11]. Inorganic minerals such as montmorillonite, sepiolite, halloysit, hydroxyapatite, attapulgite, kaolin and zeolite etc. have been loaded into the hydrogel matrix in order to increase gel strength and stability of the pure polymeric hydrogels [12-15].

In recent years, diatomite having hydrated octahedral layered magnesium aluminum silicate minerals used in the preparation of polymer composite materials due to its low density, highly porous structure, high surface area, absorption capability, active hydroxyl groups, chemical stability and low cost [13, 16-18]. The physical properties of the hydrogels can be improved by diatomite incorporating into the hydrogel structure.

In the present study, poly (HEMA-co-AAc)/diatomite hydrogel composites were synthesized using in situ free radical addition polymerization technique at different particle sizes and the amounts of diatomite. The samples were evaluated by swelling properties and were characterized using FTIR (Fourier transform infrared spectrometer), DSC (differential scanning calorimeter) and optical microscope analyses. The hydrogel composite material with 5 wt % diatomite was used for the removal of Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} metal ions from aqueous solutions.

MATERIALS AND METHODS

Materials

In the synthesis of hydrogel, 2-hydroxyethyl methacrylate (HEMA, Merck), acrylic acid (AAc, Merck) and divinyl benzene (DVB, Merck) were used as monomer pair and cross linking, respectively. Potassium per sulfate (PPS, Sigma Aldrich) and potassium meta bi sulfide (PMBS, Sigma Aldrich) chosen as initiator and accelerator pair.

$Fe(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$, $FeCl_2.4H_2O$ and $Cd(NO_3)_2.4H_2O$ (Sigma Aldrich) metal salts were used as metal ion sources in the adsorption studies.

Natural diatomite was provided from the Karaman Mining Co., Ltd., and was used at different particle size of -45, -63, -90, -125 and -180 μm. The chemical composition of diatomite is listed in Table 1.

Table 1. Chemical composition of diatomite (%, by mass)

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
83.4	5.6	1.0	1.0	0.7

Sample Preparation

The poly (HEMA-co-AAc) hydrogels were synthesized using in situ free radical addition polymerization technique [19, 20] at room temperature and atmospheric pressure. In the synthesis of hydrogel, 80% HEMA, 20% AAc (the total monomer concentration taken as 2 mol/L) and DVB (1% molar ratio of the total monomer concentration) were dissolved in deionized water in a sealed plastic cap (4.5 x 2.5 cm; length x diameter) and then the mixture was mixed for 30 min. In another place, PPS and PMBS (0.5% molar ratio of the total monomer concentration and equal in weight) were dissolved in deionized water and then added to previously prepared monomer solution, the mixture was stirred for a further 10 min. For the formation of polymerization reaction, the mixture waited in a sealed plastic cap at room temperature for 24 h. When the polymerization reaction finished, the resulting gel product was treated with 4 M NaOH solution for 4 h in order to reach the pH value of 7. The swollen hydrogel was dehydrated several times using ethanol and dried at room temperature (Fig.1).

The DHC materials were synthesized similar to the hydrogel synthesis at different particle size (-45, -63, -90, -125 and -180 μm) and amount (2, 5, 10, and 20 wt%) of diatomite. Diatomite was added to the synthesis solution after initiator and accelerator pair.

Swelling Properties

The swelling properties of hydrogel and DHC were determined by the swelling degree (SD), equilibrium swelling degree (ESD) and water retention (WR) capacity. All the experiments were carried out using 0.2 g amount of the hydrogel.

The measurement of SD was performed by dried hydrogel which immersed in excess distilled water and kept undisturbed until it reached the equilibrium swelling [13,

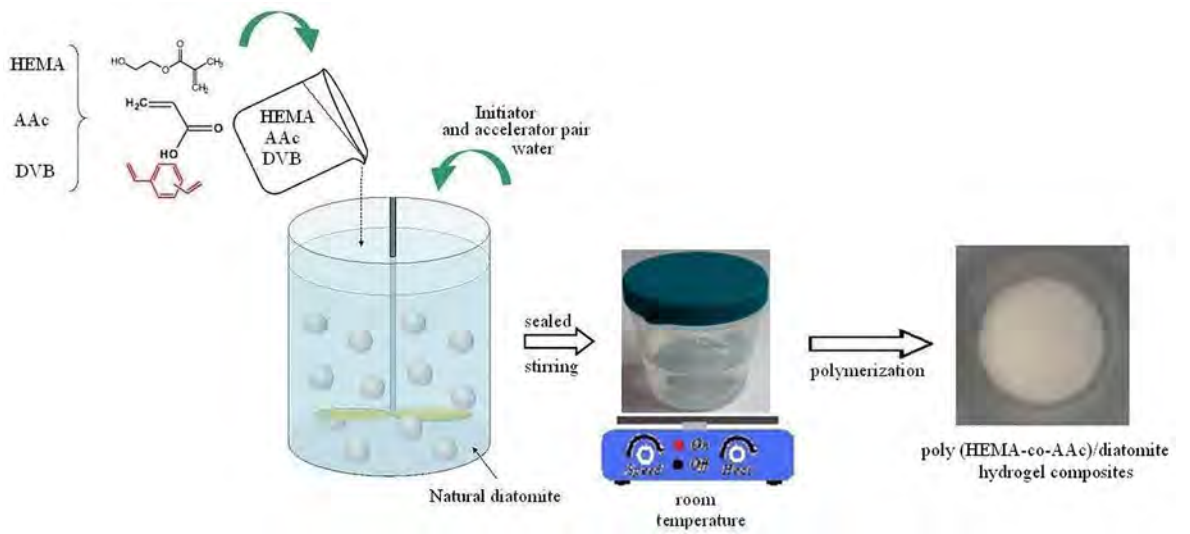

Figure 1. Schematic diagram for **the** hydrogel composite synthesis

21]. The swollen samples were dried slightly for removing the excess water of surface with paper and weighted. After weighing, the swelling capacity of hydrogel at a certain time interval was calculated according to Eq. (1).

$$SD(g/g) = (m_s - m_d)/m_d \quad (1)$$

where m_s and m_d represent the weights of swollen and dried hydrogel at room temperature, respectively.

For the equilibrium swelling degree (ESD) study, the swollen samples were dried until they reached the equilibrium at 100°C in the oven and were measured gravimetrically [15]. ESD value was calculated from Eq. (2).

$$ESD\% = [(m_s - m_{100°C})/m_s] \times 100 \quad (2)$$

where m_s and $m_{100°C}$ are the weights of swollen and dried hydrogel at 100°C, respectively.

The water retention (WR) experiments were performed after the swollen samples waited in the 0.9 wt% NaCl solution [13, 21]. The percentage of water retention was calculated using the Eq. (3).

$$WR\ \% = (m_s/m_{ds}) \times 100 \quad (3)$$

where m_s and m_{ds} are the weights of swollen hydrogel and deswollen hydrogel in 0.9 wt% NaCl solution.

Sample Characterization

Surface functional groups of the samples were investigated using a Fourier transform infrared spectrometer equipped with an ATR (Attenuated Total Reflectance) (Thermo Scientific, Nicholet IS10) in the range of 4000 to 650 cm^{-1}. The surface morphology of samples was determined by an optical microscope of 10x magnifications (Nikon eclipse LV150N, NIS-Elements 4.20). Thermal properties of the samples were performed using a differential scanning calorimetry (DSC60 Calorimeter from Shimadzu TA-60WS Instruments). The DSC thermograms of all samples were recorded in the temperature range of room temperature to 250°C at a heating rate of 10 °C/min under nitrogen atmosphere.

Adsorption Studies

The hydrogel composite having 5 wt % diatomite was used in the metal ion adsorption studies. Solutions of Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} metal ions were prepared from $Fe(NO_3)_3.9H_2O$, $FeCl_2.4H_2O$, $Cd(NO_3)_2.4H_2O$ and $Zn(NO_3)_2.6H_2O$. Adsorption experiments were performed at the metal ion concentration of 100 mg/L at natural pH and room temperature in the batch system. Firstly, approximately 0.05 g sample was added in 50 mL of metal ion solution and the mixture was stirred with a magnetic stirrer. The concentration of residual metal ions in the solution was followed by an inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Arcos) up to 24 h. The amount of metal ion adsorbed per unit mass of the hydrogel, q (mg/g) was calculated using the following Eq.(4);

$$q\ (mg/g) = [(C_o - C_e)\ V] / W \quad (4)$$

where C_o is the initial metal ion concentration (mg/L), C_e is the remaining metal ion concentration (mg/L), V is the volume of metal ion solutions (L), and W is the hydrogel mass (g) [1, 2, 4].

RESULT AND DISCUSION

The Effect of Diatomite Particle Size on the Swelling Properties of DHC

The effect of particle size of diatomite on the swelling properties of DHC was performed at particle size of -45, -63, -90, -125 and -180 µm using loading of 2 wt% diatomite which was dispersed in distilled water and added to the synthesis solution. The SD and WR properties of hydrogel composites are given in Fig. 2a and 2b, respectively.

The SD value of DHC was reached to equilibrium after 2529 min for all particle sizes. The highest values of SD, ESD and WR were obtained for particle size of -45µm as 17.2, 99.0 and 53.0, respectively (Table 2). The SD value of DHC was increased rapidly within 180 min and the water absorption capacity was increased when the particle size was reduced from -180 µm to -45 µm.

The Effect of Diatomite Amount on the Swelling Properties of DHC

The effect of the amount of diatomite was investigated using the amount of diatomite 2, 5, 10 and 20 wt% at particle size of -45µm (Fig.3). It was seen that, the SD and WR values of hydrogel composites were reached to equilibrium after 1050 min and 150 min, respectively. The synthesized hydrogel composite using diatomite loading of 5 wt% was showed the highest SD as 29.2. The highest WR value was obtained as 56.4 at the loading of

Table 2. The effect of particle size of diatomite on the swelling properties of DHC

Swelling properties	Diatomite particle size (µm)				
	-45	-63	-90	-125	-180
SD (g/g)	17.2	11.4	15.2	12.7	16.4
WR (%)	53.0	53.9	47.6	45.9	48.5
ESD (%)	99.0	98.5	98.2	97.8	98.3

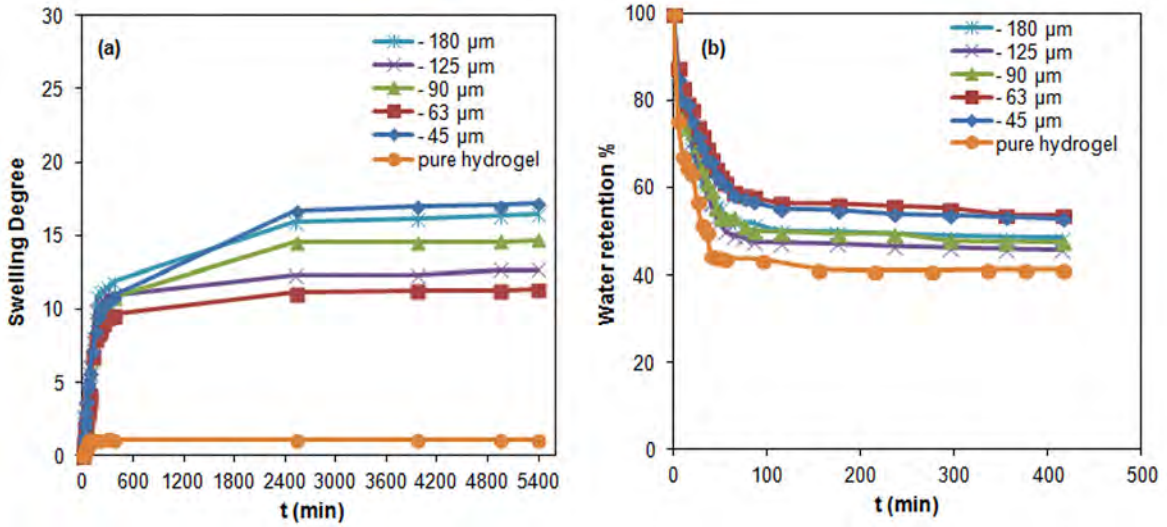

Figure 2. The effect of particle size of diatomite on (a) swelling degree and (b) water retention % of the DHC

diatomite 10 wt% (Table 3). As the hydrogel composites were compared with the pure hydrogel, it was seen that the swelling degree of composites were obtained 29 times higher than that of the pure hydrogel.

Table 3. The effect of the amount of diatomite on the swelling properties of DHC

Swelling properties	*-45µm Diatomite (wt %)*				
	0	*2*	*5*	*10*	*20*
SD (g/g)	*1.1*	*16.4*	*29.2*	*24.1*	*26.2*
WR (%)	*41.3*	*48.5*	*45.5*	*56.4*	*44.3*
ESD (%)	*89.3*	*98.3*	*96.7*	*94.9*	*97.1*

FTIR Spectrums of Samples

FTIR spectra of the pure hydrogel and DHC are given in Fig. 4. The broad band at 3000–3500 cm^{-1} is attributed to the stretching of –OH groups [21, 22-24]. The absorption bands at 2941 cm^{-1} are resulting from the C-H stretching vibrations of belong to $-CH_3$ and $-CH_2$ groups [25]. The observed peaks at 1406 cm^{-1} and 1714 cm^{-1} are due to the C-O stretching vibration of acrylic acid. The determined peak at 1406 cm^{-1} was shifted slightly to left by the increasing of amount of diatomite and the intensity of peak was decreased [12, 21]. The C=O stretching and –COOH bending of acrylic acid were observed at 1557 cm^{-1} wavenumber [15, 26].

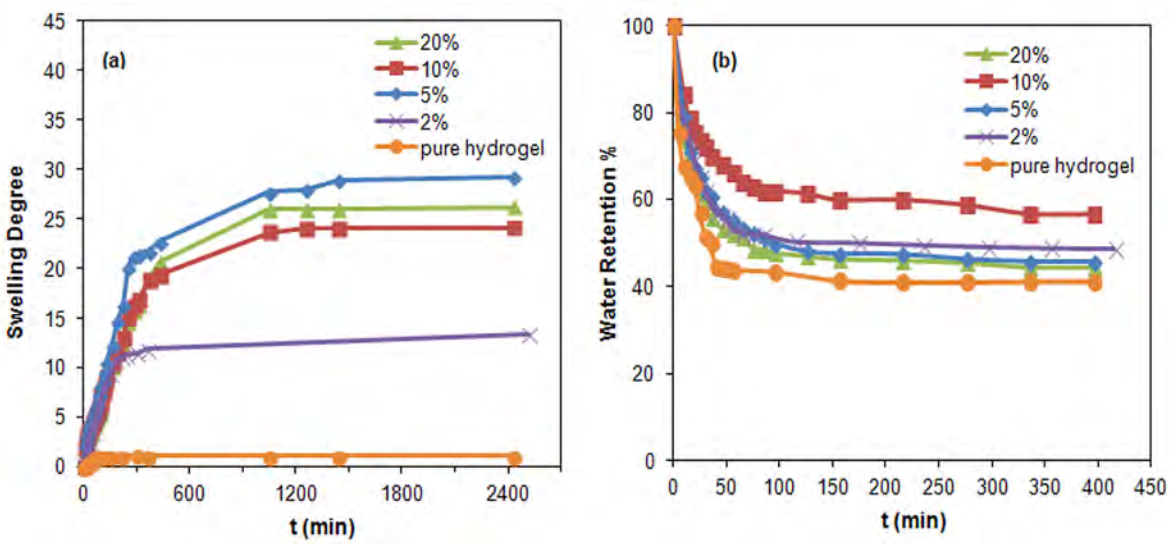

Figure 3. The effect of the amount of diatomite on (a) swelling degree and (b) water retention % of the DHC.

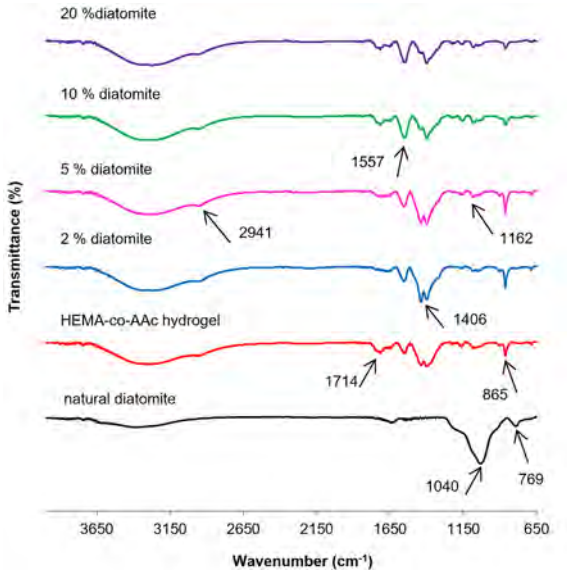

Figure 4. FTIR spectra of the natural diatomite, poly (HEMA-co-AAc) hydrogel and DHC.

Table 4. Thermal properties of the poly (HEMA-co-AAc) hydrogel and DHC.

Sample	*T_g (°C)*	*T_{m1} (°C)*	*T_{m2} (°C)*
P(HEMA-co-AAc) hydrogel	*48.89*	*110.97*	
2% diatomite	*69.79*	*124.80-135.86*	
5% diatomite	*43.59*	*74.96*	
10% diatomite	*39.57*	*91.04*	*121.31-126.55*
20% diatomite	*45.36*	*74.04*	

The absorption peak at 1162 (C–O–C) cm^{-1} was attributed to the ester group in HEMA [27]. The peaks at 769 (symmetric Si-O and Al-O) and 1040 cm^{-1} (asymmetric stretching mode of tetrahedral SiO_4, AlO_4) were resulted from silica and alumina structure of diatomite [14, 28]. These peaks disappeared in the FTIR spectra of DHC. This may be the formation of crosslinking at these bands region [22].

Analysis of Differential Scanning Calorimetry of Samples

The heating curves of the natural diatomite, poly (HEMA-co-AAc) hydrogel and DHC are presented in Fig. 5. The glass transition temperature (T_g) and melting point temperature (T_{m1} and T_{m2}) of hydrogel samples were determined from the first heating runs and results are listed in Table 4 [29]. A broad endothermic peak observed at 94.18 °C for the diatomite sample is probably due to the lost water absorbed on the diatomite structure (Fig.5) [30].

The glass transition (Tg) of P(HEMA-co-AAc) hydrogel was obtained 48.89°C. The Tg of DHC were increased from 48.89°C to 69.79°C with a loading amount of diatomite 2 wt%. The increase in the Tg arose from more regular hard domains with the incorporation of diatomite [31]. However, the Tg of the hydrogel composites with diatomite content more than 5 wt% was lowered by the addition of diatomite (Table 4). The DHC with the load of 5 and 20 wt% diatomite exhibited showed a single endothermic peak at 74.96 °C and 74.04 °C while the T_{m1} was decreased from 124.80 °C to 91.04 °C for 2 and 10 wt% diatomite loading, respectively. However,

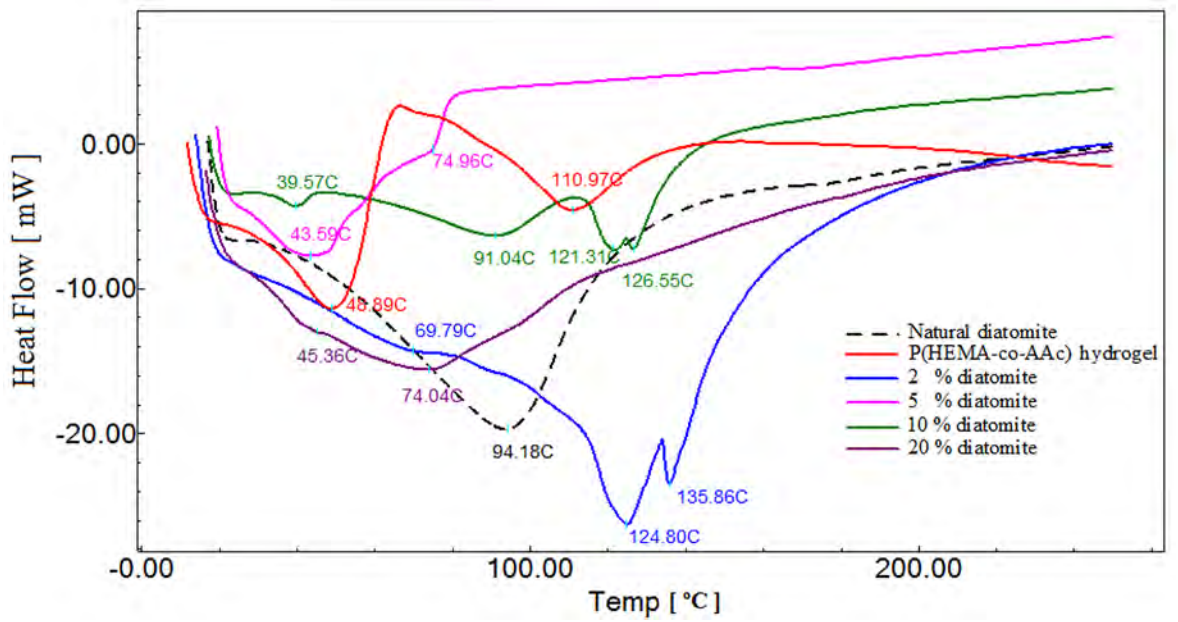

Figure 5. DSC thermograms of the natural diatomite, poly (HEMA-co-AAc) hydrogel and DHC.

the DSC curve for the DHC having content of 2 and 10 wt% diatomite showed a sharp endothermic peak at 124.80 °C (T_{m1}) and 121.31 °C (T_{m2}) followed by a small endothermic peak at 135.86 °C (T_m) and 126.55 °C (T_m), respectively. Two different endothermic melting temperature may be suggested because of recrystallization [32].

Surface Morphology of Samples

The morphology of hydrogel and DHC are given in Fig. 6. As the figure shows, macroporous structures containing interconnected crosslinked network structures were obtained. The small white particles in the optical microscope image are diatomite powders. There are many macro convex bodies in the image which are diatomite particles coated by the HEMA substrate.

Adsorption of different metal ions on the DHC

The adsorption results of Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} metal ions onto the hydrogel composite are given in Fig.7. All the metal ion adsorption experiments were done batchwise with 0.05 g hydrogel composite. As can be seen from the graph, the adsorption capacities of metal ions of Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} were found as 10.09, 3.57, 17.36 and 11.46 mg/g respectively. The shortest time to reach

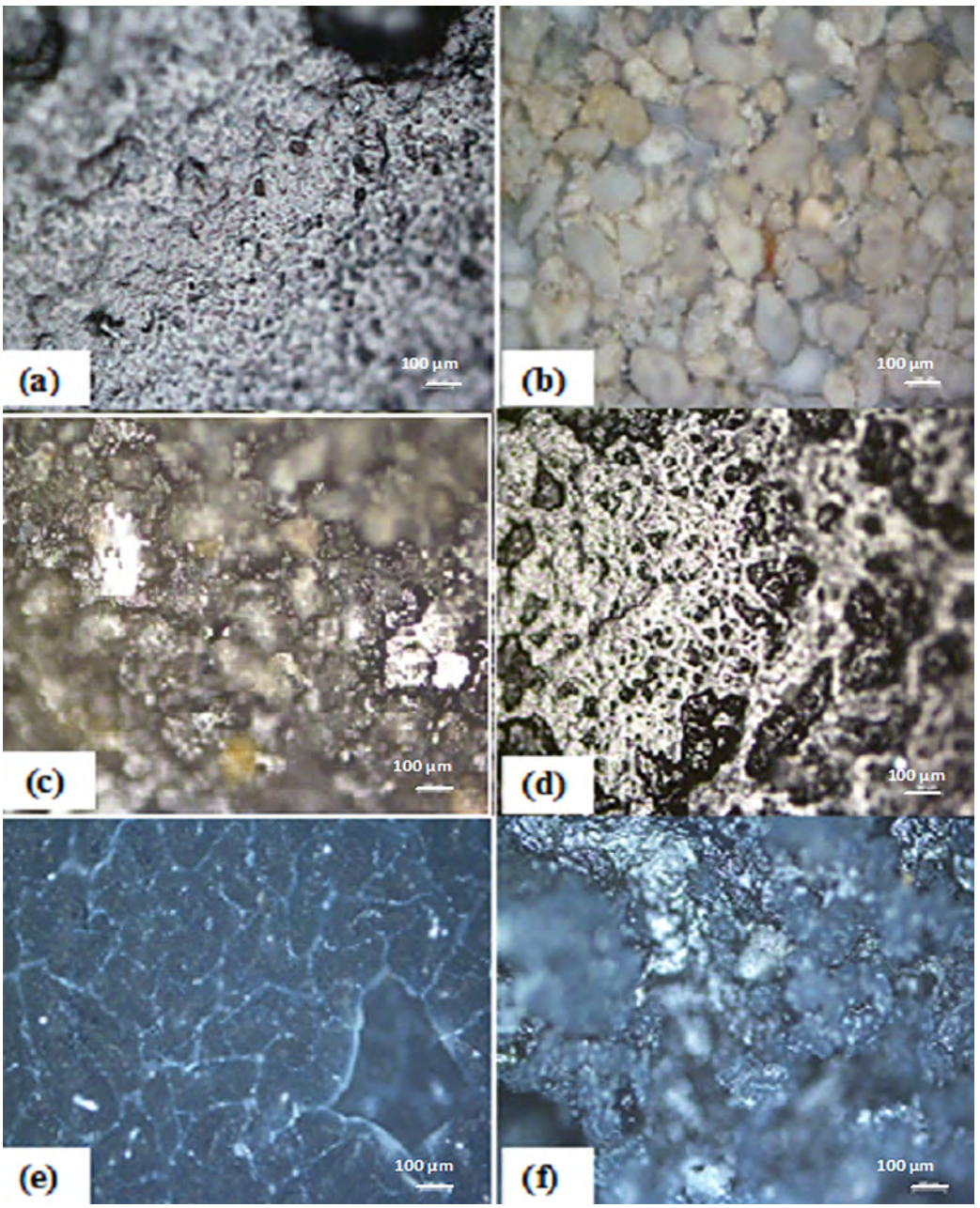

Figure 6. The images of samples (a) poly (HEMA-co-AAc) hydrogel; (b) diatomite (c-f) DHC with 2, 5, 10 and 20 wt% diatomite, respectively [Scala bar: 100 µm].

the equilibrium was achieved as 100 minutes when using Zn^{2+} solution that is quite comparable with the results reported in the literature [33-37]. These results show that the prepared hydrogel composites present great potential for Zn2+ removal having high adsorption capacity and short equilibrium time.

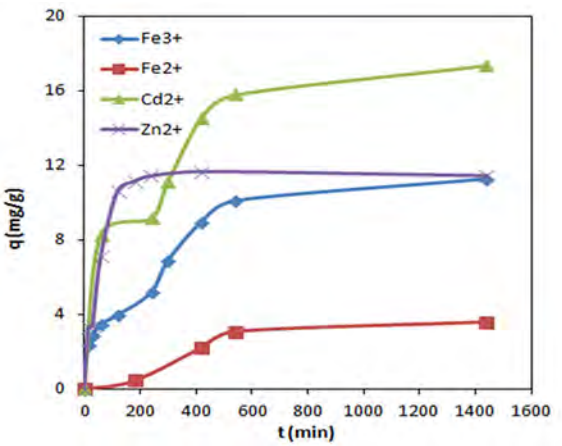

Figure 7. The adsorption capacity of Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} metal ions onto the hydrogel composite with 5 wt % diatomite.

CONCLUSION

The DHC was synthesized via in situ free radical addition polymerization technique and were characterized by FTIR, DSC and optical microscope analyses. The insertion of diatomite into the hydrogel structure was also confirmed by FTIR spectrum and optical microscope image. The maximum SD of DHC (the load of 5.0 wt% and particle size of -45μm) was found to be as 29.2 g/g while the swelling degree of the pure hydrogel was 1.1 g/g. The swelling properties of hydrogel were dramatically increased by the adding of diatomite to the hydrogel structure**.** The DSC results indicated that Tg and Tm were increased for the DHC containing 2 wt% diatomite. But, the addition more than 5 wt% of diatomite into the hydrogel structure decreased Tg and Tm. It was also determined that the hydrogel composite with 5 wt% diatomite exhibited important alternative for zinc removal.

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