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Synthesis and investigation of hydrogel nanoparticles based on natural polymer for removal of lead and copper(II) ions

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ABSTRACT

Hydrogel nanoparticles were synthesized by graft copolymerization of acrylic acid and N-isopropylacrylamide (NIPA) onto carboxymethyl cellulose (CMC) by inverse microemulsion polymerization. Ethylene glycol dimthacrylate (EGDMA) was used as crosslinker. The structure, morphology, and size of the prepared nanogels were characterized by Fourier transform infrared spectroscopy and transmission electron microscope, respectively. The prepared nanogels were used to remove copper and lead ions from aqueous solutions. The effects of pH, time, crosslinker concentrations, temperature, and initial metal ion concentration on the metal ion removal capacity were investigated.

Keywords: Nanogels; Heavy metal removal; Swelling behaviors; Stimuli pH-responsive; Carboxymethyl cellulose

1. Introduction

Hydrogels are three-dimensional hydrophilic polymers that absorb large amounts of water, swelling to form a solid gel while maintaining their physical structure without dissolving [1–5]. They have attracted considerable attention for their potential applications in water treatment [6–8].

Due to the scientific and technological progress, toxic metal contamination is a serious problem threatening human health. Heavy metal ions such as Pb(II), Cd(II), Hg(II), and Ni(II) are toxic and carcinogenic at even relatively low concentrations [9–11].

Heavy metals are generally discharged to the environments via automobile emissions, mining activities, battery industry, fossil fuels [12], metal plating, and electronic industries with diverse routes [13]. Several techniques were used in order to remove heavy metal ions from various environments. They include precipitation, adsorption, ion exchange [14], reverse osmosis, electrochemical treatments [15], hyperfiltration [16], membrane separation, evaporation, coagulation, and flotation [17].

Traditional hydrogels are highly absorbent, but maintain poor physical and mechanical properties and limited functionalities. There has been an increased effort to enhance these physical properties and functionalities by incorporating filler particles as physical cross linkers into the hydrogel network. Such filler would enhance the properties and applicability of the hydrogel [18–21].

Hydrogels based on cellulosic compounds is the most abundant one. However, the strong intermolecular and intramolecular hydrogen bonds between the

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hydroxyl groups along the chain backbone not only limit the water solubility, but also lead to the poor reactivity of cellulose [22]. In spite of the superiority of carboxymethyl cellulose (CMC) over other natural polymers, its biodegradability limits its uses considerably. To overcome this problem, grafting of copolymer on to polymeric backbone of carboxymethyl cellulose improves its applicability and also modifies its properties such as swelling and flocculation [23–25].

In the present study, some hydrogel nanoparticles were prepared and applied for copper and lead ions removal. This was achieved by graft copolymerization of acrylic acid (AA), and N-isopropylacrylamide (NIPA) along the chains of carboxymethyl cellulose substrate using inverse microemulsion method. Furthermore, the pH responsive behavior of the prepared grafted nanogels was studied at wide pH range to investigate the efficiency of these nanogels under drastic conditions and in high alkaline and high acidic media.

2. Material and method

AA, NIPA, ethylene glycol dimethacrylate (EGDMA), azobis iso butyro nitril (AIBN), and aerosol (AOT) were used as ultra pure compounds. Carboxymethyl cellulose (CMC) of commercial grade was supplied by El Nasr Pharmaceutical Chemicals Co., Egypt. Analytical grade toluene, ethanol, acetone, and diethyl acetate solvents were used. Copper nitrate and lead sulfate were used as source of cations. All the chemicals were supplied from the Fluka chemical company.

2.1. Synthesis of CMC-g-poly(NIPA-co-AAC) nanohydrogels

In a 50 ml three neck flask purged with nitrogen for 20 min (to remove oxygen before the polymerization), 0.5 g of (AOT) was added to 5 ml of hexane (oil phase). The solution was stirred at 300 rpm and purged with nitrogen for 10 min. A solution of CMC (1%) was prepared in a separate flask by slow addition of 10 g of CMC into 1,000 ml distilled water with continuous stirring to avoid flocculation. From this solution, a specific amount (namely 10, 30, 50, 70, and 100 wt/wt of the monomer, respectively) was withdrawn and added to the reaction mixture. The solution was heated to 70°C with continuous stirring. Then the desired amount of initiator (AIBN) was added and kept at 70°C for 10 min to initiate radical formation. After cooling the reaction mixture to 40°C, the equivalent weight ratios of NIPA and AA (as described in Table 1) were added drop wise during 1 h. Various amounts of EGDMA (as mentioned in Table 1) were added to the solution. The temperature rose to 70°C and maintained for 7 h to complete the reaction [26,27]. Different grafted nanohydrogel samples were obtained with varying the CMC contents and crosslinking agent concentrations as shown in Table 1. The grafted nanohydrogels were purified using selective precipitation with excess acetone and diethyl ether to disperse the micelles. After the purification process, the nanohydrogels were dispersed in ethyl acetate within 2 h with continuous stirring [27].

2.2. Confirmation of the structure of the prepared nanogels

The prepared hydrogel nanoparticles were characterized by FTIR-spectroscopy using FTIR-spectrophotometer (Mattson-infinity series bench Tab 961, Perkin Elmer Spectrum GX-USA).

2.3. Transmission electron microscope

Transmission electron micrographs, transmission electron microscope (TEM), of the colloidal nanohydrogel particles were taken using a JEM-100S transmission electron microscope (TEM, Japan). The TEM sample was prepared by mixing one dilute drop of prepared aqueous particles or latex dispersed in 5 ml acetone to become slightly turbid solution onto the copper grids and allowing it to dry. The grid was dried under IR lamp. The images of representative areas were captured at suitable magnification which clarify the morphology and the size of the nanoparticles.

2.4. Thermo-responsive behavior of the prepared nanogels

The cloud point or lower critical solution temperature (LCST) of Carboxymethyl cellulose-g-poly(NIPA-co-AAC) nanohydrogel samples was determined by differential scanning calorimetry (DSC), (TA 2920 Modulated DSC, TA instruments).

2.5. Simulated wastewater preparation

Water used throughout this work was distilled reagent grade produced by a Milli-Q SP ultra-pure-water purification system from Nihon Millipore Ltd, Tokyo. Stock solutions of Cu(II), and Pb(II) ions were prepared (1,000 mg/L). Other concentrations (10–50 mg/L) were obtained from this stock solution by serial dilution. Fresh dilutions were used for each experiment.

Table 1
Codes and composition of the prepared nanogels

Sample	CMC (wt%)	NIPA (wt%)	AAc (wt%)	EGDMA (wt%)	AIBN (wt%)
P(NIPA)	0	100	0	1	1
P(AAc)	0	0	100	1	1
CMC	100	0	0	1	1
CMC1*g*(NIPA-CO-AAc)	70	15	15	1	1
CMC2*g*(NIPA-CO-AAc)	50	25	25	1 2 3	1
CMC3*g*(NIPA-CO-AAc)	30	35	35	1	1
CMC4*g*(NIPA-CO-AAc)	10	45	45	1	1

2.6. Swelling behaviors for synthesized nanohydrogels

To determine the equilibrium swelling behavior, 100 mg freeze-dried nanogel was dispersed in 10 ml buffer solution at different pH values (2–12). The size of CMC-g-poly(NIPA-co-AAC) nanohydrogel was measured by laser particle size analyzer before and after swelling. The swelling degree was calculated from (Eq. (1)):

$$S = \frac{W - W_o}{W_o} \times 100 \quad (1)$$

where W is the weight of the sample after swelling and W_o is the initial weight of the sample.

2.7. Metal ion uptake

The uptake capability of the nanohydrogels for lead and copper ions was examined using the batch equilibrium method. An accurately weighed polymer sample (0.05 g) was then suspended in the metal solution and shaken for a specific period in atmospheric conditions. Then, the solution was filtered off and the concentration of the metal ion in the filtrate was measured by using atomic absorption spectrometer/ZEEnit 700P/Analytikjena Co./Germany.

The amount of adsorbed ions was determined by difference between the initial and final concentration of the metal.

2.8. Effect of temperature and pH on removal efficiency

The adsorption experiments were carried out at temperatures ranging from 25 to 65˚C and pH range (2–6) for solutions containing 50 mg/L (50 ppm) in order to find out the effect of these variables on absorption process. At higher pH, copper ions are precipitated in the solution. The removal efficiency was investigated after 30 min of application of the nanohydrogels on the metal ion solution.

2.9. Effect of initial metal ion concentration on removal efficiency

The equilibrium sorption was carried out at 25˚C using a concentration range of 50–250 mg/L (50–250 ppm).

3. Result and discussion

In this study, inverse microemulsion polymerization was used to synthesize CMC-g-poly(NIPA-co-AAC) nanohydrogels with various CMC and crosslinker contents as mentioned in Table 1. The structure of the prepared nanohydrogels was confirmed by the IR spectroscopy whereas their morphology was monitored by the TEM. The Fourier transform infrared spectroscopy (FTIR) spectra of NIPA, AAC, CMC, and CMC-g-p(NIPA-co-AAC) are illustrated in Fig. 1. The most important peaks and their relevance are mentioned in Table 2.

Upon comparing the FTIR spectra of NIPA, AAC, CMC, and CMC-g-p(NIPA-co-AAC) it has been observed that the spectrum of CMC-g-p(NIPA-co-AAC) shows overlapping of the band at 3,200–3,700 cm^{-1} assigned for O–H of carboxylic group with those of amines and hydroxyl groups. The characteristic absorption band of CMC at 1,000–1,166.6 cm^{-1} assigned for C–O is obviously weakened after reaction which may indicate the participation of hydroxyl of CMC in chemical reaction.

3.1. Morphology and particle size of the prepared nanohydrogels

The morphology of the prepared nanogels is spherical as shown in Fig. 2 (the provided photo is for

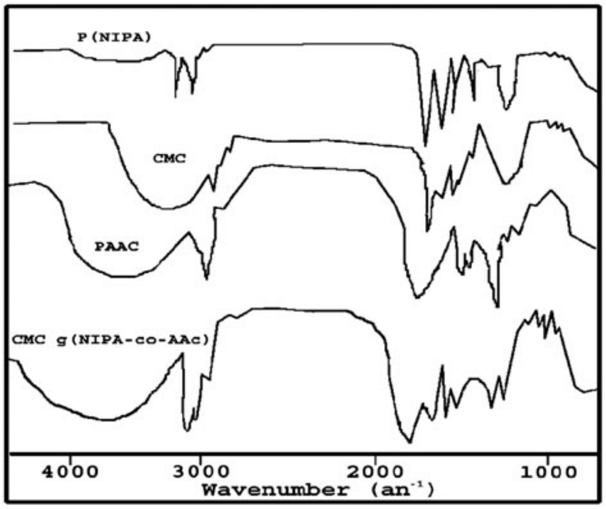

Fig. 1. FTIR spectra of NIPA, AAC, CMC, and CMC-g-p (NIPA-co-AAC).

CMC4g(NIPA-CO-AAc). The particle size of the CMC-g-p(NIPA-co-AAC) and the homo-polymers is given in Table 3. It is obvious that the particle size of the grafted polymer is much smaller than the particle size of the homo-polymers. This may be explained by that the cross-linking reduces the particle size. Gebben et al. [28] found that the intramolecularly crosslinked poly vinyl alcohol molecules are smaller in size than the initial polymer molecules and their size depends on the degree of crosslinking.

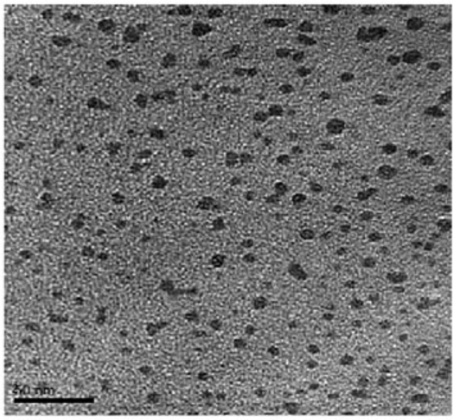

Fig. 2. TEM of CMC4g(NIPA-CO-AAc).

As the particle size depends on the degree of crosslinking, it was found that the increase in weight percent of EGDMA from 1 to 3% increases the particle size from 70 to 90 nm. This results may be explained by the fact that the more crosslinking concentration the stiffer the crosslinking network is and the smaller the cavities produced this enhance the collapse of polymer chains and made it stable in nanosize. i.e. the increase of crosslinking agent will lead to impact of polymer chains to each other, which will increase the particle sizes [29]. Furthermore, the decrease in weight percent of the CMC which represents the main backbone of the polymer chain from 70% (CMC1*g*(NIPA-CO-AAc)) to

Table 2
The most characteristic peaks of NIPA, AAC, CMC, and CMC-g-p(NIPA-co-AAC)

The compound	The most important peaks	The assignments
CMC	A strong band at 2,983 cm^{-1}	C–H stretching vibration
	A strong band at 1,166 cm^{-1}	Assigned to the ether bonds
	A strong absorption peak at 3,223 cm^{-1}	O–H stretching of the non-substituted hydroxyl groups of cellulose
	A strong absorption band at 816 cm^{-1}	C–O stretching of alcohol
PAAC	A strong band at 3,200–3,500 cm^{-1}	O–H stretching of carboxylic group
	A strong band at 2,990 cm^{-1}	C–H stretching vibration
	A strong absorption band at 1,780 cm^{-1}	C=O stretching vibration
PNIPA	The signal at 1,150 cm^{-1}	C–N of amide group
	A strong absorption band at 1,650 cm^{-1}	C=O stretching vibration
	A strong absorption band at 1,350 cm^{-1}	Stretching vibration of CH_3
	A strong absorption band at 3,300 cm^{-1}	Stretching vibration of N–H
	A strong absorption band at 2,950 cm^{-1}	Stretching vibration of C–H
CMC*g*(NIPA-*co*-AA)	A wide strong peak covering the range from 3,200 to 3,700 and overlapping other peaks	Stretching vibration of acidic O–H overlapping the O–H Alcohol and N–H amine

Table 3
The particle size and swelling degree of the prepared nanogels at 25℃

Sample	Size (nm)	Swelling degree
P(NIPA)	200	10
P(AAc)	300	5
CMC	400	4
CMC1g(NIPA-CO-AAc)	80	62
CMC2g(NIPA-CO-AAc)	70	64
	80	58
	90	50
CMC3g(NIPA-CO-AAc)	60	70
CMC4g(NIPA-CO-AAc)	50	80

10% (CMC4*g*(NIPA-CO-AAc)) decreases the particle size of the prepared nanogels from 80 to 50 nm.

3.2. Stimuli-responsive character of the prepared nanogels

3.2.1. Thermo-responsive behavior of the CMC-g-p (NIPA-co-AAC) absorbents

LCST is a key parameter of the thermally responsive polymers. It is defined as the temperature at which the polymer solution undergoes a phase transition from a soluble state (i.e. random coil form) to an insoluble state (i.e. collapsed or globule form) on elevating the temperature. LCST thermograms of nanohydrogels are shown in Fig. 3. The LCST for P (NIPA), CMC1g(NIPA-CO-AAc), and CMC4g(NIPA-CO-AAc) were 32, 43, and 48℃, respectively. It can be observed that LCST increased with increasing hydrophilicity of grafted polymer. The hydrophilicity of AAc is known to be better than that of NIPA. The more hydrophilic the moiety, the stronger hydrogen bond interaction produced in aqueous solutions. This stronger bond requires more energy to destroy and results in the increase of LCST. Thus, LCST of nanohydrogels could be adjusted by modulating wt%.

3.2.2. pH-responsive behavior of CMC-g-p(NIPA-co-AAC) absorbents

In order to investigate the removal efficiency of the prepared nanohydrogels under drastic conditions, the pH-responsive behavior was investigated in pH range 2–12 and expressed in terms of their swelling behavior. It was noted that the swelling capacity was increased with an increase in pH up to 12. Increasing the pH of the solution increases the ion dissociations of COOH and, consequently, the charges on the polymeric chains increases [30]. The pH sensitivity of CMC4-g-p(NIPA-co-AAC) as representative sample is shown in Fig. 4. It is obvious that the swelling increases with increasing pH from 2 to 12 reaching maximum swelling degree ranging from 90 to 100. Our finding agrees with those obtained by Guareño et al. [31]. They studied the effect of pH variation on the swelling of pH-sensitive polyacrylamide-grafted carboxymethyl cellulose hydrogel system composed of acrylamide and carboxymethyl cellulose. The investigated gels exhibited good pH-dependent swelling behavior as the pH of the swelling medium varied from 1.0 to 11 [31]. The minimum swelling in the acidic pH could be explained on the basis of the formation of complex structures within the gel network due to H-bonding interactions between –COOH, –OH, and –CONH– groups. These interactions resulted in the formation of a compact or tight structure which did not permit much movement of polymeric segments within the hydrogel network [32]. In the medium of pH 12, almost complete ionization of –COOH groups resulted in an extensive chain relaxation due to repulsion among similarly charged –COO– groups present along the macromolecular chains.

Moreover, this dissociation also caused an increase in ion osmotic swelling pressure. These two factors are responsible for the high degree of swelling in the high alkaline medium [33]. The maximum swelling degree was 80 obtained by CMC4-g-p(NIPA-co-AAC) which has lowest CMC where the backbone is very short that the crosslinks can be distributed uniformly on the short chain rather than on long chain which provides numerous sites for adsorption and increase its swelling degree. Furthermore, the increased swelling capacity of P(NIPA) hydrogel than the swelling of P(AAc) and CMC may be attributed to the presence of pendent chains or dangling chains in the polymeric network of P(NIPA) [34].

4. Removal of lead and copper ions from aqueous solution

The present study focused on removal of lead and copper ions from aqueous solution by synthesized CMC-g-p(NIPA-co-AAC) sorbents. The removal efficiency was calculated according to (Eq. (2)):

$$M = \frac{M_o - M_1}{M_1} \times 100 \qquad (2)$$

where M_o is the initial metal ion concentration and M_1 is the concentration of metal ion after absorption.

Upon instigating the removal efficiency of the prepared nanogels, it was found that grafting enhanced the metal ion binding capacity of the cellulosic material. The extent of enhancement depended on the

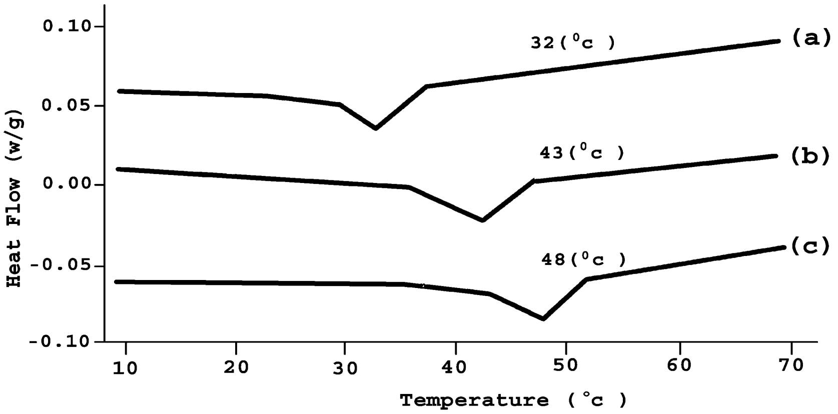

Fig. 3. DSC thermogram of (a) P(NIPA), (b) CMC1g(NIPA-CO-AAc), and (c) CMC4g(NIPA-CO-AAc).

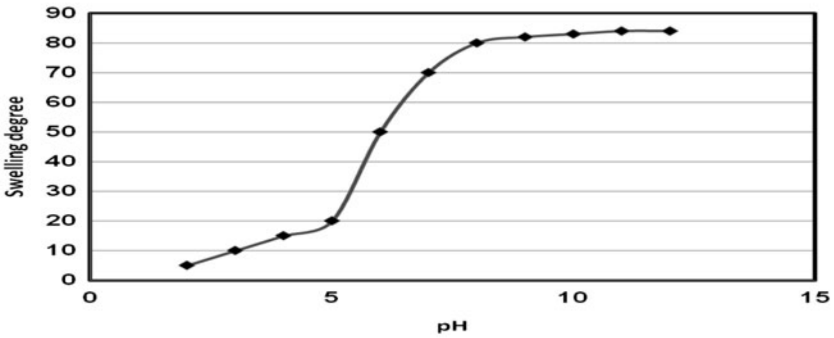

Fig. 4. Effect of pH value on swelling behavior of CMC4g(NIPA-CO-AAc) crosslinked by 1%EGDMA.

nature of metal ion, the concentration and nature of the incorporated graft polymer, pH, contact time, temperature, and initial metal ion concentrations.

4.1. Effect of crosslinker concentration on metal ion uptake

Fig. 5 shows the effect of crosslinker on metal ion uptake. It is obvious that removal efficiency of metal ion decrease by increasing crosslinker wt%. One reasonable explanation for this behavior is that denser network formation with small binding site with increasing in the crosslink density in the network leads to a decrease in the free volume and consequently lower metal binding capacity.

4.2. Effect of initial metal ion concentrations

The data in Table 4 shows the removal efficiency of the investigated nanogels for Cu(II) and Pb(II), respectively. It can be seen that the metal ion adsorption capacity increased with metal ion concentration reaching the maximum percentage metal uptake (99% for CMC4g(NIPA-CO-AAc)) at 250 ppm of Lead. This was most likely due to a greater availability of the metal ions in the vicinity of the absorbent before the absorption–desorption equilibrium was reached. In addition, a higher initial concentration provides an important driving force to overcome all mass transfer resistances of

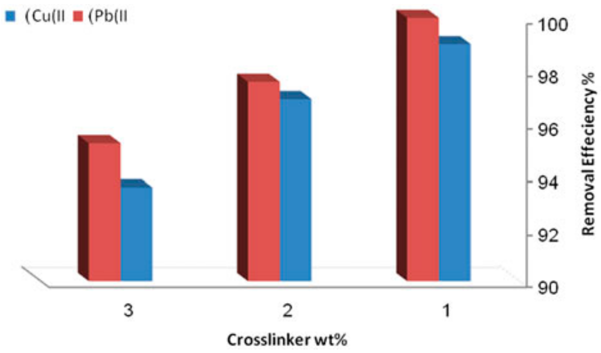

Fig. 5. Effect of crosslinker concentration on % metal ion removal efficiency at optimum conditions (40°C, pH 6 and an initial metal ion concentration 250 ppm).

the pollutant between the aqueous and solid phases, and thus increases the metal ion uptake [34].

It is obvious that the grafted CMC nanogels have high sorptivity exceed >98% under current experimental conditions. The data also reveal that the selectivity toward Pb(II) ion was slightly higher than that toward Cu(II) ion at the same conditions which shows the electivity of the prepared nanogels toward specific metal.

This selectivity increased with increasing of the carboxyl group content of polymers due to the spontaneous tendency for salt formation. The greater atomic size of lead than copper makes the salts of lead more stable than those of copper. The obtained data agree with those of the corresponding literature [35].

Furthermore, it can be seen that the unmodified CMC can bind amounts of the metal ions due to the presence of functional groups such as hydroxyl, carboxyl, etc., which provide binding sites for the metal ions [36]. The data also reveal that the carboxylic group is more efficient in binding metals than the hydroxylic group and amine group [37] thus the amounts of metal ions removed from the aqueous solutions decreased with increasing the amount of CMC substrate.

4.3. Effect of pH of the metal ion solution

The effect of pH solution on the sorption of Lead and cupper ions by grafted nanogels was investigated at pH range 2–6. This range has been chosen carefully to match the term with the industrial wastewater term (3.0–5.5 and 3.0–4.5, for Cu(II) and Pb(II) ions, respectively) [38]. Metal ion removal studies at $pH > 6$ were not conducted because of the precipitation of $Cu(OH)_2$ or $Pb(OH)_2$ from the solution. Fig. 6 shows the effect of pH on Cu ion uptake. One can see that the removal efficiency increased with the increase in pH for both Cu and Pb ion. On the other word, the higher the acidity, the lower the copper ion adsorption; this may be because of the protonation of $–NH_2$ from the acrylamide groups and the corresponding –COOH in the acrylic part under acidic conditions, generating repulsive charges between these functional groups and metal ions [39]. It is clear that the nanogels with the minimum CMC content achieved maximum absorption efficiency; this may be due to that the hydroxyl group is the least reactive group among the functional groups present in the nanogels [40].

Table 4
Effect of initial metal ion concentration on the efficiency of grafted CMC

Samples	Initial metal conc. (blank), mg/L[a]	% removal efficiency for Cu	% removal efficiency for Pb
CMC	50	18.45	20.22
	100	33.45	35.45
	150	52.44	55.67
	250	60.22	64.66
CMC1g(NIPA-CO-AAc)	50	85.51	86.71
	100	86.56	87.56
	150	89.93	90.33
	250	92.73	93.33
CMC2g(NIPA-CO-AAc)	50	88.83	89.33
	100	91.56	92.56
	150	94.77	95.77
	250	95.16	96.11
CMC3g(NIPA-CO-AAc)	50	89.12	90.12
	100	93.34	94.44
	150	95.34	96.34
	250	98.72	99.12
CMC4g(NIPA-CO-AAc)	50	91.33	92.33
	100	95.78	96.78
	150	97.66	98.56
	250	98.98	99.98

[a] 1 mg/L is equivalent to 1 ppm.

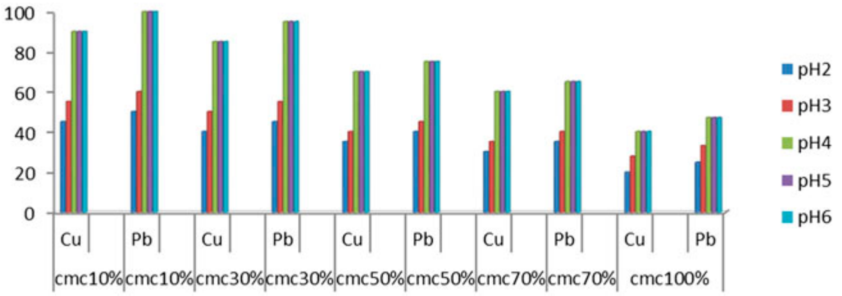

Fig. 6. Effect of pH on removal efficiency of grafted CMC.

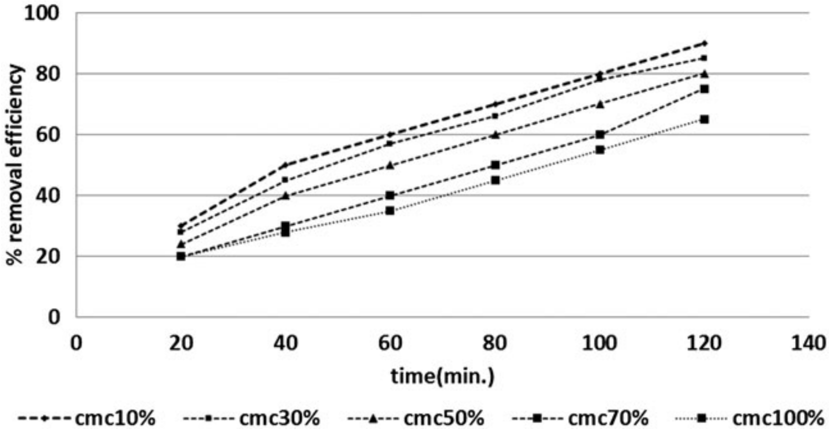

Fig. 7a. Effect of time on removal of cupper ion by using grafted CMC.

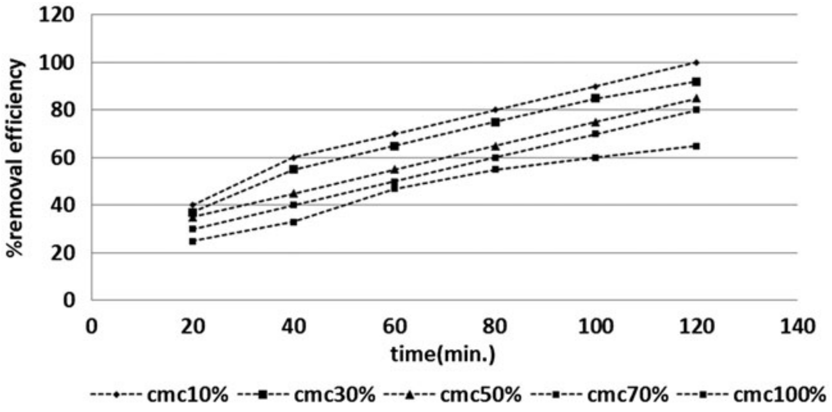

Fig. 7b. Effect of time on removal of lead ion by using grafted CMC.

4.4. Effect of contact time on ion uptake

Figs. 7a and 7b show the effect of contact time on % removal efficiency of the prepared nanogels for copper and lead ions, respectively. It was found that the removal equilibrium was reached within at 120 min for all synthesized samples. Such a fast removal rate could be attributed to the fast adsorption on the active sites of the side chains protruded from the main

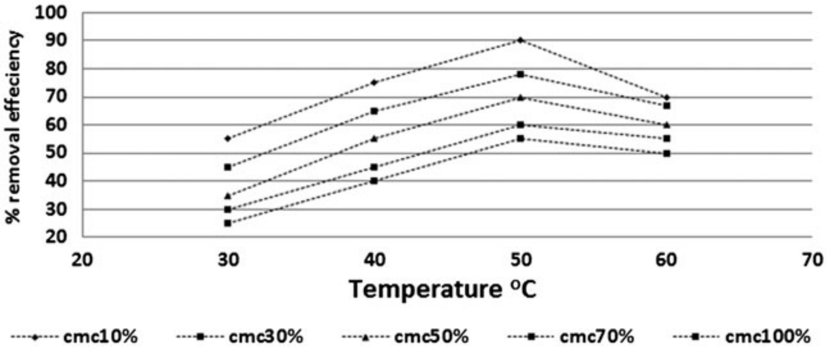

Fig. 8a. Effect of temperature on removal of Cu ions by using grafted CMC.

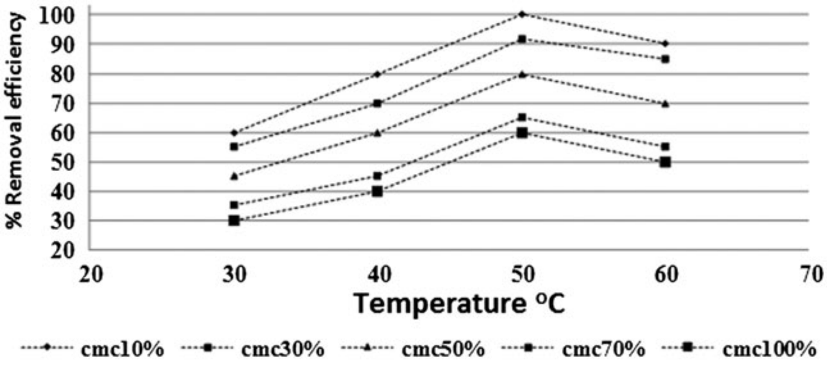

Fig. 8b. Effect of temperature on removal of Pb ions by using grafted CMC.

chains (adsorption process). This process is different from the micro-porous sorption process (absorption process). i.e. both adsorption process that occurs externally and absorption process that takes place internally cause rapid and enhanced equilibrium [41].

4.5. *Effect of temperature of the medium on ions uptake*

Furthermore, the effects of temperature on the removal of metal ions by grafted nanogels were studied at aqueous solution of pH 6 and at temperature range 20–60°C, and an initial metal ion concentration of 250 mg/L. As shown in Figs. 8a and 8b, the % removal efficiency for all the prepared nanogels increased with the increase in temperature from 30 to 50°C, revealing that the adsorption process was endothermic. But it decreased when the temperature rose from 50 to 60°C. One possible explanation was that the metal ions were well hydrated. They have to lose part of hydration sheath in order to be adsorbed. This dehydration process of metal ions needed energy [42]. At higher temperatures, the gel may shrink and releases some of the absorbed metal resulting in increasing the metal concentration in the solution again due to their thermo-responsive behavior.

5. Conclusions

The synthesized graft copolymers i.e. $\mathrm{CMC_n}$-g-p (NIPA-co-AAC) show enhanced welling capacities and pH responsive behavior. The pH sensitivity showed maximum swelling at pH 12 and minimum swelling under acidic conditions at pH 2 for all the grafted CMC which proves the readiness of these compounds to work under drastic application conditions. When the crosslinker dosage increases, the equilibrium swelling degree of the prepared nanohydrogel decreases. This makes the particles themselves very tightly. The results showed that with decreasing CMC substrate amounts, the particle size slightly decreases.

The amounts of Pd(II) and Cu(II) ions removed from the aqueous solutions by the sorbents decreased with increasing the amount of CMC substrate. The data reveals that the metal ion adsorption capacity increased with increasing metal ion concentration reaching the maximum of metal uptake, 99% for CMC4-g-(NIPA-CO-AAc), at 250 ppm lead solution. Removal efficiency for all the prepared nanogels increased with increasing temperature from 30 to 50°C. Finally, increasing number of ionic groups in the chains of networks is known to increase their swelling capacity and metal ions removal capacity.

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