New sorbent hydrogels for removal of acidic dyes and metal ions from aqueous solutions

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Summary

Poly(N-hydroxymethylacrylamide), PHMA, hydrogels were prepared by using N-hydroxymethylacrylamide, HMA, monomer and polyethyleneglycol(400)diacrylate as a crosslinking agent in aqueous medium and then amine groups were incorporated onto PHMA hydrogels by amination reaction with different diamines. The obtained hydrogels were characterized by determination of amine value, hydroxymethyl group content and FTIR spectra. The amine value of hydrogels changed from 2.23 to 4.64 mmol/g by depending on the amine compounds used in amination reaction. Their swelling degree increased at acidic pH values and they showed pH dependent swelling behaviour. They were used as sorbent for removal of indigo carmine and Cu(II) ion, as a model dye molecule and metal ion, respectively, from aqueous solutions. The adsorption properties of the hydrogels were investigated by depending on pH, time and initial indigo carmine or Cu(II) ion concentration. It was seen that the amine group incorporated hydrogels have quite high adsorption rate and adsorption capacity, and their adsorption capacities changed with pH of the solution. Langmuir isotherm model was the best fit for adsorption of both indigo carmine and Cu (II) ion.

Keywords

N-hydroxymethylacrylamide, hydrogel, amination, dye adsorption, metal ion removal

Introduction

Since the environmental pollution is increasing day-by-day due to the increase in industrialization and urbanization, the need to reduce the pollution particularly in wastewater streams of hydrometallurgical and other industries is important. Among the environmental pollutions, heavy metal ions and dyes have gained relatively more significance due to their toxicity. Heavy metal ions in wastewater come from battery manufacturing, automobile emissions, mining activities and alloy industries [1]. Also, many industries such as plastics, paper, textile and cosmetics use dyes in order to colour their products. Moreover, the colour they impart is very desirable to the water consumers. Therefore, colour removal from wastewater is a major environmental

problem. Several treatment techniques such as precipitation, filtration and neutralization have been developed in recent years, but adsorption is generally preferred for the removal of metal ions and dyes from wastewater because of its high efficiency, easy handling and availability of different adsorbents [2].

Removal of heavy metal ions and dyes by using polymers having different functional groups would be of great importance in environmental applications [3,4] due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes. For this purpose, different polymeric adsorbents especially hydrogels having different functional groups, which have complexing ability with metal ion and dyes, have been investigated in the preceding literature [5-7]. Hydrogels can be defined as three-dimensional networks of polymers that are water-swollen. According to the type of the functional group in polymer matrix, the properties of hydrogels can be changed with temperature, pH, solvent composition and salt concentration [8,9]. The hydrogels having functional groups can be obtained by copolymerization of the monomers with different functional groups or post-modification of polymerized products. The second option is generally preferred to prepare materials, which are difficult to obtain by direct polymerization of the corresponding monomers.

The aim of this work is to prepare and characterize new hydrogels having functional groups that can be complex with metal ions and dyes and investigate their adsorption properties. To obtain amine group containing hydrogels the amination reaction was applied by using different diamines. Amines are very hazardous compounds [10] and the products obtained by the synthesis must not contain any free amine remaining at the end of the synthesis. In this work, the poly(N-hydroxymethylacrylamide) (PHMA) hydrogels were prepared by using N-hydroxymethylacrylamide (HMA) monomer in the presence of a crosslinking agent (polyethyleneglycol(400)diacrylate-(PEG(400)DA)) and aminofunctionalized by amination reaction by using different diamines; ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), for the first time. The obtained hydrogels were characterized by the determination of amine value, hydroxymethyl group content, swelling degree and FTIR spectra. Also, they were used as new sorbents for the removal of indigo carmine and Cu(II) ion from aqueous solution and the effect of adsorption parameters such as pH, time and initial concentration on their adsorption properties was investigated.

Experimental

Materials and instruments

HMA obtained from Aldrich Chemicals was used without purification in polymerization reactions. EDA, DETA, TETA, ammonium persulfate and N,N,N,N tetra methyl ethylenediamine (TEMED) were Merck "for synthesis". PEG(400)DA having molecular weight of 508 g/mole was kindly supplied by Sartomer Chemicals (SR-344). All of the other reagents used were extra pure chemicals. Indigo carmine (disodium salt of 3,3-dioxobi-indolin-2,2-ylidine-5,5-disulfonate) obtained from Merck (the purity is >80 and λ_{max} is 608 nm) was used without further purification. The structure of indigo carmine was given in Figure 1. Cu(II) ion solutions used in adsorption experiments were prepared by dissolving Cu(CH3COO)2 of Merck.

The FTIR spectra of dried polymers were obtained by Digilab Spectrometer, Excalibur- FTS 3000 MX model (Digilab, USA) in the range from 4000 to 400 cm⁻¹. In order to achieve a 2 cm⁻¹ resolution, 64 scans were made in each spectrum. Spectrophotometric measurements were carried out using Carry 1 E (Varian) UV/Vis Spectrophotometer having a scan rate of 600 nm/min and a spectral resolution of 1 nm. Cu(II) ion determinations were carried out by using Orion 720A (Thermo Elc. Corp., USA) plus ion-meter.

Figure 1. Chemical structure of indigo carmine.

Preparation of hydrogels

PHMA hydrogel was prepared by free radical solution polymerization of HMA monomer in the presence of PEG(400)DA as a crosslinking agent. The preparation conditions and materials used are written in Table 1 as a footnote. Prior to the polymerization, dried nitrogen was bubbled into the HMA/PEG(400)DA/water mixture for 10 min to remove the oxygen dissolved in the reaction mixture. Amonium persulfate and TEMED were added into the mixture as an initiator and activator, respectively. The pH of this solution was adjusted to 6.0 with diluted NaOH. The reaction mixture was sealed and left at 50°C, for 2 h.

For the preparation of amine group incorporated PHMA hydrogels, the resulting gel obtained from polymerization reaction was recovered, cut into pieces and placed into round-bottom flask, and then amine compound was added with stirring to provide R=1:4 (R= HMA/amine mol ratio). Different diamines (EDA, DETA and TETA) were used in amination reactions. The mixture was heated to 90°C and kept at this temperature for 4 h. Then, it was poured into the excess methanol and filtered, followed by washing with water until free from amine, as determined by colour reaction with ninhydrine. Polymers were washed with methanol again and dried to constant weight under vacuum at ambient temperature, to give yellowish fine powders.

Characterization

Determination of amine value (AV): The polymers (50 mg) were equilibrated with HCl (20 ml, 0.1 N) by stirring 24 h in a sealed flask, followed by filtration and washing the residue with distilled water to remove unreacted HCl and titration of filtrate with NaOH (0.1 N) in the presence of phenolphthalein indicator. The results are given as mmol/g dry polymer.

Determination of hydroxymethyl group (HMG) content: The polymers (50 mg) were kept in NaOH solution (10 ml, 2N) for 48 h in a sealed flask. Then, the pH was

adjusted to 4.0 in the presence of bromophenol blue indicator and hydroxylamine hydrochloride (10 ml, 10% aqueous solution) was added and after 5 min the mixture was titrated with KOH (N/3)[11]. The results are given as mmol/g dry polymer.

Determination of unreacted monomers: After polymerization reaction of HMA, the PHMA hydrogel was purified by extracting-disintegrating with blender in methanol, followed by drying to constant weight in vacuum at ambient temperature. The total amounts of unreacted monomers were determined in the extraction solvent by the bromate-bromide method [12].

Determination of swelling degree: The polymers were swollen in distilled water and buffer solutions with different pH values of 2.2, 5.3, 6.5, 7.0 and 8.0 at ambient temperature. KHphatalate/HCl, KHphatalate/NaOH and K₂HPO₄/NaOH buffer solutions were used for the desired pH values. Ionic strength of all solutions was adjusted to 0.03 M. The swelling degree of polymers was determined gravimetrically at regular time intervals and calculated from the following expression:

$$S(g water/g polymer) = (W_s-W_d)/W_d$$
 (1)

where W_s and W_d are the weights of swollen and dry polymer, respectively. The amount of water adsorbed by polymers under equilibrium conditions is 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 indigo carmine solution (25 ml) and Cu(II) ion solution (25 ml) with the concentrations of 1000 mg/l and 500 mg/l, respectively, for the determination of adsorption capacity. The amount of residual dye in the solution was determined spectrophotometrically after 24h. Also, the amount of residual Cu(II) ion in solution was determined by using ion-meter. For the determination of changes in adsorption capacities by the time, polymers were stirred with the dye and Cu(II) ion solution under the experimental conditions described above and the residual dye and Cu(II) ion concentrations were determined at regular time intervals. Also the adsorption capacity of polymers were determined in the pH range of 3-8 and 3-5.5 for indigo carmine and Cu(II) ion adsorption, respectively. The pH of initial solutions was adjusted by using dilute HCl or NaOH solutions. Furthermore, adsorption isotherms were obtained by stirring H-TETA polymer, prepared by using TETA, in the dye and Cu(II) ion solutions with various initial concentrations for a period of time equal to the respective equilibrium times. The residual concentrations of dye and Cu(II) ion were determined as described above. All of the experiments were carried out triplicate. The adsorption capacity, Q (mg dye or Cu(II) ion per g polymer), of polymers was calculated by using the following expression:

$$Q(mg/g) = (C_i-C_e) V/m$$
 (2)

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

Results and Discussion

Properties of hydrogels

PHMA was obtained by radical polymerization of HMA monomer in aqueous solution in the presence of PEG(400)DA as a crosslinking agent. The unreacted monomer content analysis showed that PHMA was obtained with a yield of 98.3% and HMG content was found as 8.94 mmol/g (Table 1). This value is low by considering its theoretical value (9.52 mmol/g). It is supposed that such slight difference is coming from the some of the hydroxymethyl groups reacting with each other to form ether linkages under current experimental conditions. According to the literature [13,14], the crosslinking reactions between methylol groups are promoted by the acidic environment (pH 2-3) and could be described by the following mechanism [15]:

-CO-NH-CH₂OH
$$\longrightarrow$$
 -CO-NH-CH₂-O-CH₂-NH-CO- $+$ H₂O heat
-CO-NH-CH₂-O-CH₂-NH-CO- \longrightarrow HCHO + CO-NH-CH₂-NH-CO

In the current experimental conditions, it was observed that studies at pH value of 6 prevented this crosslinking reactions to some extent.

The amination reaction was applied to PHMA hydrogel by using different diamines to obtain modified hydrogels having primary and secondary amine groups. EDA, DETA and TETA were used in these reactions. The amination reaction of hydroxymethylol groups with diamine is represented in Scheme 1. When diamines are used for the amination reaction, the possibility of the reaction with both amino groups of a diamine molecule may cause to the additional crosslinking reaction. To prevent this, the excess amount of diamine was used in amination reactions.

PHMA Hydrogel Diamine compounds Aminofunctionalized hydrogel Scheme 1. The amination reaction of poly(N-hydroxymethylacrylamide) hydrogel with diamine compounds.

The FTIR spectra of PHMA and its modification product, H-EDA, obtained by using EDA in amination reaction, are shown in Figure 2. As can be seen from this figure, the characteristic absorption peaks originating from C=O group at 1655 cm⁻¹ and hydroxymethylol group at 1023 cm⁻¹ of N-hydroxymethyl acrylamide units are present. In spectrum of H-EDA, it was observed that the intensity of the peak due to the hydroxymethyl group decreased greatly and also the new peaks between 550 and 870 cm⁻¹ due to the amino groups were present. These confirm the amination reaction of hydroxymethyl groups with the amines.

The properties of the amine group incorporated PHMA hydrogels were given in Table 1. The amine value of these hydrogels changed between the values of 2.23-4.64 mmol/g depending on the amine compound used in the amination reaction and the highest amine value was obtained for H-TETA polymer (4.64 mmol/g) prepared by

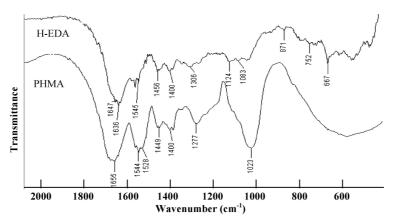


Figure 2. The FT-IR spectrum of PHMA and amine group incorporated hydrogels.

using TETA in the reaction. In Table 1, although PHMA has lower EDS value (11.31 g water/g), the modified polymers have higher swelling abilities in distilled water and their EDS values changed between the values of 23.09-37.72 g water/g. The amine groups incorporated into the polymer matrix by modification reaction increased their swelling degree. Also, the swelling isotherms of PHMA and amine group incorporated PHMA hydrogels in distilled water at ambient temperature are depicted in Figure 3. It is clearly seen from the figure that the swelling degree of modified polymers are higher than that of the PHMA. Furthermore, the swelling degree of the hydrogels almost reaches to the equilibrium within 60 min. In Figure 4, the effect of pH value of the external solution on the swelling ability of the hydrogels is given. The EDS value of PHMA did not change by the pH of the external solution, but of modified hydrogels changed. It is seen from the figure that, the EDS of all modified hydrogels are higher at the lower pH value of the external solutions and these EDS values decreased with increasing the pH value of the solution. This is attributed to the protonation of the amino groups on the polymer chain at low pH.

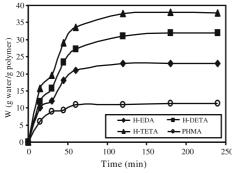


Figure 3. Swelling isotherms of PHMA and amine group incorporated PHMA hydrogels in distilled water at ambient temperature.

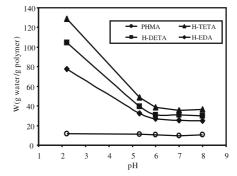


Figure 4. Effect of pH on the swelling degree of the hydrogels.

Adsorption studies

The indigo carmine and Cu(II) ion were selected as model compounds to investigate the use of the amine group incorporated PHMA hydrogels for the removal of acidic dyes and heavy metal ions. Adsorption properties of these hydrogels were evaluated by depending on different adsorption conditions such as pH value of the initial solutions, initial dye and metal ion concentration and also hydrogel properties. The indigo carmine and Cu(II) ion adsorption capacities of polymers are given in Table 1.

Table 1. The properties of PHMA and amine group incorporated PHMA hydrogels.

	Amine	AV	HMG	EDS b)	Q ^{c)} (n	ng/g)
Polymer	compound used for amination reaction	(mmol/g)	(mmol/g)	(g water/g polymer)	Indigo carmine	Cu(II)
PHMA ^{a)}	-	-	8.94	11.31±0.1	-	-
H-EDA	EDA	2.23	1.24	23.09±0.2	149.7	113.7
H-DETA	DETA	3.51	0.15	32.82±0.3	167.7	208.3
H-TETA	TETA	4.64	0.10	37.72±0.3	237.6	274.0

AV: Amine value, HMG: Hydroxymethyl group content, EDS: Equilibrium degree of swelling. a : HMA (4.66 ml), PEG(400)DA(0.25 ml), water(25 ml), (NH₄)S₂O₈(0.05 g), TEMED (0.125 ml, 25% aqueous solution) were used in polymerization reaction. Reaction temp:50°C, reaction time: 2h

These values were obtained by using dye and metal ion solutions with the concentration values of 1000 mg/l and 500 mg/l, respectively. The experiments were carried out at 25° C, for 24 h under the natural pH value of the solutions (pH of 6 for indigo carmine solution and 5.5 for Cu (II) ion solution).

PHMA did not adsorb indigo carmine effectively as determined in the preliminary experiments, but the functionalized hydrogels adsorbed quite high amount of dye (see Table 1). The indigo carmine adsorption capacity of functionalized hydrogels varied between 149.7 and 237.6 mg/g. Although their amine values were quite high (2.23-4.64 mmol/g), their capacities were found to be lower than the expected ones from their amine values. It is supposed that the amine groups in polymer surfaces complexed with the acidic species (especially SO₃Na groups) of dye molecule, so the diffusion of the big dye molecules into the polymer matrix is prevented and amine groups placed inner part of the hydrogel network can not complex with these species. Also, the lower swelling degree of hydrogels at pH value of 6 affects their adsorption capacities. In literature, various organic and inorganic based adsorbents such as ash, silica gel, zeolite, lignin, chitin, chitosan and clay materials [16-18] have been studied for the removal of different types of dye from aqueous solutions. Prado et al [19]

b: EDS was determined in distilled water.

 $^{^{\}rm c}$: Adsorption conditions: 1000 mg/l initial indigo carmine and 500 mg/l initial Cu(II) ion solutions, 25°C, 24 h,160 rpm.

reported that the maximum amount of indigo carmine adsorbed was 1.24x10⁻⁵ and 1.54x10⁻⁴ mol/g by chitin and chitosan, respectively. Also, Otero et al. [20] stated that the indigo carmine adsorption capacities of activated carbons based on sewage sludge were 30.82 and 60.04 mg/g. Sahiner et al. [21] studied the removal of indigo carmine from aqueous solutions by N-vinyl-2-pyrollidone/acrylonitrile hydrogels having adsorption capacity of 2.0 mg/g. It is clearly seen that these functionalized hydrogels have quite high adsorption capacity compared with those given in literature.

The Cu(II) ion adsorption capacity of amine group incorporated hydrogels varied between 113.7 and 274.0 mg/g as it is seen from Table 1. Although the PHMA was not effective in removal of Cu(II) ion, the modified gels have very high Cu(II) ion adsorption capacity. H-TETA polymer having the higher amount of secondary amine groups compared with EDA has the highest Cu(II) ion adsorption capacity (274.0 mg/g, 4.31 mmol/g). This shows that not only primary amine groups but also the secondary amine groups contributed to the formation of Cu-amine complexes.

pH effect on the adsorption capacity

To evaluate the effect of the pH on the adsorption capacity of polymers, the adsorption experiments were carried out in solutions having different pH values. The indigo carmine adsorption was investigated in solutions having pH values between 3-8. The Cu (II) adsorption experiments were limited between 3 and 5.5 because the precipitation of cupric hydroxide was observed at the pH value over 6. In Figure 5(a and b), the pH effects on the indigo carmine and Cu(II) ion adsorption capacity of modified polymers are seen. The indigo carmine adsorption capacity of polymers increased by decreasing of pH value of the solution and it was the highest at pH value of 3. (760,0 mg/g for H-TETA polymer). This phenomenon can be explained by the increasing of the electrostatic effects between protonated amine groups and anionic species of indigo carmine. The ionization degree of functional groups in polymer chain decreased at higher pH values. Also, it is supposed that the higher swelling degree of polymer at acidic pH was effective in the diffusion of the dye into the polymer matrix and increased their adsorption capacity.

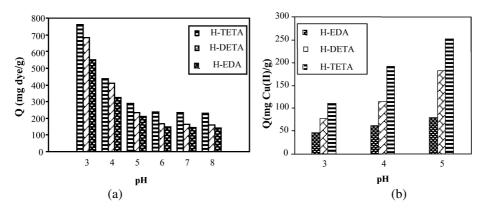


Figure 5. Effect of pH on the adsorption capacity of polymers. a: Indigo carmine, b: Cu(II) ion. Adsorption conditions: 1000 mg/l indigo carmine and 500 mg/l Cu(II) ion initial concentration, 25°C, 160 rpm, 2 h.

The Cu(II) ion adsorption capacity of amine group incorporated PHMA hydrogels increased by increasing of pH as seen in Figure 5b. At low pH, the protonization of amino groups prevent the complexation of Cu(II) ion with the polymer. This protonization decreased at higher pH and Cu(II) ions interact with unprotonated amine groups by chelating [22].

Adsorption rate

Figure 6 (a) and (b) shows the change in the amount of adsorbed indigo carmine and Cu(II) ion by functionalized PHMA hydrogels as a function of time. Adsorption conditions are given in the figure legend. The initial slopes of these curves represent the adsorption rates. High adsorption rates are observed at the beginning (approximately within 10 min) and then plateau values are gradually reached within 30 min. This high initial rate suggests that the adsorption occurs mainly on the polymer surface. The adsorption behaviour of dyes and metal ions is directly related to some experimental factors such as pH of the solution, characteristics of the adsorbent, dimensions of the dye molecule and metal ion. Various polymeric sorbents having different properties adsorbed different dyes from aqueous solutions within range of 2h-5 day [20,21,23,24]. Furthermore, different sorbents adsorbed indigo carmine within different times (165 min-5 days) [20,21,23]. Also, several polymeric sorbents have adsorbed different metal ions from solutions with different adsorption rates changing between 0.5h to 24 h [25-27]. It is possible to say that the adsorption rate of the amine group incorporated PHMA hydrogels for both indigo carmine and Cu(II) ion are very fast compared with those obtained in the previous works [25,26]. These higher adsorption rates and higher capacity of functionalized PHMA hydrogels and reaching the equilibrium condition in short times will provide many advantages in using of these gels for dye and metal ion adsorption process.

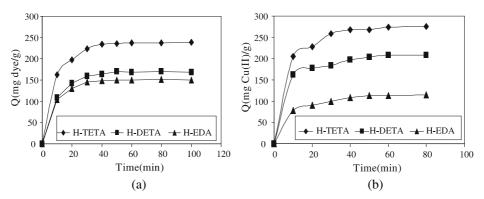


Figure 6. Plots of adsorbed indigo carmine(a) and Cu(II) ion(b) amount by functionalized hydrogels versus time. Adsorption conditions: 1000 mg/l indigo carmine and 500 mg/l Cu(II) ion initial concentration, 25°C, 160 rpm.

Adsorption isotherms

It is necessary to establish the most appropriate correlations for the equilibrium data in the design of adsorption systems. Equilibrium adsorption capacity of an adsorbent is dependent upon the concentration of the adsorbed molecule, together with the other process parameters. In order to investigate the initial concentration effect on the adsorption capacity, H-TETA polymer was chosen as a model polymer and adsorption experiments were carried out at initial concentrations between 40 and 1000 ppm and 10-500 ppm for indigo carmine and Cu(II) ion, respectively. The adsorption experiments were carried out at 25°C for 2 h (Fig. 7). The results obtained from the adsorption isotherm were evaluated by using Langmuir and Freundlich adsorption models.

Langmuir isotherm model:
$$C_e/q_e = 1/(Q_o.b) + (1/Q_o)C_e$$
 (3)

In Eq. (3), q_e (mg/g) is the amount of the adsorbed dye or metal ion per unit weight of adsorbent at the final equilibrium concentration (C_e , mg/l). Q_o (mg/g) and b (l/mg) are the Langmuir constants related to the capacity and energy of adsorption, respectively. From a plot of C_e / q_e vs C_e , Q_o and b can be determined from the slope and intercept. In this model, it is assumed that a dye molecule or metal ion monolayer is formed on a relatively regular polymer surface by complex formation with the amino groups of the polymer matrix [28] and the adsorbed amount of molecules depends on the equilibrium concentration of adsorbed molecules.

Langmuir isotherm constants of indigo carmine-H-TETA and Cu(II) ion-H-TETA polymer systems are given in Table 2 and Figure 8 represents the Langmuir isotherms of these systems. It is seen in Table 2 that the Langmuir isotherm model gave the best results for indigo carmine and Cu(II) ion adsorption by the H-TETA polymer. Regression coefficients were 0.9912 and 0.9596 for indigo carmine and Cu(II) ion, respectively. Also, the maximum adsorption capacities calculated from the equation are close to the experimental results (Tables 1 and 2). When the Freundlich isotherm model was applied to these systems, a good fit was not obtained (for indigo carmine-H-TETA system; R²=0.5981 and for Cu(II) ion-H-TETA system; R²=0.8961).

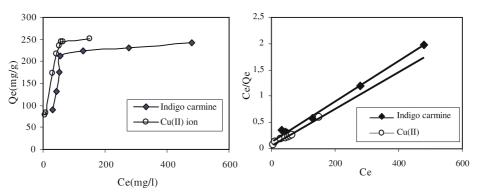


Figure 7. Equilibrium adsorption of indigo carmine (a) and Cu(II) ion (b) on the H-TETA polymer.

Figure 8. Langmuir isotherms of Indigo carmine and Cu(II) ion – H-TETA system.

Table 2. Constants of Langmuir isotherm model for Indigo carmine and Cu(II) ion adsorption by H-TETA polymer.

Langmuir constants						
	Q_0	b	R^2			
Indigo carmine	256.4	0.031	0.9912			
Cu(II) ion	243.9	0.121	0.9596			

Conclusion

The PHMA hydrogel was obtained by the polymerization of HMA in the presence of PEG(400)DA as a crosslinking agent. Amine group incorporated derivatives of PHMA were prepared for the first time by the reaction of this polymer with various diamines. The AV of the last hydrogels changed by depending on the amine compound used in reaction and the highest AV was obtained for TETA incorporated hydrogel (4.64 mmol/g). Increasing the AV of the hydrogels decreased their HMG content and EDS values increased due to the amine groups in polymer chain after modification. The protonization of amine groups in polymer increased the swelling ability at acidic pH values. The amine group incorporated PHMA hydrogels having amide, hydroxymethyl and amine groups adsorbed the indigo carmine and Cu(II) ion effectively while PHMA having only amide and hydroxymethyl groups did not. It is seen that the indigo carmine adsorption capacity increased (760.0 mg/g for H-TETA polymer at pH=3.0) and Cu(II) ion adsorption capacity decreased by decreasing of pH value of the initial solutions. Both adsorption capacities increased by increasing of the initial solution concentration and the Langmuir isotherm model gave the best results for indigo carmine and Cu(II) ion. The high adsorption rate and high capacity showed that these amine group incorporated hydrogels can be used as a sorbent for the removal of acidic dyes and some metal ions from aqueous solutions effectively.

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