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Preparation of poly (DMAEM)-cross linked pregelled starch graft copolymer and its application in waste water treatments

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ABSTRACT

Pregelled starch (PS) was first cross linked with epichlorohydrin (ECH) to obtain insoluble cross-linked pregelled starch (CPS). The latter was graft co-polymerized with different amounts of dimethylaminoethyl methacrylate (DMAEM) using potassium permanganate/sulphuric acid redox system. This was done to obtain six levels of poly (DMAEM)-cross linked pregelled starch graft copolymers (PDMAEM-CPS) having different graft yields (expressed as N%) with increasing order and designated as (PDMAEMCPS 1 to PDMAEMCPS 6). The latter copolymers were dispersed in aqueous solution of heavy metal ions Cu (II) ions and filtered to form polymer–metal ions complex. Different factors affecting the heavy metal ions removal such as pH, extent of grafting, treatment time and starch dose were studied in detail. It was found from the obtained results that; the residual metal ions removal from their aqueous solutions increased with (a) increasing the extent of grafting of PDMAEMCPS i.e. from PDMAEMCPS 1 to PDMAEMCPS 6; (b) increasing the pH of the metal ions solution complex from 1 to 8; (c) increasing the starch dosage from 0.25 to 2.0% (w/v), then leveled off thereafter and (d) increasing the time of the reaction up to 20 min then leveled off after that. On the other hand, Pb, Cd and Hg ions were also removed from their solutions with different extent. Furthermore, the prepared copolymer could be recovered by washing the metal ions from the complex with weak acid 1 N HNO_3 (pH 2) and the metal-binding activity of the starch was slightly reduced by this process. Finally, the ability of PDMAEMCPS to remove three types of acid dyes from their solutions was also reported.

1. Introduction

It is well known that, heavy metal ions and organic compounds as well as dyes remain a serious environmental problem facing the world for water pollution, as a result of their numerous industrial applications. In addition many of them are known to be toxic or carcinogenic even at low concentration, not biodegradable and tend to accumulate in living organisms causing a serious diseases and disorders (Crini, 2005). Therefore, their presence in water should be controlled. Different methods such as precipitation, ion-exchange, reverse osmosis, solvent extraction, electro dialysis techniques (Barcicki, Pawlowski, & Cichocki, 1980; Boto and Pawlowski, 1987), biological treatments (Fu and Viraraghhavan, 2001; Pearce, Lloyd, & Guthrie, 2003), membrane process (Bruggen and Vandecasteele, 2003; Ning, 2002), advanced oxidation process (Al-Momani, Touraud, Degorce-Dumas, Roussy, & Tomas, 2002), chemical and electrochemical techniques (Von Gunten, 2003) and adsorption procedure (Calace, Nardi, & Pietroletti, 2002; Gupta, Jain, Ali, Sharma, & Sanin, 2003; Li-Ming and Dan-qing, 2002; Xu, Shun, Gui, Ji-De, & Alayiding, 2005a) have been developed for the removal and recovery of metal ions and organic compounds from sewage and industrial wastewater. Amongst all the techniques proposed, adsorption-using sorbents is one of the most fascinating and popular methods for high quality treated effluents. Recently, a great attention and faster publications rate on developing cheaper and effective adsorbents containing natural polymers to overcome the non-biodegradability and high cost of the adsorbent resins were reported. Amongst these, natural polysaccharides, such as chitin and Chitosan (Kumar, 2000), cyclodextrin (Crini and Morcellet, 2002), cellulose (Guclu, Gurdag, & Ozgumus, 2003), amino functionalized silica (Heidari, Younesi, & Mehraban, 2009), as well as starch derivatives (Keles and Guclu, 2002; Mostafa and Samerkandy, 2004; Niu, Wu, Wang, Li, & wang, 2007; Sanford and Baird, 1983; Wurzburg, 1986) deserve particular attention with respect to their ability to remove heavy metal ions and dyes from aqueous solutions (Arami, Yousefi Limaee, & Mohammad Mahmoodi, 2008; Muthukumar, Sargunamani, Selvakumar, & Venkata Rao, 2004). In this respect, starch is abundant, biodegradable and renewable resources and has the capacity to associate by

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physical and chemical interaction with a wide variety of molecules (Li, Xiang, & Ni, 2004; Polaczek, Starzyk, Malenki, & Tomasik, 2000). In recent years, many approaches have been made to utilize starch as a metal absorbent by introducing various functional groups, such as carboxylate (Khalil and Abdel-Halim, 2001; Xu, Feng, Peng, Wang, & Yushan, 2005b), xanthate (Bose, Bose, & Kumar, 2002), acrylamide (Chauthan et al., 2006), acrylonitrile (Abdel-Aal, Gad, & Dessouki, 2006), phosphate (Gue, Zhang, Ju, & Yang, 2006) and dithiocarbamate (Yin, Ju, Zhang, Wang, & Yang, 2006). Some derivatives of starch dialdehyde like dihydrazone, semicarbazone and dioxime have also been prepared (Para and Karolczyk-Kostuch, 2002a,b; Para, Karolczyk-Kostuch, & Fiedorowicz, 2004; Para, 2004). Nevertheless, the problem here was these absorbents have low effective functional groups. In order to solve the problem, high content of functional groups are wanted to get by the most important fascinating method for chemical modification of polymer i.e. graft copolymerization. This was done by our research team using novel Pregelled starch (highly reactive substrate) and a new DMAEM (as a non reported monomer), in addition to $KMnO_4$/sulphuric acid as a redox system. Adsorbent obtained by this method is more effective in removal of heavy metal ions from aqueous solution.

Therefore, in the present work, our research team attempt to explore the adsorption behavior on the newly prepared poly (DMAEM)-cross linked pregelled starch graft copolymer (PDMAEMCPS) as a cheaper, low cost, non toxic and biodegradable polymer, having different graft yields expressed as nitrogen (%) (a point that has not been reported in the literature). The latter were prepared by grafting different amount of dimethylaminoethyl methacrylate onto cross linked pregelled starch using potassium permanganate/sulphuric acid redox system towards Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} ions removal from their solutions. For this purpose, various factors affecting the adsorption, such as pH, treatment time, extent of grafting, starch dose and recovery of starch were studied in detail. In addition, the ability of PDMAEMCPS to remove acid dyes from their solutions was also reported.

2. Materials and methods

2.1. Materials

Pregelled starch was kindly supplied by Cairo Company for Starch and Glucose, Cairo, Egypt. Dimethylaminoethyl methacrylate (Aldrich) stabilized with 0.01% hydroquinone was freshly distilled at 75 °C and pressure of 100 mm Hg. It was stored at −10 °C until used. Epichlorohydrin, sodium chloride, potassium permanganate were obtained from Fisher Scientific Co. Ltd. (Canada). Sulphuric, hydrochloric and nitric acids (E-Merck, India). sodium hydroxide (Modern lab., Chemicals, Egypt). $CuSO_4{\cdot}5H_2O$, $Pb(CH_3CO_2)_2{\cdot}3H_2O$, $Hg(CH_3CO_2)_2$, and $CdSO_4$ were analytical reagent grade chemicals and used without further purification.

2.2. Preparation of cross-linked pregelled starch

100 g pregelled starch was slurred in 150 ml water containing 1.5 g sodium chloride and 8 ml epichlorohydrin. To this slurry, 6 g sodium hydroxide in 40 ml water was added slowly over 30 min. The mixture was stirred for 16 h at room temperature. The slurry now containing cross linked pregelled starch, was adjusted to pH 6.5 with 2% HCl. The product was washed with water, filtered, and then washed with water and ethanol and finally air-dried.

2.3. Preparation of poly (dimethylaminoethyl methacrylate)-cross linked pregelled starch graft copolymer having different graft yields

Six levels of poly (DMAEM)-cross linked pregelled starch graft copolymers with different graft yields (expressed as N%), used as adsorbents for (Cu^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+}) ions in this study, were synthesized by keeping all the grafting reaction conditions constant and varying only the monomer concentration. Details of the conditions used as well as characterization of PDMAEMCPS are given in Table 1.

Unless other wise indicated, the graft polymerization reaction was carried out in 100 ml stoppered flasks containing an aqueous solution of monomer (5, 10, 20, 30, 40 and 50% based on weight of substrate ows). The flasks were stoppered and placed in a thermostatic water bath until the required temperature was reached. Nitrogen gas was purged through this solution to remove the dissolved oxygen. The cross-linked pregelled starch (10 g), (20 mmol/l) $KMnO_4$ and 50 mmol/l sulphuric acid were then added and the reaction mixture was mixed thoroughly. The total volume was adjusted to be 75 ml. The contents were shaken occasionally during polymerization for 2 h at 45 °C. After the desired reaction time, the flask contents were poured over 500 ml of ethanol where a precipitate was formed, which consisted of cross-linked pregelled starch graft copolymer and the homopolymer. The homopolymer poly (dimethylaminoethyl methacrylate) was removed from the reaction mixture by washing the precipitate five times with 400 ml of water/ethanol mixture (30:70, v/v) for 15 min at room temperature on magnetic stirrer, filtered and finally dried in an electric oven at 60 °C for 2 h. It was found experimentally that washing five times with a mixture of water/ethanol mixture (30/70, v/v) is quite enough for complete removal of homopolymer in physical mixture of pregelled starch/poly (dimethylaminoethyl methacrylate), by estimating N% of the mixture after each wash until constant value.

2.4. Determination of nitrogen

It was estimated by a well known kejeldhal method (Vogel, 1975).

2.5. Proof of grafting

This was done via measuring the N% of the grafted samples three times for each sample, as well as their standard deviation. On other word, both the N% and standard deviation were taken as an evidence or confirmation of grafting of dimethylaminoethyl methacrylate onto cross-linked pregelled starch that is free from nitrogen groups as a starting substrate (Mostafa, Samerkandy, & El-Sanabary, 2010a,b).

2.6. Heavy metal ions removal

An aqueous solution of copper ions (Cu 203 ppm) was prepared by dissolving cupric sulphate ($CuSO_4$. $5H_2O$, 0.8 g) in distilled water 1 l. Poly (DMAEM)-cross linked pregelled starch graft copolymer (0.25–3.0%) was then added to the copper solution (100 ml), and the dispersion was stirred for 20 min at room temperature (26 °C ± 0.5) to form a complex with the metal ions. The grafted cross linked starch-heavy metal ions complex was then removed by filtration and the filtrate was used for the residual metal analysis. On the other hand, to evaluate the removal effect of other metal ions, Pb (203 ppm), Cd (194 ppm) and Hg (208 ppm) solutions were prepared by dissolving lead acetate (Pb $(CH_3CO_2)_2{\cdot}3H_2O$, 0.374 g), mercuric acetate (Hg $(CH_3CO_2)_2$, 0.33 g) and cadmium sulphate ($CdSO_4$, 0.359 g) in distilled water (1 l) respectively.

Table 1
Preparation of poly (DMAEM)-cross linked pregelled starch graft copolymer having different graft yields (expressed as N%) as well as their main characteristics.

Starch type	Dimethylaminoethyl methacrylate concentration (based on weight of substrate)	N% of the resultant copolymer	Apparent viscosity (m Pa s) of the resultant copolymer
Blank	0	0.005	235
PDMAEMCPS1	5	0.45	239
PDMAEMCPS 2	10	1.01	246
PDMAEMCPS 3	20	1.35	253
PDMAEMCPS 4	30	1.72	260
PDMAEMCPS 5	40	2.10	267
PDMAEMCPS 6	50	2.45	273

Reaction conditions: cross linked pregelled starch, 10 g; [$KMnO_4$], 20 mmol/l; [sulphuric acid], 50 mmol/l, material to liquor ratio, 1:7.5; time, 2 h; and temperature, 45 °C.
N.B.
Blank: cross linked pregelled starch prior to grafting
PDMAEMCPS 1: poly (DMAEM)-cross linked pregelled starch graft copolymer with 0.45 N%
PDMAEMCPS 2: poly (DMAEM)-cross linked pregelled starch graft copolymer with 1.01 N%
PDMAEMCPS 3: poly (DMAEM)-cross linked pregelled starch graft copolymer 1.35 N%
PDMAEMCPS 4: poly (DMAEM)-cross linked pregelled starch graft copolymer with 1.72 N%
PDMAEMCPS 5: poly (DMAEM)-cross linked pregelled starch graft copolymer with 2.1 N%
PDMAEMCPS 6: poly (DMAEM)-cross linked pregelled starch graft copolymer with 2.45 N%

After the metal solution was treated with the grafted cross-linked starch, residual metal ion content in the filtrate was measured by a colorimetric method using Atomic Absorption Spectrophotometer.

2.7. Recovery of the prepared copolymer

Poly (DMAEM)-cross linked starch graft copolymer (1 g) at pH 8 used to remove copper ions was redispersed in distilled water (40 ml), and the dispersion was adjusted to pH 2 by adding 1 N HNO_3 solution. After stirring for 10 min, the dispersion was filtered. The starch residue was washed with water and readjusted to pH 8 with 1 N NaOH and dried at 40 °C overnight. The degree of Cu removal using the recovered starch was measured and compared with the unrecovered one.

2.8. Dye removal

0.5 g of poly (DMAEM)-cross linked pregelled starch graft copolymer and 100 ml of an aqueous solution of dye (100 mg/l) were placed in 125 glass-stoppered flasks without pH adjustment and automatically shaken for 12 h at room temperature (26 °C ± 1 °C). The flasks content were filtered and the concentration of the dye in the filtrate was measured using a Shimadzu UV/visible Spectrophotometer at maximum wavelength of each dye. The sorption capacity was then calculated and expressed in percentage uptake (R in %), which represents the ratio between the amount-adsorbed dye and the starting amount dye.

$$R\% = \frac{\text{Amount of dye adsorbed}}{\text{Total amount of dye}} \times 100$$

The Acid Orange 12 (AO12), Acid red 14 (AR14) and Acid Orange 7 (AO 7) dyes (Aldrich) were used for dye removal on the prepared copolymer.

3. Results and discussion

3.1. Tentative mechanism for heavy metal ion/dye polymer interaction

$$\text{St-N-R3} + H^+ \rightarrow \text{St-NH}^+\text{-R3}$$

where St- = cross-linked pregelled starch substrate; while St-N-R3 represents poly (DMAEM)-cross linked pregelled starch graft copolymers.

The above reaction was introduced to reinforce explanation of the effect of pH on the adsorption of acid dyes and metal ions over the newly prepared poly (DMAEM)-cross linked pregelled starch graft copolymers. It is well known that, the heavy metal/acid dyes in questions are mostly removed via protonation and deprotonation at lower and higher pH respectively of the tertiary amine groups on the surface of cross linked pregelled starch graft copolymer (Mostafa et al., 2010b).

3.2. Effect of pH

Fig. 1 represents the effect of changing pH of poly (DMAEM)-cross linked pregelled starch graft copolymer (expressed as N%) on the Cu removal from its solution at fixed N% i.e. 2.45. It is seen Fig. 1 that, residual Cu ion concentration in the filtrate decreased when pH increased from 1 to 8. This is in accordance with the results published by Xu et al. (2005a,b), Shi-Mei, Feng, Peng, Wang, & Yushan, 2005, Gue, Shu-Fen, Zhi, & Zong, 2005, Kweon, Choi, Kim, & Lim, 2001 and Zhang and Chen (2002).

Due to the protonation and deprotonation of the tertiary amine groups on the surface of cross linked pregelled starch graft copolymer, its adsorption behavior for metal ions is influenced by the pH values as shown in Fig. 1. The examined test were limited to the pH range from 1 to 8 because of the known precipitate of $Cu(OH)_2$ in alkaline medium.

For more detail, at pH 8 the residual metal ion content decreases from 203 ppm as a starting concentration in absence of cross-linked starch copolymer to 65 ppm in presence of it. Further more, the residual metal ion concentration increases by decreasing the pH from 6 to 4 to 2 and finally to 1 but with lesser extent. The decrement in the residual metal ion concentration follows the order: pH 8 > pH 6 > pH 4 > pH 2 > 1.

When the starch pH was 6 or 4, the residual Cu content in the filtrate decreased to 92 ppm or 101 ppm respectively. While at lower pH i.e. 2 and 1 the starch was no longer effective in removing Cu from the solution (i.e. the starch did not show Cu binding activity i.e. not amenable. This can be explained by the fact that at lower pH value most of tertiary amine groups in the copolymer are protonated. Then cationic repulsion can occur between metal ion species and protonated grafted chains. The opposite hold true at higher pH values (6–8). On the other word, most of tertiary amine groups in the copolymer are less protonated which lead to strong complexation between the copolymer and metal ion in question (Dhodapkar, Rao, Pande, & Kaul, 2006).

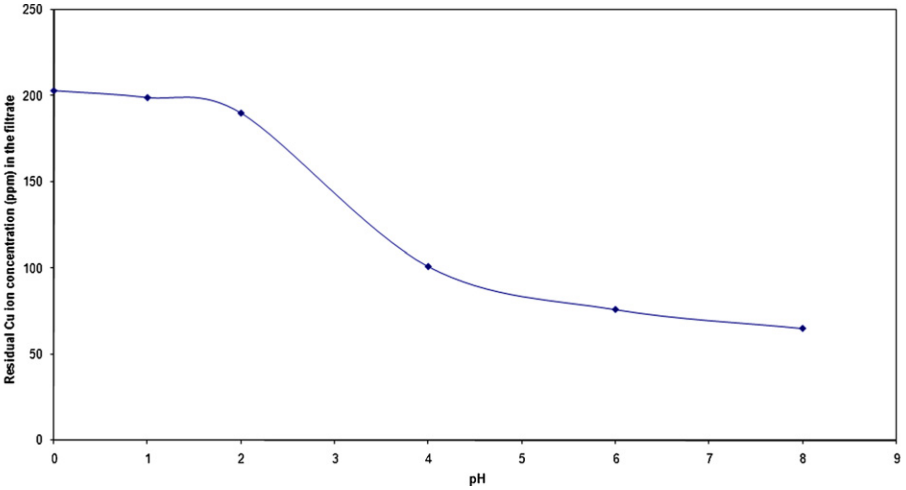

Fig. 1. The relation between residual Cu ion content and pH in the metal–copolymer complex solution. *Reaction conditions*: PDMAEMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 ml; N%, 2.45; time, 20 min; temperature, 26 °C ± 1 °C.

3.3. *Effect of extent of grafting on metal removal*

Fig. 2 declares the effect of changing the extent of grafting (expressed as N%) of poly (DMAEM)-cross linked pregelled starch graft copolymer (expressed as N%) on the Cu removal from its solution at pH 8. It is seen from Fig. 2 that, for Cu removal, residual metal ion concentration in the solution decreased when N% of poly (DMAEM)-cross linked grafted starch copolymer increased. So, by increasing the N% of the copolymer from 0.45 to 2.45 would lead to a decrease in residual metal ion concentration from 203 to 65 as shown before at pH 8. This indicates that the metal ions in the solution interact more likely with higher extent with the tertiary aminated groups of poly (DMAEM)-cross linked starch graft copolymer, which reflect the role of extent or degree of grafting on the heavy metal ions binding activity or removal. The latter was not reported for our knowledge in the literature until now.

3.4. *Effect of treatment time on the metal removal*

Fig. 3 shows the effect of treatment time on the removal of Cu ions with poly (MAA) – cross-linked starch graft copolymer at optimum conditions observed before. It is seen from Fig. 3 that, the Cu removal was completed within the first 20 min induction period, which indicate that the copper ions rapidly form chelates or interaction with the tertiary amine groups of the cross linked pregelled starch graft copolymer. This rapid interaction will be beneficial for practical application, i.e. the latter copolymer could be used as a filtering resin for a short period of treatment of wastewater during filtration.

3.5. *Effect of PDMAEMCPS dose used*

When the dose of poly (DMAEM)-cross-linked pregelled starch graft copolymer added to the copper solution (203 ppm Cu) was increased from 0.25 to 3.0% (w/v), the residual Cu content in the filtrate decreased gradually (Fig. 4). At 2.45 N%, the copper ions in the solution were almost completely removed with 2.0% starch addition based on solution volume, and then leveled off after that. This corresponds to an increase in copolymers active sites as well as saturation occurred at 2.0% (w/v) at which further increase in starch dosage had little or no effect on metal removal. A point should be useful for establishing the optimum economical dose of PDMAEMCPS in metal removal.

3.6. *Removal of other heavy metal ions*

Six levels of poly (DMAEM)-cross-linked pregelled starch graft copolymers their graft yields ranged from (0.45 to 2.45 N%) were

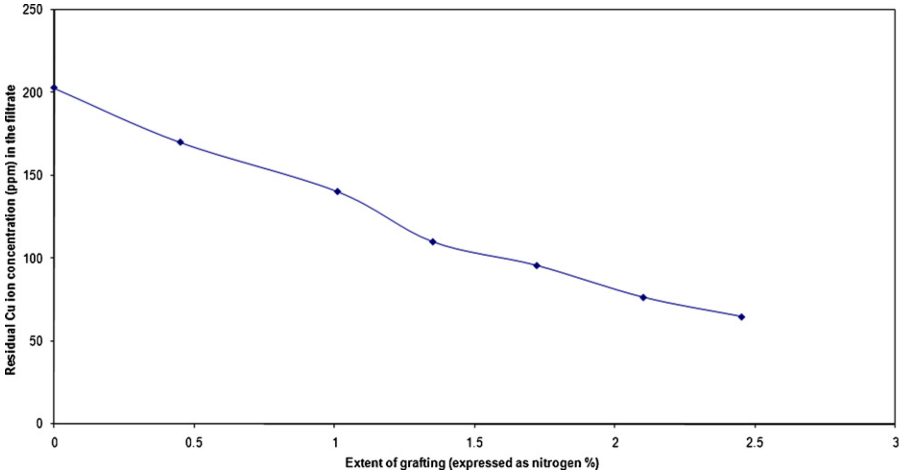

Fig. 2. Effect of varying the extent of grafting (expressed as N%) on the residual Cu ion in the metal–copolymer complex solution. *Reaction conditions*: PDMAEMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 ml; pH, 8; time, 20 min; temperature, 26 °C ± 1 °C.

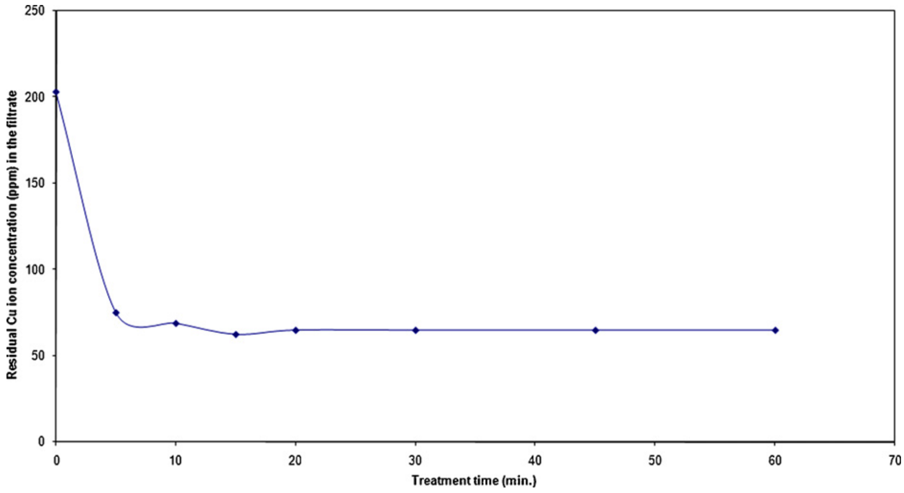

Fig. 3. Effect of treatment time on the residual Cu ions removal using PDMAEMCPS. *Reaction conditions*: PDMAEMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 ml; N%, 2.45; pH, 8; temperature, 26 °C ± 1 °C.

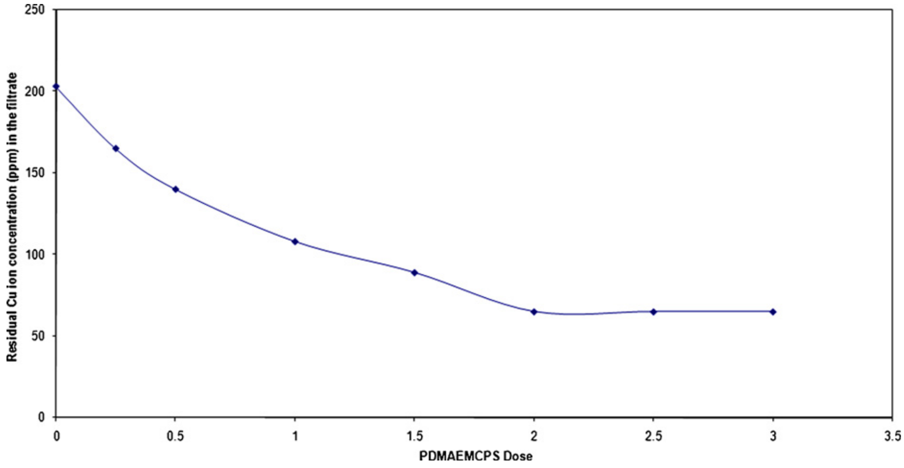

Fig. 4. Effect of dosage of PDMAEMCPS on the residual Cu ions concentration (ppm) removal from metal–copolymer complex solution. *Reaction conditions*: initial Cu conc., 203 ppm; total volume, 100 ml; N%, 2.45; time, pH 8, 20 min; temperature, 26 °C ± 1 °C.

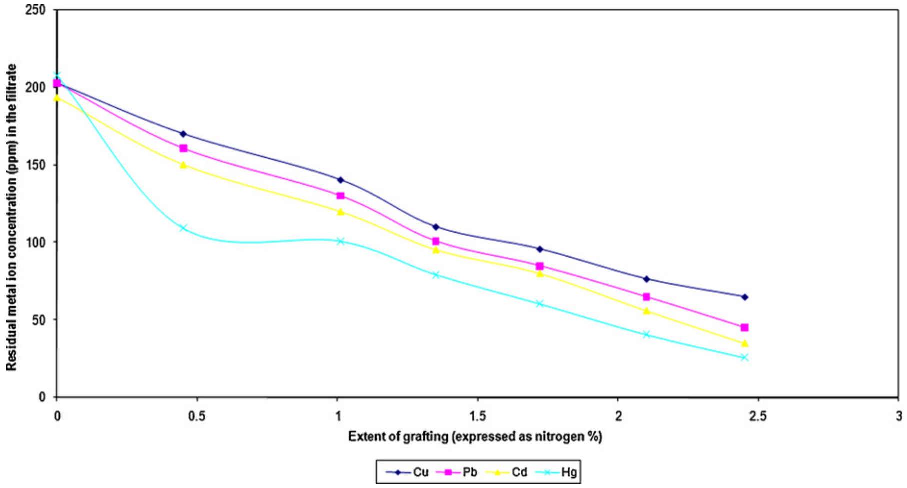

Fig. 5. The relation between changing the extent of grafting (expressed as N%) on the removal of different heavy metal ions in questions. *Reaction conditions*: PDMAEMCPS, 2 g; initial metal ion conc., about 202 ppm; total volume, 100 ml; pH, 8; time, 20 min; temperature, 26 °C ± 1 °C.

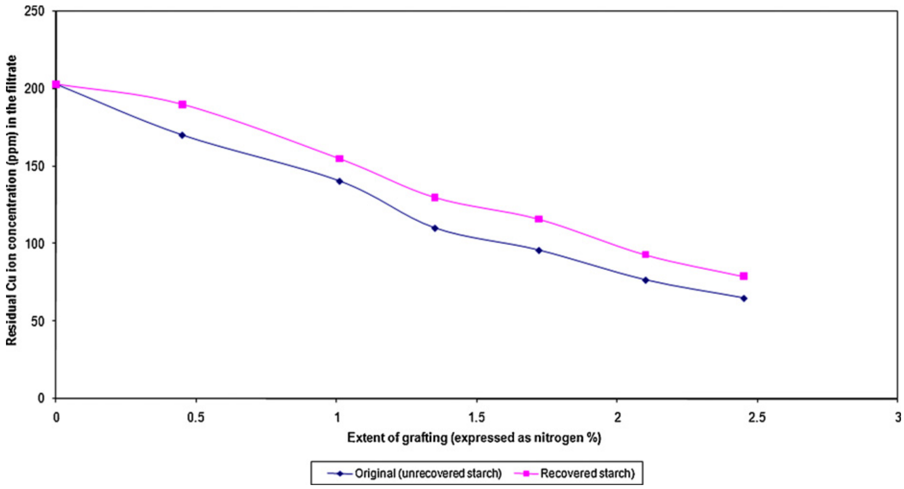

Fig. 6. The difference between original unrecovered starch and recovered one of PDMAEMCPS towards Cu ions removal from the metal–copolymer complex solution. *Reaction conditions*: PDMAEMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 ml; pH, 8; time, 20 min; temperature, 26 °C ± 1 °C.

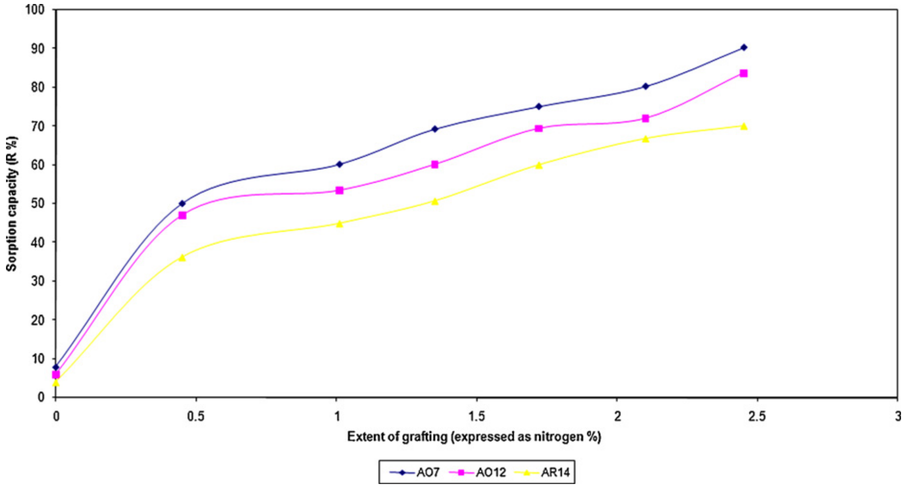

Fig. 7. Relation between extent of grafting (expressed as N%) and sorption capacity of dye adsorbed (*R*%) on PDMAEMCPS. *Reaction conditions*: PDMAEMCPS, 0.5 g; dye conc., 100 mg/l; total volume, 100 ml; time, 12 h; temperature, 26 °C ± 1 °C.

used for removing different heavy metal ions from their solutions at a similar concentration (about 200 ppm). The different heavy metal ions used were Pb^{+2}, Cd^{+2} and Hg^{+2}.The obtained results are set out in Fig. 5. Details of the conditions used are set out elsewhere.

It is seen from Fig. 5 that, the residual amount of heavy metal ions removed is governed by the % nitrogen (graft yield) as well as the nature of metal ion used. So, when the N% increased from 0.45 to 2.45 the residual removal of heavy metal increased irrespective of the nature of metal ion used. It is also seen that, the synthesized poly (DMAEM)-cross linked pregelled starch graft copolymers are more effective in removing Hg^{+2} than all other metal ions in question and follow the order:

$$Hg^{2+} > Cd^{2+} > Pb^{2+}$$

This can be explained in terms of, the differences between the metal ions in questions with respect to; (a) relative atomic size; (b) ability for metal ion to interact with the polymer; (c) metal ion charge density and (d) reactivity of the metal ion. In addition, Khalil and Abdel-Halim (2000) said that, Hg^{2+} acquires the high-

Table 2
Maximum adsorption capacity for the adsorption of Cu^{2+}. Pb^{2+} and Cd^{2+} onto different adsorbents cited in the literature.

Adsorbents	Maximum adsorption capacity (Q_m(mmol g^{-1}))			Cited references in the text
	Cu^{2+}	Pb^{2+}	Cd^{2+}	
Cellulose-g-acrylic acid copolymer	0.286	0.296	0.240	16
Starch-g-acrylic acid copolymer	0.080	0.603	0.170	17
Amino functionalized Silica	–	0.279	0.161	21
Cross linked carboxymethyl KGM	0.434	0.201	0.208	22
Our prepared PDMAEMCPS copolymers as residual metal ion conc. in the filtrate	65/203 ppm	45.2/194 ppm	35.2/203 ppm	Present work

est sorption value amongst the variable studied metal ions used i.e. Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}; hence, Hg^{2+} will be used in comparing the sorption behavior of different legends. Furthermore, this is in accordance with the results also published by Khalil and Farag (1999) for the stability of various legends with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.

3.7. Recovery of starch

Fig. 6 shows the comparison of original (unrecovered) starch and recovered one for poly (DMAEM)-cross linked starch graft copolymer under the same condition shown before in the experimental part on copper removal. It is seen from the figure that, the removal efficiency of the recovered starch appears slightly less than that of fresh starch. In case of Cu removal, the recovered starch of 2.45 N% (pH8) reduced the copper ion content to 79 ppm in comparison to 65 ppm unrecovered starch.

3.8. Dyes removal

The sorption capacity (dye uptake *R*%) was investigated using three types of acid dyes namely Acid Orange 12 (AO12), Acid Red 14 (AR14) and Acid Orange 7 (AO 7) .The measurement of each dye must be at the maximum wave length of each dye which was as follows: 484, 514 and 484 nm respectively. This was done under the optimized experimental conditions as shown in Section 2.

On the other hand, to evaluate the influence of the tertiary amine groups on the sorption capacity of anionic dye removal of the prepared copolymers, different tests were carried out using the six copolymers (PDMAEMCPS 1 to PDMAEMCPS 6) having different tertiary amine groups in addition to blank experiment with the polymer with zero nitrogen groups just for comparison. It seen from Fig. 7 that, at any graft yield, the capacity of dyes removal follows the order: Acid Orange 7 (AO 7) > Acid Orange 12 (AO 12) > Acid Red 14 (AR 14).

Furthermore, the amount of dye adsorbed for all dyes in questions increases by increasing the extent graft yields of the prepared copolymers. In other word, the acid dyes display the best interaction or sorption capacity with the copolymers in question containing higher tertiary amine groups (i.e. interaction between tertiary amine groups on the polymer and acid groups in the basic dyes). This was confirmed by the higher sorption capacities of the prepared copolymers that reach a maximum at 90.3 in case of Acid Orange 7 (AO 7), 83.8 for Acid Orange 12 (AO 12) and 70.2 for Acid Red 14 (AR 14) at higher N% i.e. 2.452. Moreover, acidity, molecular size and stereochemistry of the dyes appeared to influence the amount of dye adsorbed on PDMAEMCPS.

3.9. Comparison with other adsorbents

In order to justify the efficiency (validity) of the new prepared poly (DMAEM)-cross linked starch graft copolymers having 2.45 N% as an adsorbent of Cu^{2+} and other heavy metals like Cd^{2+} and Pb^{2+}, its adsorption potential must be compared with other various adsorbents reported in the literature (Dhodapkar et al., 2006; Khalil and Abdel-Halim, 2000; Khalil and Farag, 1999; Zhang and Chen, 2002). Table 2 represents the values of maximum adsorption capacity on different adsorbents cited in the literature compared with that of the present study. It is shown that poly (DMAEM)-cross linked starch graft copolymers having 2.45 N% has good adsorption capacity as shown in the text when compared with other adsorbents. Taking in mind that, all the maximum adsorptions capacity of all adsorbents in the table have been measured in mmol g^{-1} not in ppm as in our case, which reflect the degree of efficiency and selectivity of our prepared adsorbent in comparison with other cited adsorbents.

4. Conclusion

By cross linking followed by grafting with DMAEM, pregelled starch could become an active and relatively insoluble metal scavenger for heavy toxic divalent cations such as Cu, Pb, Cd and Hg ions contaminated in water as well as efficient acid dyes removal. At low N% 0.45 of the copolymer, valuable amount of these metal ions (ppm) could be effectively removed from water by dispersing 2.0% (w/v) of the copolymer for (20 min) at pH 8 and subsequent filtering the starch–metal complex. The starch could be regenerated by a weak acidic washing. For effective metal removal, the metal solution should not to be acidic. By raising the levels of grafting, metal scavenging activity of the copolymer could be increased up to the level required for industrial application. On the other hand, the latter prepared copolymers could be used also to remove acid dyes from their aqueous solutions and follows the order: Acid Orange 7 (AO 7) > Acid Orange 12 (AO 12) > Acid Red 14 (AR 14).

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