

Preparation of Poly (MAA)-Crosslinked Pregelled Starch Graft Copolymer and Its Application in Waste Water Treatments

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ABSTRACT: Propelled starch (PG) was first crosslinked with epichlorohydrin to obtain insoluble crosslinked pregelled starch (CPS). The latter was graft copolymerized with different amounts of Methacrylic acid using potassium persulphate as initiator. This was done to obtain six levels of poly (MAA)-crosslinked pregelled starch graft copolymers (PMCPs) having different graft yields (expressed as meq COOH/100 g starch) with increasing order and designated as (PMCPs 1 to PMCPs 6). The latter copolymers were dispersed in aqueous solution of heavy metal ions (Cu^{2+} , Pb^{2+} , Cd^{2+} , and Hg^{2+}) 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 PMCPs i.e., from PMCPs 1 to PMCPs 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, (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 1N HNO_3 (pH 2) and the metal-binding activity of the starch was slightly reduced by this process. Finally, the ability of PMCPs to remove three types of basic dyes from their solutions was also reported. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2838–2846, 2009

Key words: pregelled starch; epichlorohydrin; crosslinking; methacrylic acid; grafted starch; heavy metal ions removal; dyes

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.¹ Therefore, their presence in water should be controlled. Different methods such as precipitation, ion-exchange, reverse osmosis, solvent extraction, electro dialysis techniques,^{2,3} biological treatments,^{4,5} membrane process,^{6,7} advanced oxidation process,⁸ chemical and electrochemical techniques⁹ and adsorption procedure^{10–13} have been developed for the removal and recovery of metal ions and organic compounds

from sewage and industrial wastewater. Among 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 nonbiodegradability and high cost of the adsorbent resins were reported. Among these, polysaccharides, such as chitin and chitosan,¹⁴ cyclodextrin¹⁵ as well as starch derivatives^{16–18} deserve particular attention with respect to their ability to remove heavy metal ions and dyes from aqueous solutions.

In this work, our research team attempt to explore the adsorption behavior on the newly prepared poly (MAA)-crosslinked pregelled starch graft copolymer (PMCPs) having different graft yields expressed as carboxyl contents (a point that has not been reported). The PMCPs were prepared by grafting different amount of MAA onto crosslinked pregelled starch using potassium persulfate as initiator toward Cu^{2+} , Pb^{2+} , Cd^{2+} , and Hg^{2+} ions removal from their solutions. For this purpose, various factors affecting

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TABLE I
Preparation of Poly (MAA)-Crosslinked Pregelled Starch Graft Copolymer Having Different Graft Yields (Expressed as meq/COOH/100 g Starch) as well as their Main Characteristics

Starch type	Methacrylic acid concentration (based on weight of substrate)	Carboxyl content (meq/COOH/100 g starch)	Graft Yield % (G.Y. %)	Graft Reaction Efficiency % (G.R.E. %)	Apparent Viscosity (m.pa.s) ^a
Blank	0	1.01	0.084	–	235
PMCPS 1	5	50.5	4.431	88.62	239
PMCPS 2	10	88.2	8.001	80.01	246
PMCPS 3	20	110.9	9.643	48.22	253
PMCPS 4	30	150.2	14.440	47.48	260
PMCPS 5	40	175.1	17.245	43.11	267
PMCPS 6	50	198.2	19.975	39.95	273

Reaction conditions:

Cross linked pregelled starch, 10 g; K₂S₂O₈, 40 mmol/L; material to liquor ratio, 1:7.5; Time, 2 hr; and temperature, 60°C.

Blank: Crosslinked Pregelled starch prior to grafting.

PMCPS 1: Poly (MAA)-cross linked pregelled starch graft copolymer with 50.5 meq COOH/100 g starch.

PMCPS 2: Poly (MAA)-cross linked pregelled starch graft copolymer with 88.2 meq COOH/100 g starch.

PMCPS 3: Poly (MAA)-cross linked pregelled starch graft copolymer with 110.9 meq COOH/100 g starch.

PMCPS 4: Poly (MAA)-cross linked pregelled starch graft copolymer with 150.2 meq COOH/100 g starch.

PMCPS 5: Poly (MAA)-cross linked pregelled starch graft copolymer with 175.1 meq COOH/100 g starch.

PMCPS 6: Poly (MAA)-cross linked pregelled starch graft copolymer with 198.2 meq COOH/100 g starch.

^a Apparent viscosity was measured for completing a full characterization of the prepared copolymer.

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 PMCPS to remove basic dyes from their solutions was also reported.

MATERIAL AND METHODS

Materials

Pregelled starch was kindly supplied by Cairo Company for Starch and Glucose, Cairo, Egypt. Methacrylic acid 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 persulphate, hydrochloric acid, Nitric acid, sodium hydroxide, CuSO₄ 5H₂O, Pb(CH₃CO₂)₂·3H₂O, Hg(CH₃CO₂)₂, and CdSO₄ were reagent grade chemicals.

Preparation of crosslinked pregelled starch

Pregelled starch (100 g) 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 crosslinked 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.

Preparation of poly (methacrylic acid)-crosslinked pregelled starch graft copolymer having different graft yields

Six levels of poly (MAA)-crosslinked pregelled starch graft copolymers with different graft yields (expressed as meq COOH/100 g starch), used as adsorbents for (Cu²⁺, Pb²⁺, Cd²⁺, and Hg²⁺) 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 PMCPS are given in Table I.

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). 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 crosslinked pregelled starch (10 g) and (40 mM) K₂S₂O₈ initiator 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 60°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 (methacrylic acid) 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 (methacrylic), by estimating carboxyl content of the mixture after each wash until constant value.

Determination of carboxyl content

This was determined as per the procedure of Mitchell and Wijnberg, 1995.¹⁹ To 0.5 g of grafted crosslinked pregelled starch, 25 mL 0.1N HCl was added and the mixture was allowed to stand for 30 min with occasional stirring. The slurry was filtered through a filter glass crucible (G 4) and washed with distilled water until it was free from chlorine. The grafted starch was then transferred to a 500 mL beaker to which 300 mL distilled water was added. It was then boiled for 15 min. for complete gelatinization, followed by titration with standard 0.1N NaOH solutions with phenolphthalein as indicator. A blank test was also performed with crosslinked pregelled starch prior to grafting.

Carboxyl content was calculated as follows:

$$\text{Milli-equivalents of acidity/100g starch} = \frac{(\text{Sample} - \text{Blank})\text{mL} \times \text{Normality of NaOH} \times 100}{\text{Sample weight (dry basis) in g}}$$

Proof of grafting

This was done via measuring the carboxyl content of the grafted samples using a well known method three times for each sample, as well as their standard deviation. On other word, both the carboxyl content and standard deviation were taken as an evidence or confirmation of grafting of MAA onto crosslinked pregelled starch that is free from carboxyl groups as a starting substrate.

Heavy metal ions removal

An aqueous solution of copper ions (Cu 203 ppm) was prepared by dissolving cupric sulfate (CuSO₄·5H₂O, 0.8 g) in distilled water 1 liter. Poly (MAA)-crosslinked pregelled starch graft copolymer (0.25–3.0%) was then added to 100 mL in 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 crosslinked starch-heavy metal ions complex was then removed by filtration and the filtrate was used for the residual metal analysis.

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 (CH₃CO₂)₂·3H₂O, 0.374 g], mercuric acetate [Hg (CH₃CO₂)₂, 0.33 g], and cadmium sulfate (CdSO₄, 0.359 g) in distilled water (1 L), respectively.

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

Recovery of the prepared copolymer

Poly (MAA)-crosslinked 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 1N HNO₃ solution. After stirring for 10 min, the dispersion was filtered. The starch residue was washed with water and readjusted to pH 8 with 1N NaOH and dried at 40°C overnight. The degree of Cu removal using the recovered starch was measured and compared with the unrecovered one.

Dyes removal

Poly (MAA)-crosslinked pregelled starch graft copolymer (0.5 g) 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) to be ensure about the complete adsorption. 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.

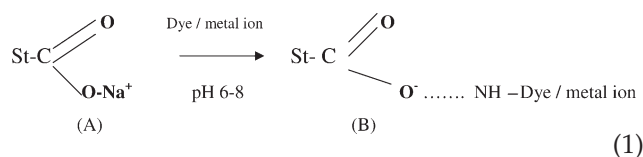
The sorption capacity was then calculated and expressed in percentage uptake (R in %), which represents the ratio between the amount-adsorbed dye and the starting amount dye.

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

The basic dyes safranin T (ST), methylene blue (MB) and crystal violet (CV) (E. Merck) were used for dye removal on the prepared copolymer.

RESULTS AND DISCUSSION

Tentative mechanism for heavy metal ion/Dye Polymer interaction:



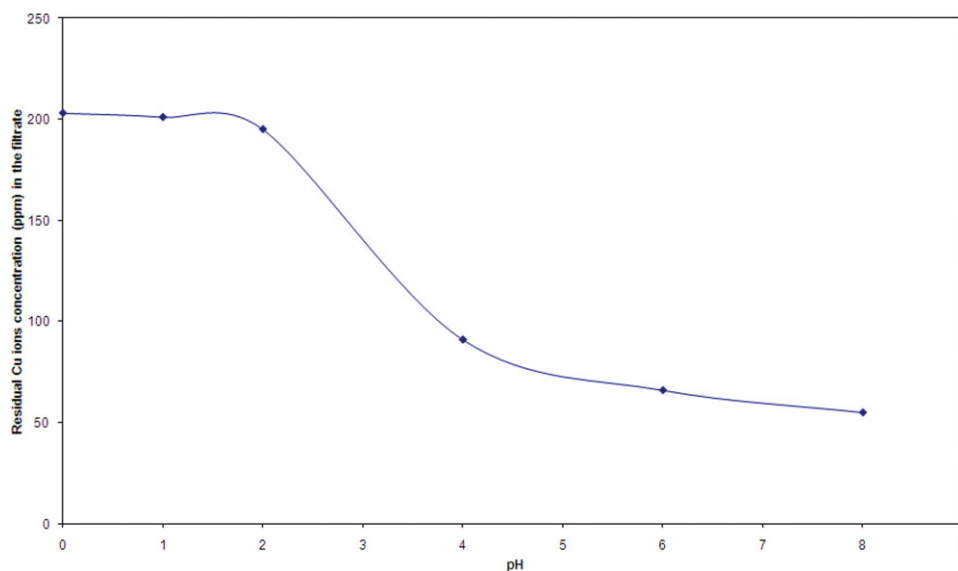


Figure 1 The relation between residual Cu ion content and pH in the metal-copolymer complex solution. Reaction conditions: PMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 mL; carboxyl content, 198.2 meq COOH/100 g starch; time, 20 min; temperature, $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where St- = Crosslinked Pregelled Starch substrate.

The aforementioned reaction step was introduced mainly to explain and follow up the effect of pH on the adsorption of basic dyes and metal ions over poly (MAA)-crosslinked pregelled starch graft copolymers. It is well known that, the heavy metal/basic dyes (cationic) in questions are mostly removed via ion-exchange process; i.e., A particular adsorbent is applicable to a particular class of dye/heavy metal has a high adsorption capacity for cationic dyes/metal ions.^{20–23}

Effect of pH

Figure 1 represents the effect of changing pH of poly (MAA)-crosslinked pregelled starch graft copolymer (expressed as meq-COOH group/100 g starch) on the Cu removal from its solution at fixed carboxyl content i.e., 198.2 meq COOH/100 g starch. It is seen Figure 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., 2005,²⁴ Gue et al., 2005,²⁵ Kweon et al., 2001,²⁶ and Zhang and Chen, 2000.²⁷

This indicates that the metal ions in the solution interact more likely with the carboxyl groups of the copolymer at higher pH because of the transformation of carboxyl groups from an acid form at lower pH to sodium salt form at higher one.

It was found experimentally that, the cupric sulfate solution tested had weak acidity (pH about 5). When 1% (W/V) of pH 2 grafted crosslinked preg-

elled starches was added to the solution, the pH of the solution become 3.3. With the starches of pH 4, 6, and 8, the pH values of the solution become 4.5, 5.0, and 5.4, respectively.

For more detail, at pH 8 the residual metal ion content decreases from 203 ppm as a starting concentration in absence of crosslinked starch copolymer to 55 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 82 ppm or 91 ppm, respectively. While at lower pH i.e., 2 and 1 the starch was no longer effective in removing Cu from the solution (the starch did not show Cu binding activity i.e., not amenable).

In addition to the above, the proposed tentative mechanism explains also the observed pH effect on the adsorption of metal ions over PMCPS within the pH studied range. At lower pH, the introduced reactive functional groups (COONa^+) as shown in eq. (1A) exist predominately in the protonated carboxyl group, and this prevent positive metal ions from adsorbing on the PMCPS substrate. This exhibits a weaker force of attraction between oppositely charged ions compared to COO^- eq. (1B) group at higher pH. So, adsorption of metal ions/dye at lower pH is found to be very poor. The opposite hold true at higher pH values (6 to 8). On the other word, the ionic interaction between the negative

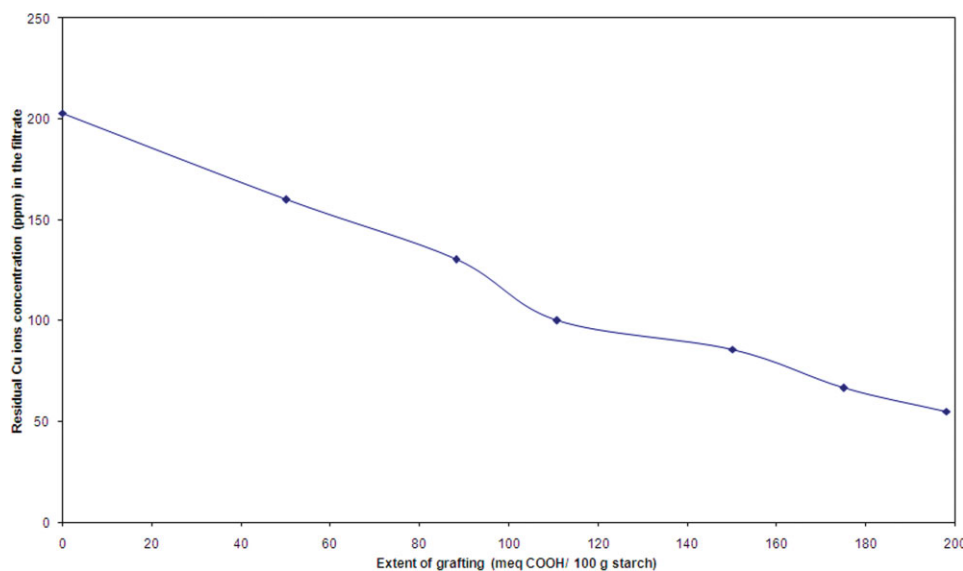


Figure 2 Effect of varying the extent of grafting (meq COOH/100 g starch) on the residual Cu ion in the metal-copolymer complex solution. Reaction conditions: PMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 mL; pH, 8; time, 20 min; temperature, $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

carboxyl groups in the PMCPS and positive charged metal ions in question is the main factors in the adsorption process.²⁸

Effect of extent of grafting on metal removal

Figure 2 declares the effect of changing the extent of grafting or graft yield of poly (MAA)-crosslinked pregelled starch graft copolymer (expressed as meq-COOH group/100 g starch) on the Cu removal from its solution at pH 8. It is seen Figure 2 that, for Cu removal, residual metal ion concentration in the solution decreased when carboxyl contents of poly (MAA)-crosslinked grafted starch copolymer increased. So, by increasing the carboxyl contents of the copolymer from 50.2 to 198.2 meq-COOH/100 g starch would lead to a decrease in residual metal ion concentration from 203 to 55 as shown before at pH 8. This indicates that the metal ions in the solution interact more likely with higher extent with the carboxyl groups of poly (MAA)-crosslinked 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.

Effect of treatment time on the metal removal

Figure 3 shows the effect of treatment time on the removal of Cu ions with poly (MAA)-crosslinked starch graft copolymer at optimum conditions observed before.

The adsorption time was changed from 0 to 60 min, and the residual Cu ion contents during this

period were examined. It is seen Figure 3 that, Cu ion removal increases with the treatment time during the first 20 min, then level off. In general, there are three main steps involved in Cu ion removal onto the crosslinked grafted polymer: (i) the transport of the Cu ions from the bulk solution to the adsorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the adsorbent particle. Because the adsorption is a chemical process, Step (ii) is fast. On the other hand, grafted polymer was prepared in solid-state form, so most of the active groups are on the particle surface, which makes Step (iii) rapid. So, 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 carboxyl groups of the crosslinked 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.²⁹

Effect of PMCPS dose used

When the dose of poly (MAA)-crosslinked 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 198.2 meq-COOH/100 g starch, 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

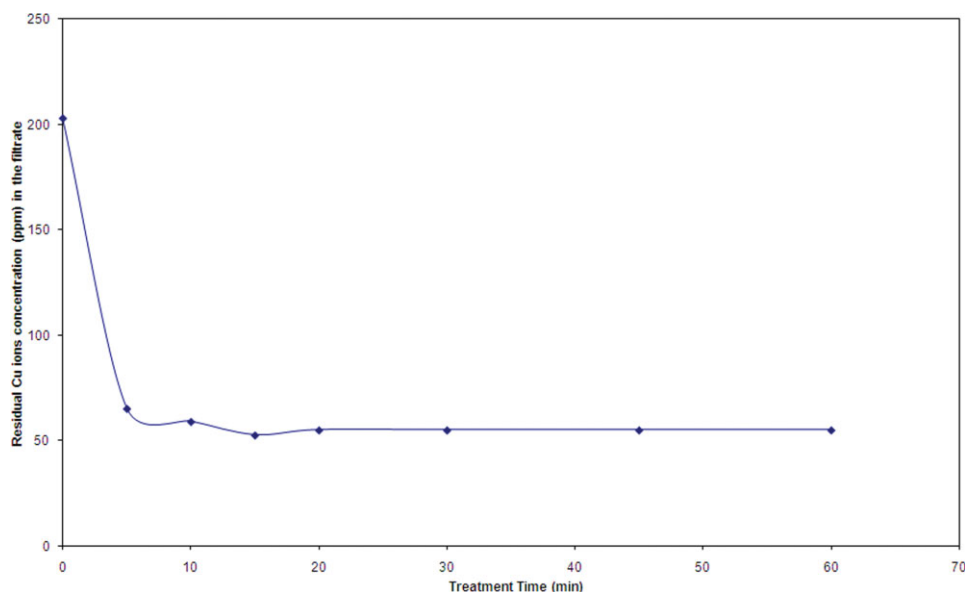


Figure 3 Effect of treatment time on the residual Cu ions removal using PMCPS. Reaction conditions: PMCPS, 2 g; initial Cu conc., 203 ppm; total volume, 100 mL; carboxyl content, 198.2 meq COOH/100 g starch; pH, 8; temperature, 26°C ± 1°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 PMCPS in metal removal.

Removal of other heavy metal ions

Six levels of poly (MAA)-crosslinked pregelled starch graft copolymers their graft yields ranged

from (50.2–198.2 meq COOH/100 g starch) were 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 Figure 5. Details of the conditions used are set out elsewhere.

It is seen from Figure 5 that, the residual amount of heavy metal ions removed is governed by the %

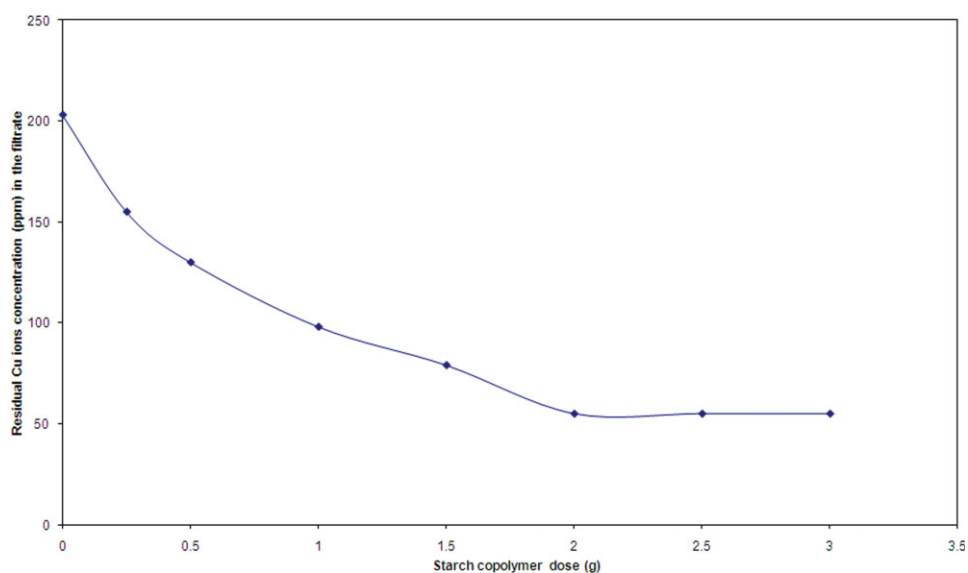


Figure 4 Effect of dosage of PMCPS on the residual Cu ions concentration (ppm) removal from metal-copolymer complex solution. Reaction conditions: Initial Cu conc., 203 ppm; total volume, 100 mL; carboxyl content, 198.2 meq COOH/100 g starch; time, pH 8, 20 min; temperature, 26°C ± 1°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

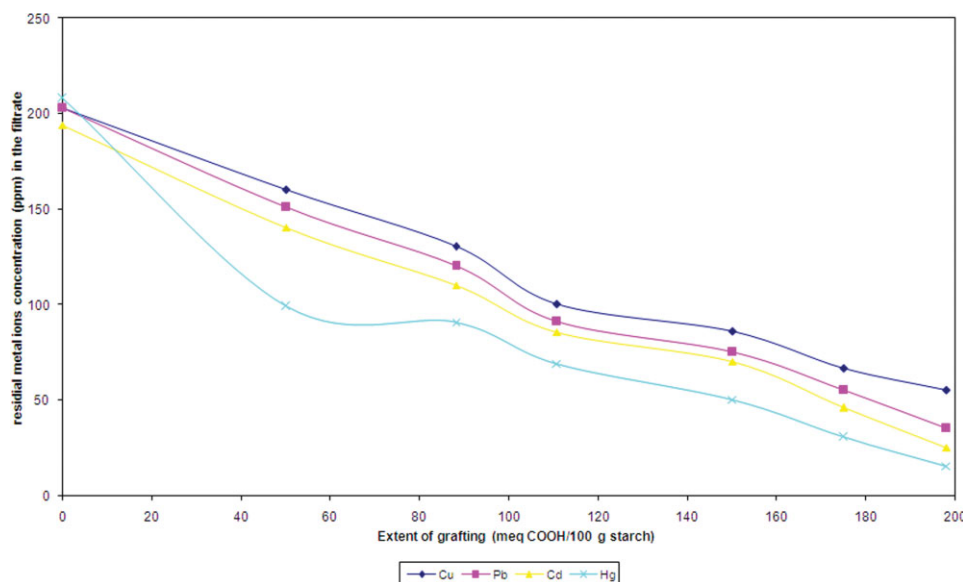


Figure 5 The relation between changing the extent of grafting (meq COOH/100 g starch) on the removal of different heavy metal ions in questions. Reaction conditions: PMCPs, 2 g; initial metal ion conc., about 202 ppm; total volume, 100 mL; pH, 8; time, 20 min; temperature, $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

carboxyl content (Graft yield) as well as the nature of metal ion used. So, when the carboxyl contents increased from 50.2 to 198.2 the residual removal of heavy metal increased irrespective of the nature of metal ion used. It is also seen that, the synthesized poly (MAA)-crosslinked pregelated starch graft copolymers are more effective in removing Hg^{+2} than all other metal ions in question and follow the order:



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 Mohammed, 2000,³⁰ said that Hg^{2+} acquires the highest sorption value among the

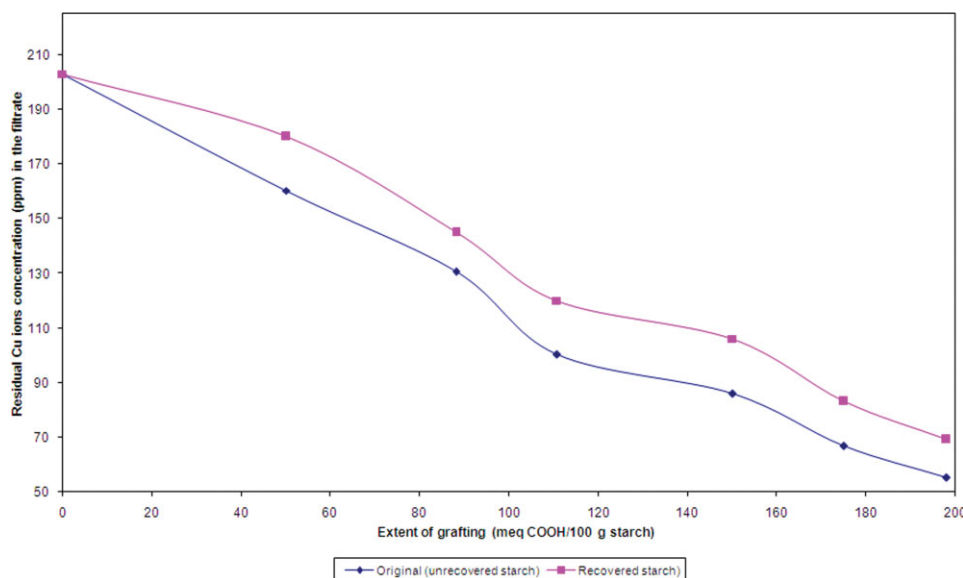


Figure 6 The difference between original unrecovered starch and recovered one of PMCPs toward Cu ions removal from the metal-copolymer complex solution. Reaction conditions: PMCPs, 2 g; initial Cu conc., 203 ppm; total volume, 100 mL; pH, 8; time, 20 min; temperature, $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

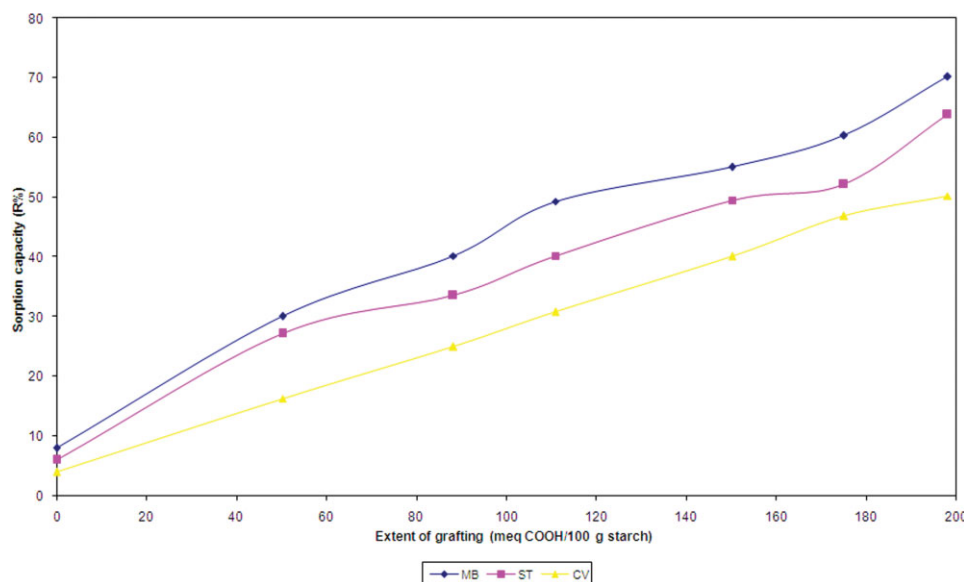


Figure 7 Relation between extent of grafting (meq COOH/100 g starch) and sorption capacity of dye adsorbed (R %) on PMCPS. Reaction conditions: PMCPS, 0.5 g; Dye conc., 100 mg/L; total volume, 100 mL; time, 12 h; temperature, 26°C ± 1°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

variable studied metal ions used i.e., Cu²⁺, Zn²⁺, Co²⁺, Cd²⁺, Pb²⁺; hence, Hg²⁺ 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, 1999,³¹ for the stability of various legends with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.

Recovery of starch

Figure 6 shows the comparison of original (unrecovered) starch and recovered one for poly (MAA)-crosslinked 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 198.2 meq COOH/100 g starch (pH 8) reduced the copper ion content to 69 ppm in comparison to 55 ppm unrecovered starch.

Dyes removal

The sorption capacity (dye uptake R %) was investigated using three types of basic dyes namely Methylene Blue (MB), Safranin T (ST) and Crystal Violet (CV). For each dye, it was followed the absorption maximum from UV-vis-spectrum located at 667, 520, and 590 nm, respectively. This was done under the optimized experimental conditions as shown in the experimental part.

On the other hand, to evaluate the influence of the carboxylic groups COOH on the capacity of dye removal of the prepared copolymers, different tests were carried out using the six copolymers (PMCPS 1 to PMCPS 6) having different carboxyl groups in addition to blank experiment with the polymer with zero carboxyl groups just for comparison. It seen from Figure 7 that, at any graft yield, the capacity of dyes removal follows the order: Methylene Blue (MB) > Safranin T (ST) > Crystal Violet (CV)

The amount of dye adsorbed for all dyes in questions increases by increasing the graft yields of the prepared copolymers. In other word, the basic dyes display the best interaction or sorption capacity with the copolymers in question containing higher carboxylic groups (i.e., interaction between carboxylic groups on the polymer and basic groups in the basic dyes). This was confirmed by the higher sorption capacities of the prepared copolymers that reach a maximum at 70.2 in case of Methylene Blue (MB), 63.8 for Safranin T (ST) and 50.2 for crystal violet (CV) at higher carboxyl contents i.e., 198.2 meq COOH/100 g starch. Moreover, Basicity, molecular size and stereochemistry of the dyes appeared to influence the amount of dye adsorbed on PMCPS.

CONCLUSIONS

By crosslinking followed by grafting with MAA, 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 basic dyes removal. At low carboxyl content 50.2 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 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 basic dyes from their aqueous solutions and follows the order: Methylene Blue (MB) > Safranin T (ST) > Crystal Violet (CV).

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