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

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ABSTRACT

Propelled starch(PG) was first cross linked with epichlorohydrin to obtain insoluble cross-linked pregelled starch(CPS). The latter was graft co polymerized with different amounts of Methacrylic acid (MAA) using potassium persulphate as initiator. This was done to obtain six levels of poly(MAA)-cross linked pregelled starch graft copolymers(PMCPS) having different graft yields(expressed as meq COOH/100g 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 expressed as (carboxyl contents) of PMCPS i.e. from PMCPS 1 to PMCPS 6; (b) Increasing the pH of the metal ions solution complex from 2-8; (c) increasing the starch dosage from 0.25 to 2.0 % based on total volume of the solution, then leveled off thereafter, (d) increasing the time of the reaction up to 20 minute then leveled off after that. On the other hand, Pb, Cd and Hg ions were also removed from their solutions with different extent according to their atomic size and reactivity. Further more, 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.

KEYWORDS

Pregelled starch;
Epichlorohydrin;
Cross-linking;
Methacrylic acid;
Grafted starch;
Heavy metal ions removal;
Dyes.

INTRODUCTION

It is well known that, heavy metal ions, organic compounds and 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]. So, 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 techniques[9] and adsorption procedure[10-13] 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. Among these, polysaccharides, such as chitin and chitosan[14], cyclodextrin[15] 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 the present work, our research team attempt to explore the adsorption behavior on the newly prepared poly (MAA)-cross linked pregelled starch graft copolymer (PMCPS) having different graft yields expressed as carboxyl contents(a point that has not been reported). The latter were prepared by grafting different amount of MAA onto cross linked 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 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 75^0C and pressure of 100mm Hg. It was stored at -10^0C until used. Epichlorohydrin, sodium chloride, potassium persulphate, hydrochloric acid, Nitric acid, sodium hydroxide, $CuSO_4.5H_2O$, $Pb(CH_3CO_2)_2.3H_2O$, $Hg(CH_3CO_2)_2$, and CdSO4 were reagent grade chemicals.

Preparation of cross-linked pregelled starch

100g pregelled starch was slurred in150ml water containing 1.5g sodium chloride and 8ml epichlorohydrin. To this slurry, 6g sodium hydroxide in 40ml water was added slowly over 30min. The mixture was stirred for 16hrs 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.

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

Six levels of poly (MAA)-cross linked pregelled starch graft copolymer with different graft yields (expressed as meq COOH/100g starch), 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 as shown in TABLE 1.

The graft polymerization reaction was carried out in 100ml stoppered flasks containing an aqueous solution of monomer(5,10,20,30,40 and 50 % based on

TABLE 1 : Preparation of poly(MAA)-cross linked pregelled starch graft copolymer having different graft yields (expressed as meq/COOH/100g starch)

Starch type	Methacrylic Acid concentration (based on weight of substrate)	Graft Yield (expressed as meq/ COOH/100g starch
PMCPS 1	5	50.5
PMCPS 2	10	88.2
PMCPS 3	20	110.9
PMCPS 4	30	150.2
PMCPS 5	40	175.1
PMCPS 6	50	198.2

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 (10g) and (40mmol/l) $K_2S_2O_8$ initiator were then added and the reaction mixture was mixed thoroughly. The total volume was adjusted to be 75ml. The contents were shaken occasionally during polymerization for 2hr at 60°C. After the desired reaction time, the flask contents were poured over 500ml 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 15min. at room temperature on magnetic stirrer, filtered and finally dried in an electric oven at 60°C for 2h. 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.

Reaction conditions

Cross linked pregelled starch, 10g; $K_2S_2O_8$, 40 mmol/L; material to liquor ratio, 1:7.5; Time, 2hr; and temperature, 60°C

N.B.

PMCPS 1: Poly (MAA)-cross linked pregelled starch graft copolymer with 50.5 meq COOH/100g starch; PMCPS 2: Poly (MAA)-cross linked pregelled starch graft copolymer with 88.2 meq COOH/100g 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/100g starch; PMCPS 5: Poly (MAA)-cross linked pregelled starch graft copolymer with 175.1 meq COOH/100g starch; PMCPS 6: Poly(MAA)-cross linked pregelled starch graft copolymer with 198.2 meq COOH/ 100g starch

Carboxyl contents

It was traced according to a reported method[19].

Heavy metal ions removal

An aqueous solution of copper ions (Cu 203 ppm) was prepared by dissolving 0.89g cupric sulfate ($CuSO_4$. $5H_2O$) in 1 litter distilled water. Poly (MAA)-cross linked pregelled starch graft copolymer (0.25-4.0% w/v) was then added to 100ml of copper solution, with continuous stirring at automatic shaker for 20min at room temperature (26°C±1.0) to form a complex with the metal ions. The grafted cross linked starch-heavy metal ions complex was then removed by filtration on centered glass funnel and the filtrate was used for the residual metal analysis by using Atomic absorption (Varian. A.A 200), Austria.

Under the above optimum condition in case of Cu, other heavy metal ions were prepared to compare the efficiency of metal removal with respect to the Cu as shown below:

Pb(203ppm), Cd(194ppm) and Hg(208ppm) solutions were prepared by dissolving 0.19g lead acetate Pb $(CH_3CO_2)_2.3H_2O$, 0.33 g mercuric acetate Hg $(CH_3CO_2)_2$, and 0.25 g cadmium sulfate $CdSO_4$ in(1 L) distilled water.

Recovery of the prepared copolymer

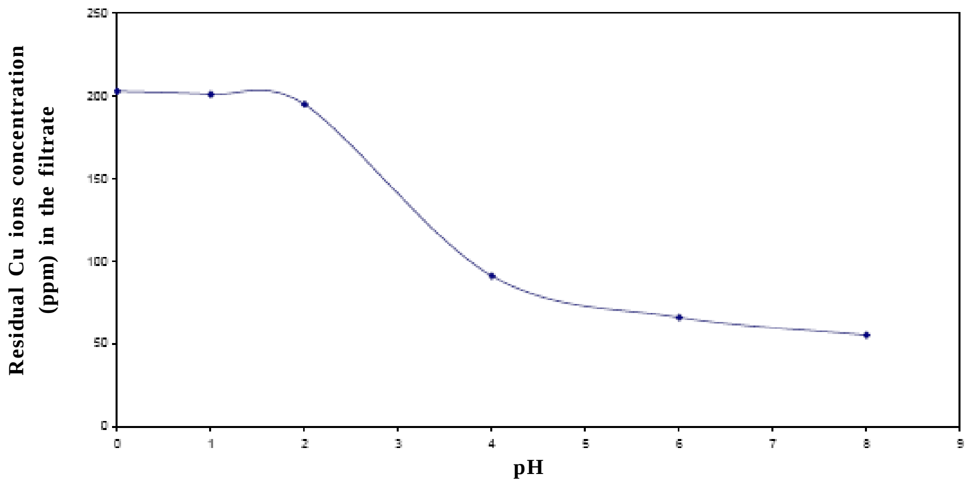
Poly (MAA)-cross linked starch graft copolymer (1g) at pH 8 used to remove copper ions was redispersed in distilled water (40ml), and the dispersion was adjusted to pH 2 by adding 1N HNO_3 solution. After stirring for 10 min, the dispersion was filtered. The starch residue was washed with water and readjusted 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.

Dyes removal

0.5g of Poly (MAA)-cross linked pregelled starch graft copolymer and 100 ml of an aqueous solution of dye(100mg/L) were placed in 125 glass-stoppered flasks without pH adjustment and automatically shaken for 12h 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.

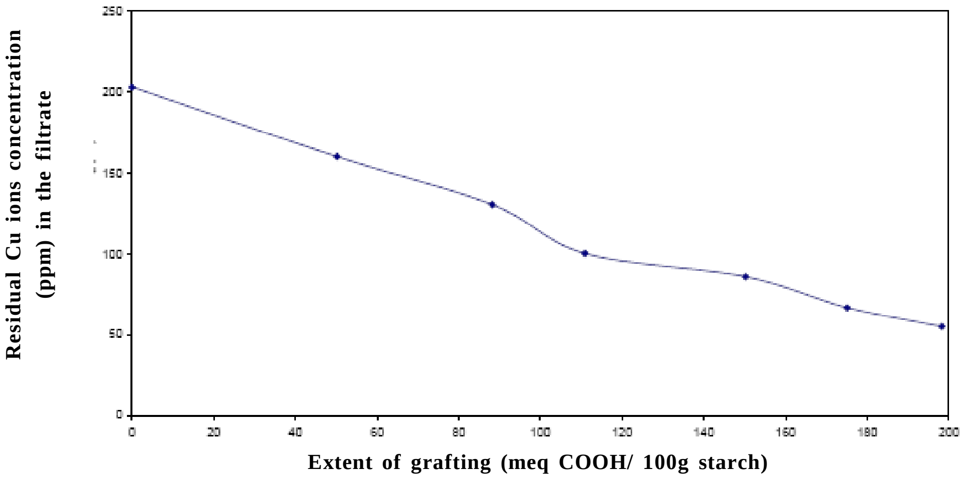
The sorption capacity was then calculated and expressed in percentage uptake (R in %), which represents the ration between the amount-adsorbed dye and the starting amount dye.

R% = Amount of dye adsorbed/ Total amount of dye×100



Reaction conditions: PMCPS, 2g; initial Cu conc., 203ppm; total volume, 100ml; carboxyl content, 198.2meq COOH/100g starch; time, 20min; temperature, 26°C±1°C.

Figure 1: The relation between residual Cu ion content and pH in the metal-copolymer complex solution



Reaction conditions: PMCPS, 2g; initial Cu conc., 203ppm; total volume, 100ml; pH, 8; time, 20 min; temperature, 26°C±1°C

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

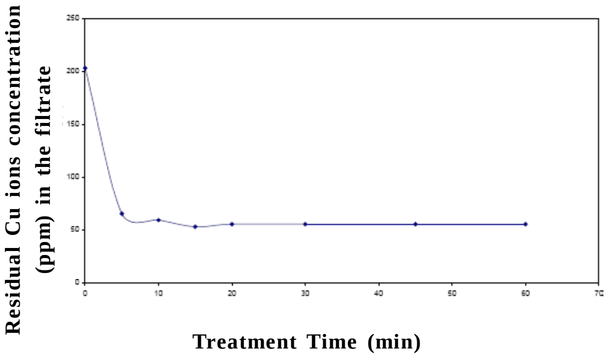
The basic dyes safranine T(ST), methylene blue (MB) and crystal violet(CV) (E. Merck) were used for dye removal on the prepared copolymer.

RESULTS AND DISCUSSION

Effect of pH

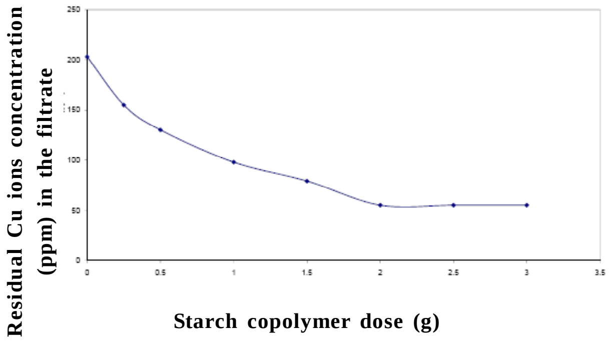
Figure 1 represents the effect of changing pH of poly(MAA)-cross linked pregelled starch graft copolymer (expressed as meq-COOH group/100g starch) on the Cu removal from its solution at fixed carboxyl content i.e. 198.2 meq COOH /100g starch. It is seen figure 1 that, for Cu removal, residual metal ion concentration in the filtrate decreased when pH increased from 1 to 8. This indicates that the metal ions in the solution interact more likely with the carboxyl groups of the copolymer at higher pH duo to the transformation of carboxyl groups from an acid form at lower pH to sodium salt form at higher one.

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 55 ppm in presence of it. Further more, the residual metal ion concentration decreases also 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.



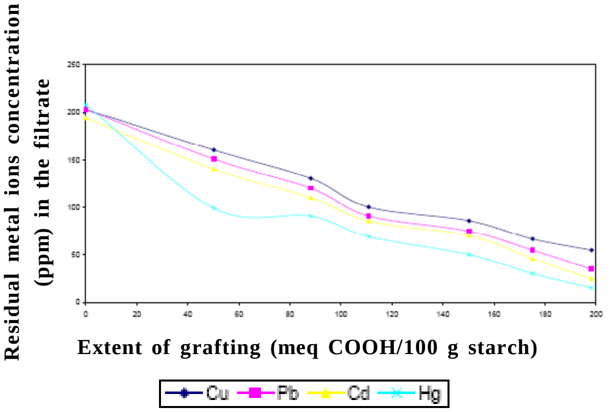
Reaction conditions: PMCPS, 2g; initial Cu conc., 203ppm; total volume, 100ml; carboxyl content, 198.2meq COOH/100g starch; pH, 8; temperature, 26°C±1°C

Figure 3: Effect of treatment time on the residual Cu ions removal using PMCPS



Reaction conditions: Initial Cu conc., 203ppm; total volume, 100ml; carboxyl content, 198.2meq COOH/100g starch; time, pH 8, 20 min; temperature, 26°C±1°C.

Figure 4: Effect of dosage of PMCPS on the residual Cu ions concentration (ppm) removal from metal-copolymer complex solution



Reaction conditions: PMCPS, 2g; initial metal ion conc., about 203ppm; total volume, 100ml; pH, 8; time, 20min; temperature, 26°C±1°C.

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

When the starch pH was 6 or 4, the residual Cu content in the filtrate decreased to 82ppm 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 (i.e. the starch did not show Cu binding activity i.e. not amenable.

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)-cross linked 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)-cross linked grafted starch copolymer increased. So, by increasing the carboxyl contents of the copolymer from 50.2 to 198.2 meq-COOH /100g 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)-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.

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)-cross-linked starch graft copolymer at optimum conditions observed before.

It is seen figure 3 that, the Cu removal was completed within the first 20min. induction period, which indicate that the copper ions rapidly form chelates or interaction with the carboxyl 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.

Effect of PMCPS dose used

When the dose of poly(MAA)-cross-linked pregelled starch graft copolymer added to the copper solution(203ppm Cu) was increased from 0.25 to 3.0% w/v, the residual Cu content in the filtrate decreased gradually(Figure 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 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)-cross-linked pregelled starch graft copolymers their graft yields ranged from(50.2-198.2meq COOH/100g 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.

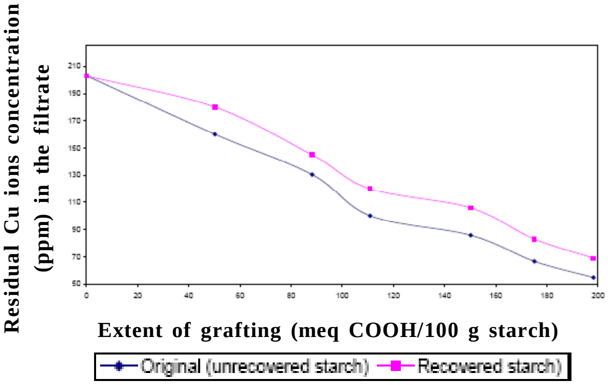
It is seen from figure 5 that, the residual amount of heavy metal ions removed is governed by the % carboxyl content(Graft yield) as well as the nature of metal ion used. So, when the carboxyl contents increased from 50.2-198.2 the residual removal of heavy metal increased irrespective of the nature of metal ion used. It is also seen that, the synthesized poly (MAA)-cross linked pregelled starch graft copolymers is more effective in removing Hg^{+2} than all other metal ions in question and follow the order:

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

This is in accordance with the results published by Khalil et al.[20] for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent transition metal ions. In addition to relative atomic size and reactivity.

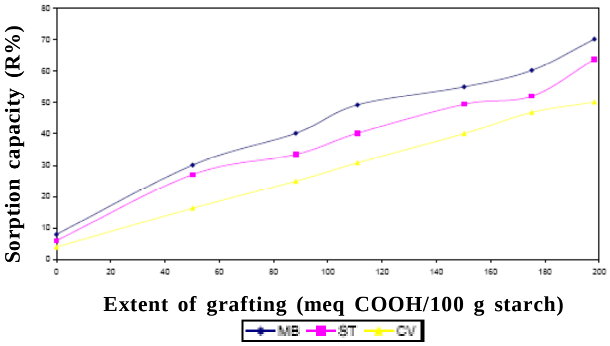
Recovery of starch

Figure 6 shows the comparison of original (unrecovered) starch and recovered one for poly (MAA)-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 198.2 meq COOH /100g starch (pH8) reduced the copper ion content to 69ppm in comparison to 55 ppm unrecovered starch.



Reaction conditions: PMCPS, 2g; initial Cu conc., 203ppm; total volume, 100ml; pH, 8; time, 20 min; temperature, 26^{O}C±1^{O}C.

Figure 6: The difference between original unrecovered starch and recovered one of PMCPS towards Cu ions removal from the metal-copolymer complex solution



Reaction conditions: PMCPS, 0.5g; Dye conc., 100mg/L; total volume, 100ml; time, 12hr; temperature, 26^{O}C±1^{O}C

Figure 7: Relation between extent of grafting (meq COOH/ 100 g starch) and sorption capacity of dye adsorbed (R %) on PMCPS

Dyes removal

The sorption capacity(dye uptake R%) was investigated using three types of basic dyes namely Methylene Blue(MB), Safranine T(ST) and Crystal Violet(CV). The measurement of each dye must be at the maximum wave length of each dye which was as follows: 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 figures 7 that, at any graft yield, the capacity of dyes removal follows the order: Methylene Blue (MB)> Safranine T(ST)>Crystal Violet (CV)

While by increasing the graft yields of the prepared copolymers, the amount of dye adsorbed for all dyes in questions increases. Or 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 Safranine T (ST) and 50.2 for crystal violet (CV) at higher carboxyl contents i.e. 198.2 meq COOH/10 g starch. Moreover, Basicity, molecular size and stereochemistry of the dyes appeared to influence the amount of dye adsorbed on PMCPS.

CONCLUSION

By cross linking 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(20min.) 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 basic dyes from their aqueous solutions and follows the order: Methylene Blue (MB)>Safranine T(ST)>Crystal Violet(CV).

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