



Trade Science Inc.

August 2007

Volume 2 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ, 2(2), 2007 [25-32]

Modification Of Carbohydrate Polymers Part 2: Grafting Of Methacrylamide Onto Pregelled Starch Using Vanadium-Mercaptosuccinic Acid Redox Pair

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Received: 4th April, 2007 ; Accepted: 9th April, 2007

ABSTRACT

Pregelled starch (PGS) as a reactive carbohydrate polymer has been chemically modified via graft co polymerization with methacrylamide (MAam) as a reactive monomer using vanadium-mercaptosuccinic acid redox pair as a new initiation system. This was done to maximize the graft yield and graft reaction efficiency percent and minimize the homopolymerization. The major factors affecting the polymerization reaction such as vanadium, mercaptosuccinic acid, MAam and sulphuric acid concentrations, liquor ratio as well as reaction time (duration) and temperatures have been studied systematically. The grafting parameters were studied with respect to graft yield and graft reaction efficiency percent as well as % homopolymerization. On the other hand, the newly prepared poly (MAam)-pregelled starch graft copolymers were characterized for heavy metal ions removal from their solutions. Based on the results obtained, appropriate conditions for grafting methacrylamide onto pregelled starch was established and the graft yield is higher under the following conditions: using 60 m mol/L Vanadium ion, 40 m mol/L mercaptosuccinic acid, 50 mmol/L sulphuric acid; 50% methacrylamide concentration (based on weight of substrate), liquor ratio, 7.5, reaction time, 90 min; and polymerization temperature, 35°C. Finally, the potential value of the resultant copolymers for heavy metal ion removal was assessed through measurements of critical properties such as removal of different heavy metal ions as well as durability.

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KEYWORDS

Grafting;
Pregelled starch;
Methacrylamide;
Heavy metals;
Durability.

INTRODUCTION

It is well known that starch is one of the most important naturally abundant polysaccharides and a low cost carbohydrate polymer. It is one of the few carbohydrate polymers that have been used extensively in industry. In recent years, particular attention has been directed to synthesize starch graft copolymers due to a great interest of synthesizing a new low cost-effective polymer^[1-8].

Choice of the initiator is one of the main controlling factors in the graft copolymerization reaction with respect to graft yield and graft reaction efficiency percent. Many researchers have studied the graft copolymerization onto starch with vinyl monomers initiated by ceric salts; due to the latter can form efficient redox system in presence of organic reductants^[9-10]. On the other hand, according to Hebeish et-al, poly (MAA)-starch graft copolymer is the main product of polymerization reaction only when starch was pre-swelled prior to grafting^[11]. Our previous studies have also disclosed that the precipitation technique of MnO₂ onto starch in presence of citric acid as activator induces the graft copolymerization onto starch without homopolymer formation^[12].

In this paper, synthesis of poly(methacrylamide)-pregelled starch graft copolymer is studied by using new initiation system namely vanadium-mercaptoposuccinic acid redox pair. The major factors affecting grafting reaction were studied systematically. This was done to establish the optimum conditions for producing grafted starch with higher graft yield and graft reaction efficiency percent. In addition, the application of the resultant copolymers for heavy metal ions removal was assessed via measuring the critical properties such as heavy metal ions removal as well as durability.

EXPERIMENTAL

Materials

Pregelged starch was kindly supplied by Egyptian starch and Glucose Manufacturing Company, Cairo Egypt. Ammonium metavanadate (E.Merck), mercaptosuccinic acid (Sigma), Sulphuric acid

(E.Merck), methacrylamide, ethyl alcohol, hydrochloric acid, sodium hydroxide, nitric acid, mercuric chloride, copper sulphate, zinc acetate, lead acetate, nickel chloride, and cobalt nitrate were reagent grade chemicals.

Polymerization procedure

The graft polymerization reaction was carried out in 100ml stoppered flasks containing an aqueous solution of monomer. 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 pregelled starch and calculated amounts of mercaptosuccinic acid, methacrylamide, and sulphuric acid solutions were added and the reaction mixture was mixed thoroughly. To initiate the reaction a known amount of ammonium metavanadate was added. The contents were shaken occasionally during polymerization. After the desired time interval, the flask contents were poured over 500 ml ethyl alcohol. At this end, a precipitate was formed which consisted of starch graft copolymer and the homopolymer (poly methacrylamide). The latter can be removed by washing with 400ml water-ethanol mixture (30:70) several times (for 15min.each) on the magnetic stirrer at room temperature, filtered and finally dried in an electric oven at 60°C for 3h. It was found experimentally that washing five times with a mixture of water/ethanol (30:70,v/v) is quite enough for complete homopolymer removal in physical mixtures of starch/poly(methacrylamide), that can be proven by tracing the nitrogen content of these mixtures after each wash.

Proof of grafting

This was done via measuring the nitrogen % of grafted samples by a well-known Kjeldahl method^[13]. three times for each samples, as well as their standard deviation. On other words, both the nitrogen % and the standard deviation for each sample were taken as an evidence of grafting onto pregelled starch as a carbohydrate polymer that is free from nitrogen groups as a starting substrate.

Characterization

The graft yield was traced by estimating the nitrogen% and the graft yield was calculated as follows

$$\text{Graft yield (\%)} = \frac{100(N(\%)6.07)}{100 - (N(\%)6.07)}$$

On the other hand, the graft reaction efficiency percent (G.R.E. %) was calculated as follows:

$$\text{G.R.E. (\%)} = \frac{\text{Graft yield (\%)}}{\text{Percent of monomer}} \times 100$$

$$\text{Homopolymer \%} = 100 - \text{GRE \%}$$

Heavy metal ions removal

Aqueous solutions of 0.05M of different metal ions were prepared and its pH was adjusted to the specific values. Poly(MAam)-pregelged starch graft copolymers (0.25 g) having different graft yields were put into a glass bottle containing 100 ml of metal salt solution and the mixture was occasionally shaken at magnetic stirrer for 24 hr at room temperature. After the desired contact time, the solutions were filtered and the residual metal ions concentration in the filtrate was estimated by using atomic adsorption.

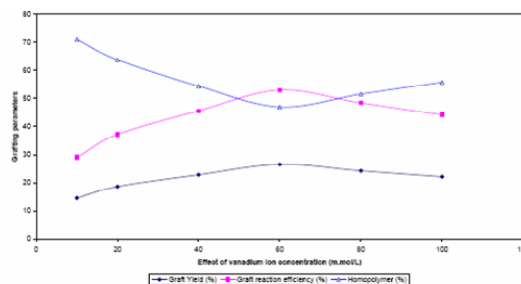
Desorption of metal ions

The treated poly(methacrylamide)-pregelged starch graft copolymers with metal ions solution was stirred with 50ml of 0.1N nitric acid for 2 hours at room temperature and then filtered. Then the metal ion in the filtrate was estimated.

RESULTS AND DISCUSSION

Effect of vanadium(V) ions concentration

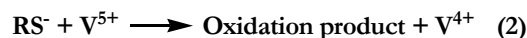
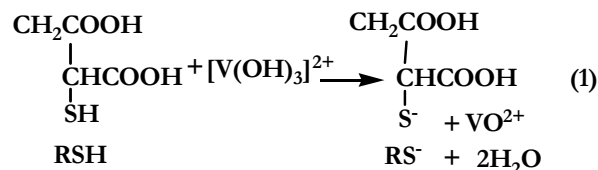
Figure 1 shows the relation between vanadium(V) ions concentrations and the grafting parameters (graft yield and graft reaction efficiency %) of poly(MAam)-pregelged starch graft copolymers. It is seen from the figure 1 that the graft yields and graft reaction efficiency % increased by increasing the vanadium ions concentration from 10 to 60mmol/L but decreased thereafter. The increase in grafting parameters may be due to increase in the formation of primary free radical species, that leads to an increment in the free radical concentrations, which participate mainly in graft initiation reaction. While on the other hand, the reduction in grafting parameter after 60mmol/L Vanadium ions may be explained in terms of oxida-



Reaction conditions: [Pregelged starch], 3g; [mercaptosuccinic acid], 40mmol/L; [MAam], (50% b.o.w.s.); [sulphuric acid], 50mmol/L; liquor ratio, 7.5; time, 90min, temperature, 35°C

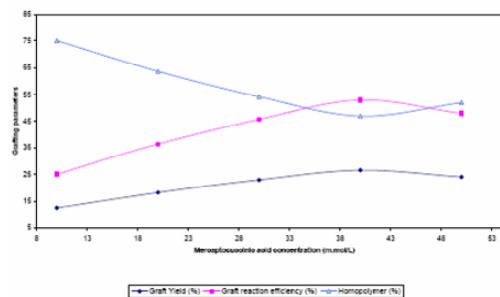
Figure 1: Effect of vanadium ion concentrations on the grafting parameters of poly (MAN) - pregelged starch graft copolymers

tive termination of growing grafted chain via presence of abundance of free radical species as shown below in equations (1) and (2):



Effect of mercaptosuccinic acid concentrations

Figure 2 shows the effect of varying mercaptosuccinic acid concentrations from 10-50mmol/L on



Reaction conditions: [Pregelged starch], 3g; [V⁵⁺], 60mmol/L; [MAam], (50 % b.o.w.s.); [sulphuric acid], 50mmol/L; liquor ratio, 7.5; time, 90 min, temperature, 35°C

Figure 2: Effect of mercaptosuccinic acid concentrations on the grafting parameters of poly (MAam)-pregelged starch graft copolymers

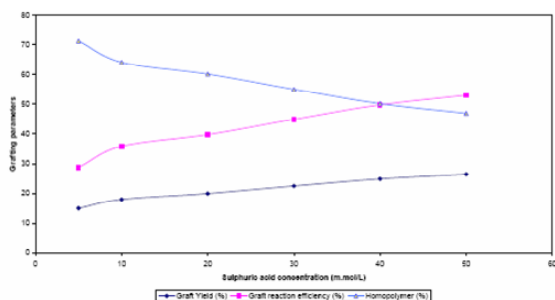
the grafting parameters of poly(MAam)-pregelged starch graft copolymers. It was observed that the graft yield and graft reaction efficiency % increased by increasing the mercaptosuccinic acid concentration up to 40mmol/L but decreased thereafter. The enhance-

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ment in grafting may be duo to the increase in the mercaptosuccinic acid concentration, which generates a larger number of free radical species at faster rate at which addition of monomer takes place. While the decrement in grafting parameters beyond the cited concentrations of mercaptosuccinic acid, may be attributed to the higher formation of homopolymer as evident from the data of homopolymer in figure 2.

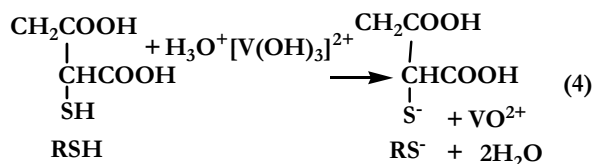
Effect of sulphuric acid concentration(hydrogen ions)

Figure 3 shows the effect of sulphuric acid



Reaction conditions : [Pregelged starch], 3g; [V⁵⁺], 60mmol/L; [mercaptosuccinic acid], 40mmol/L; [MAam], (50% b.o.w.s.); li-
quor ratio, 7.5; time, 90 min, temperature, 35°.

Figure 3: Effect of sulphuric acid concentration on the grafting parameters of poly (MAam)- pregelged starch graft copolymers

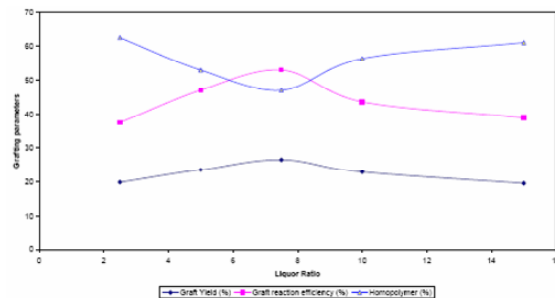


concentrations(H⁺) on the grafting parameters. Or on the other word, H⁺ concentration was changed from 5-50mmol/L. It was seen from Figure 3 that, the grafting parameters increase by increasing the sulphuric acid concentration within the studied range. This observation may be explained in the manner of, in the aqueous medium vanadium(V) present as VO²⁺ and by increasing hydrogen ion concentration it reacts with ions to give[V(OH)₃]²⁺ species(as shown below in equation 3), which is a better oxidant(littler 7 waters(1959). The latter species reacts with mercaptosuccinic acid producing primary free radical(as in equation 4). Thus, by increasing hydro-

gen ion concentration, the production of primary free radical species increases thereby leading to an increase in graft yield and graft reaction efficiency%.

Effect of liquor ratio

Figure 4 reveals the dependence of changing the



Reaction conditions: [Pregelged starch], 3g; [V⁵⁺], 60mmol/L; [mercaptosuccinic acid], 40mmol/L; [MAam], (50% b.o.w.s.); [Sulphuric acid], 50mmol/L; time, 90 min, temperature, 35°C.

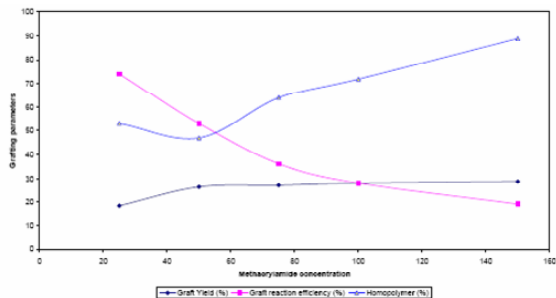
Figure 4: Effect of changing liquor ratio on the grafting parameters of poly (methacrylamide) - pregelged starch graft copolymer

liquor ratio on the grafting parameters of poly (methacrylamide)-pregelged starch graft copolymer. It is seen figure 5 that, increasing the liquor ratio up to 7.5 is accompanied by an increase in the grafting parameter, then decrease when the liquor ratio increases up to 15. So, it is logically to say that, of all liquor ratio studied, a liquor ratio 7.5 constitute the best. It is likely that at this particular liquor ratio a good grafting environment is created through intimate association of the monomer and initiator with the pregelged starch macromolecules. Once this is the case, greater availability of the monomer and initiator in the vicinity of the pregelged starch macromolecules occurs, thereby leading to higher grafting. Opposite situation is encountered at higher liquor ratio.

Effect of MAam concentration

Figure 5 shows the dependence of methacrylamide concentration on the grafting parameters of poly (methacrylamide)-pregelged starch graft copolymer. It is clear that there is a direct relation between the graft yield and monomer concentration within the range studied. This is truly duo to greater availability of the monomer molecules at higher methacrylamide concentration in the proximity of pregelged starch(grafting sites).

While on the other hand, with respect to G.R.E.,



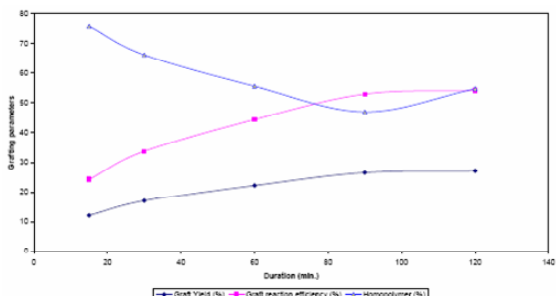
Reaction conditions : [Pregelged starch], 3g; $[V^{5+}]$, 60 m mol; [mercaptosuccinic acid], 40m mol/L; Material to liquor ratio, 7.5; [Sulphuric acid], 50m mol/L; time, 90 min, temperature, 35°C

Figure 5: Effect of methacrylamide concentrations on the grafting parameters of poly(MAN)-pregelged starch graft copolymers

the results reflect that G.R.E. decreases as the methacrylamide concentration increases, unlike the graft yield. This suggests that, beside its favorable effect on grafting reaction, the concentration of methacrylamide seems to have an outstanding effect on the homopolymerization reaction as evidenced by the down data in figure 5. Since the grafting reaction competes with the homopolymerization and since the concentration of methacrylamide acts more in favor of the latter, and the observed decrement in G.R.E. by increasing methacrylamide concentration can be explained.

Effect of polymerization time

Figure 6 shows the effect of reaction time(period) on the grafting parameters by changing the time of polymerization reaction from 15 to 120min. There is an increase in the graft yield and graft reaction efficiency percent as the reaction time increased from 15



Reaction conditions: [Pregelged starch], 3g; $[V^{5+}]$, 60mmol/L; [mercaptosuccinic acid], 40mmol/L; [Methacrylamide], 50 % (b.o.w.s.); Material to liquor ratio, 7.5; [Sulphuric acid], 50mmol/L; time, temperature, 35°C.

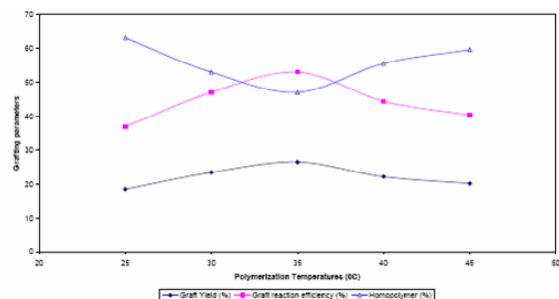
Figure 6: Effect of duration on the grafting parameters of poly(methacrylamide)-pregelged starch graft copolymer

to 90min. then leveled off by increasing the reaction time to 120min. This is seen irrespective of the polymerization temperature used. Increasing the grafting parameter from 15 to 90min. may be attributed to addition of greater number of methacrylamide molecules to the growing grafted chains. While leveling off grafting parameter after that, could be associated with depletion in monomer and initiator concentration as the reaction proceeds. Beside, it is may also likely that, during the course of grafting, pregelged starch undergoes modification and the modified starch derived thereof is not as amenable to grafting as the unmodified starch, a point which may be taken into consideration when explaining leveling off grafting.

Effect of polymerization temperature

The effect of polymerization temperature on the graft yield and graft reaction efficiency percent of poly(MAN)-pregelged starch graft copolymers has been shown in figure 7. However, the extent of grafting is determined by temperature; the extent of grafting increases by raising the polymerization temperature from 25°C to 35°C then decreases by raising the polymerization temperature thereafter. Results of grafting reaction efficiency are in accordance with those of grafting reaction.

The increment in grafting parameters is attributed to the increase in the production of primary free radical species with consequent increased in the number of grafting sites at polymer backbone, beside, increase in the rate of diffusion of Methacrylamide onto the polymer backbone. While,



Reaction conditions : [Pregelged starch], 3g; $[V^{5+}]$, 60mmol/L; [mercaptosuccinic acid], 40mmol/L; [Methacrylamide], 50% (b.o.w.s.); Material to liquor ratio, 7.5; [Sulphuric acid], 50mmol/L; time, 90min.

Figure 7 : Effect of polymerization temperature on the grafting parameters of poly(MAam)-pregelged starch graft copolymers

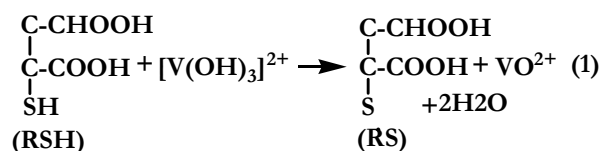
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the decrease in the grafting parameters after 35°C is attributed to the early termination of growing grafting chains at elevated polymerization temperature. Nevertheless, the possibility of greater amount of homopolymer formation at higher temperature and the adverse effect of this on the graft yield and grafting and graft reaction efficiency % cannot be ruled out.

Tentative mechanism of grafting

Based on the experimental results, the following tentative mechanism for grafting has been proposed:

The primary free radical species (RS·) is formed as follows:

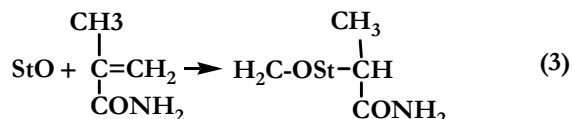


Once the free radical species (RS·) are formed, they produce pregelled starch macro radical St-O· via direct abstracting of hydrogen atoms from pregelled starch molecules. This reaction may be represented as follows:

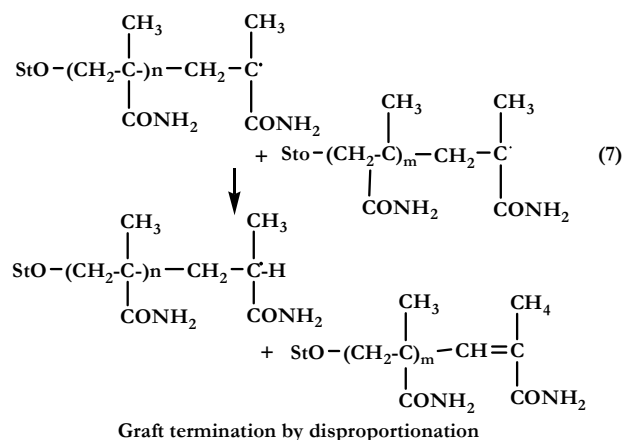
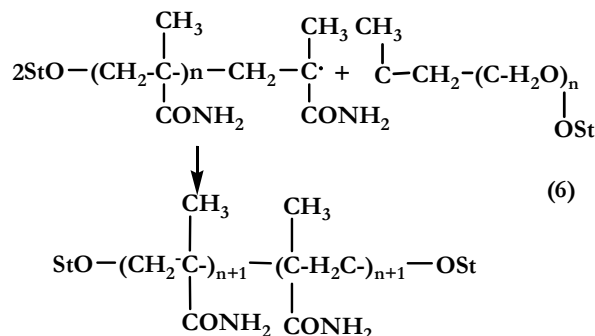
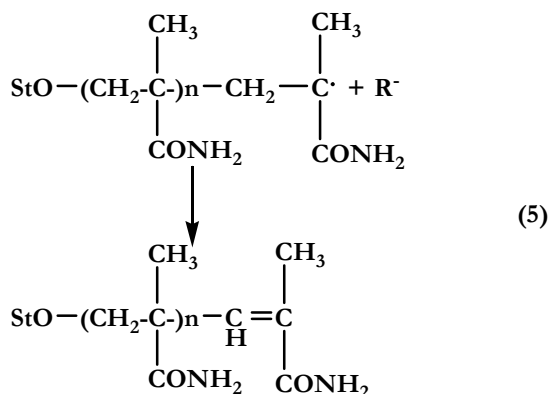
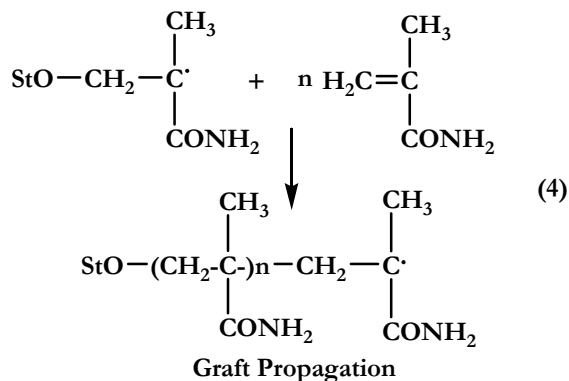


Where St-OH represent the pregelled starch molecule.

In the presence of methacrylamide as a vinyl monomer, the pregelled starch is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and pregelled starch with creation of a free radical on the monomer, i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto pregelled starch as follows:



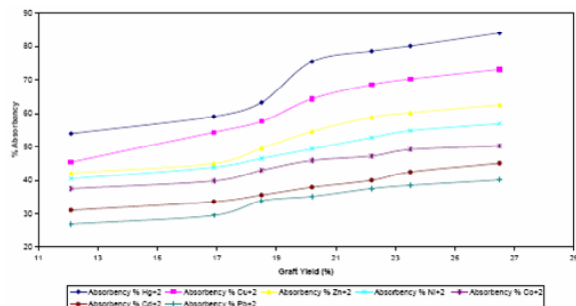
Finally, termination of the growing grafted chain may occur via reaction with the initiator, coupling or combination and disproportionation as follows:



CHARACTERIZATION

Heavy metal ions removal

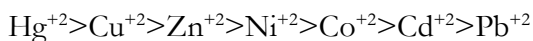
Poly (methacrylamide)- pregelled starch graft copolymers, their graft yields ranged from (12.1-26.5%) were used for removing different heavy metal ions from their solutions. The different heavy metal ions used were Hg^{+2} , Cu^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , Cd^{+2} and Pb^{+2} . The obtained results are set out in figure 8.



Reaction conditions : Poly (MAam)-pregelled starch graft copolymer, 0.25 g; Metal ion concentration, 0.05M; Time, 24hr; Temperature; room temperature; total volume, 100ml

Figure 8: Effect of changing the graft yields of poly(MAam)-pregelled starch graft copolymers on the % adsorbency of different heavy metal ions from their solution

It is seen from the figure that, the amount of heavy metal ions removed (expressed as % adsorbency) is governed by the % grafting as well as the nature of metal ion used. So, when the graft yields increased from 12.1-26.5%, the magnitude of removal of heavy metal increased irrespective of the nature of metal ion used. It is also seen that, the synthesized poly(methacrylamide) pregelled starch graft copolymers is more effective in removing Hg^{+2} than all other metal ions in question and follow the order:



This is in accordance with Irving-William, series(14) for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.

Durability

Poly(methacrylamide)-pregelled starch graft copolymer having 26.5% graft yield was used in adsorption and desorption of different metal ions several times up to 4 cycles at room temperature to ex-

amine their durability.

Figure 9 reflects the adsorbency of different metal ions on the above copolymer after four cycles (adsorption and desorption).

It is seen that:

- The adsorbed metal ions were easily desorbed by treatment with 0.1 M HNO_3 at room temperature.
- The adsorbed amount of the different metal ions decreases slightly after each washing cycle;

In other word, the decrease in adsorption capacity of the copolymer in question after each washing cycle may be due to solubility of some highly substi-

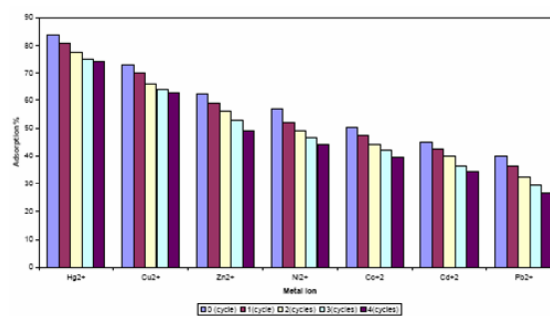


Figure 9: The Durability of poly (MAam)-pregelled starch graft copolymer

tuted derivatives ($CONH_2$) after each washing cycle.

CONCLUSIONS

Approximately 26.5% graft yield and 53% graft reaction efficiency as well as 47% homopolymerization were obtained when methacrylamide as a reactive monomer was graft copolymerized onto pregelled starch as a reactive substrate using a new redox initiation system namely vanadium-mercaptosuccinic acid redox pair. This was obtained by applying the following optimum grafting conditions: using 60mmol/L Vanadium ion, 40mmol/L mercaptosuccinic acid, 50mmol/L sulphuric acid; 50% monomer concentration (based on weight of substrate), liquor ratio, 7.5, reaction time, 90min; and polymerization temperature, 35°C. Furthermore, application of the synthesized copolymers for removal heavy metal ion in question follows the order: $Hg^{+2} > Cu^{+2} > Zn^{+2} > Ni^{+2} > Co^{+2} > Cd^{+2} > Pb^{+2}$

REFERENCES

- [1] Y.F.Cao, J.Z.Yang, Z.L.Liu; Journal of Chemical Industry and Engineering, **55**, 325-327 (2004).
- [2] F.E.Okieimen; Indian Journal of Chemical Technology, **10**, 197-200 (2003).
- [3] J.P.Gao, R.C.Tian, J.G.Yu, M.L.Duan; Journal of Applied Polymer Science, **53**, 1091-1102 (1994).
- [4] Kh.M.Mostafa, Abdul Rahem Samarkandy; Journal of Applied science Research, **1**(5), 335-340 (2005).
- [5] Kh.M.Mostafa, M.S.Morsy; Starch/Starke, **56**, 254-261 (2004).
- [6] Kh.M.Mostafa, A.A.El-Sanabary; Journal of Applied Polymer Science, **88**, 959-965 (2003).
- [7] M.I.Khalil Kh.M.Mostafa, A.Hebeish; Die Angewandte Macromoleculare Chemie., **213**, 14 (1993).
- [8] J.P.Gao, J.G.Yu, W.Wang; Journal of Applied Polymer Science, **68**, 1965-1972 (1998).
- [9] M.Z.Liu, R.S.Cheng, J.J.Wu; Journal of Polymer Science, A., **31**, 3181-3186 (1993).
- [10] H.Song, X.C.Ma; Specialty Petrochemicals, **20**, 30-33 (2003).
- [11] A.Hebeish, M.K.Beliakova, A.Bayazeed; J.Appl. Polym. Sci., **68**, 1709-1715 (1998).
- [12] Kh.M.Mostafa; J.Appl.Polym.Sci., **56**, 263 (1995).
- [13] A.I.Vogel; Elementary Practical Organic Chemistry, Part 3, 'Quantitative Organic Analysis, Longman Group Ltd', (London), 2nd Ed. 652 (1975).
- [14] H.Irving, R.J.P.Williams; Nature, **162**, 764 (1984); Chem.Rev., **56**, 271 (1958).