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## Synthesis of new low cost carbohydrate polymers for dyes removal from their solutions

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### ABSTRACT

Synthesis of new low cost natural carbohydrate polymers based on cross-linking pregelled starch-using epichlorohydrin as a cross-linking agent via graft copolymerization was studied in detail using potassium monopersulphate in presence of Fe<sup>2+</sup> redox pair as initiator. Different factors affecting the graft polymerization reaction such as potassium monopersulphate, ferrous ion, sulphuric acid and methacrylamide concentrations, material to liquor ratio in addition to polymerization time and temperature were studied systematically. This was done to prepare poly (MAam)-cross-linked pregelled starch graft copolymers having different graft yields and their uses for removal of different classes of dyes namely acid, disperse and basic dyes from their solutions. In addition, the grafting parameters were studied with respect to graft yield and graft reaction efficiency %. Based on the results obtained, appropriate conditions for grafting methacrylamide onto cross linked pregelled starch were established and the graft yield is higher under the following conditions: using 60mmol/L potassium monopersulphate as initiator, 40m mol/L ferrous ion concentration, 50mmol/L, sulphuric acid; material to liquor ratio 1:7.5; 50% methacrylamide concentration (based on weight of substrate), reaction time, 60 min; and polymerization temperature, 40°C. Finally, utilization of the resultant copolymers for dyes removal reflects the role of the copolymer as effective adsorbent for the removal of acid and disperse dyes from aqueous solutions, beside little or no affinity to basic dye. It would be interesting to use these copolymers as sorbent for the economic treatment of effluent containing particularly acid dyes.

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### KEYWORDS

Pregelised starch;  
Cross linking;  
Grafting;  
Methacrylamide;  
Dyes.

### INTRODUCTION

The wastewater disposed by textile and other industries is causing major hazards to the environment

and drinking water due to presence of a large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and color (dyes). Out of all such contaminants, the color seems to be the most undes-

ired one, as human eye can most easily recognize it. It is now a well-established fact that the coloration of water is mainly caused by dyes, which are generally toxic, non-degradable and stable. The stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures. Hence, their removal methods are selected with a great deal of care<sup>[1-8]</sup>. Formerly, conventional methods adopted by textile industries for removal of coloration from their disposal waste include, froth flotation, flocculating, etc. However, all such methods were found inefficient and incompetent. During the last decade, the attention has been shifted towards adsorption technique, which has emerged as one of the widely accepted methods for the removal of all such contaminants. The literature survey reveals that a large number of waste products have been utilized as adsorbent; these include peat<sup>[9,10]</sup> and bagasse fly ash<sup>[11,12]</sup>.

Starch is probably the most abundant and low cost natural commercially available biodegradable and renewable carbohydrate polymer. So, considerable research work have been reported so far that, chemical modification of starch or modified starch via the most important fascinating field i.e. grafting were done for improving the starch properties and enlarging the range of its utilization<sup>[13-21]</sup>.

In this work we attempt to explore the possibility of synthesizing a novel type of grafted starches based on pregelled starch. This was done first by cross linking the pregelled starch with epichlorohydrin as a cross linking agent in presence of NaOH, then graft the cross linked starch with methacrylamide as a reactive monomer using potassium monopersulphate in presence of  $Fe^{+2}$  redox pair as initiator. Different factors affecting the polymerization reaction were studied with respect to initiator, monomer and  $Fe^{+2}$  ion concentrations, material to liquor ratio polymerization time as well as polymerization temperature. Finally, the work was further extended to study the suitability of selected samples of the prepared poly (methacrylamide)-cross linked grafted starch having different graft yields (i.e. different  $CONH_2$  groups) for different classes of dyes removal.

## Experimental part

### 1. Materials

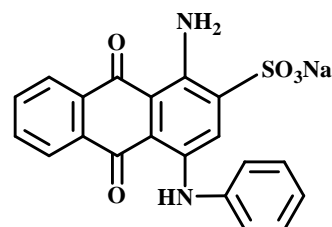
Pregelged starch was kindly supplied by Egyptian

starch and Glucose Manufacturing Company, Cairo Egypt. Epichlorohydrin, sodium chloride, methacrylamide, hydrochloric acid, potassium monopersulphate (Aldrich USA), ferrous sulphate (AR, BDH), ethyl and methyl alcohol were purchased from different suppliers.

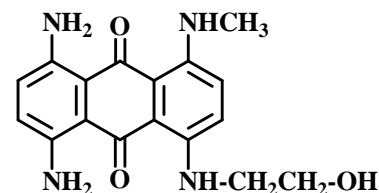
### 2. Dyes

Acid dye (C.I. Acid Blue 25), disperse dye (C.I. Disperse Blue 3) and basic dye (C.I. Basic Blue 3) were commercial products and used without purification.

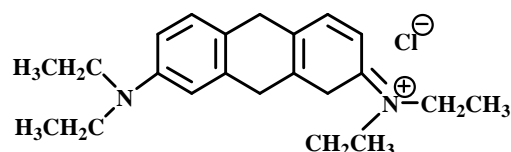
#### Dyes structure



C.I. Acid blue 25



C.I. Disperse blue 3



C.I. Basic blue 3

#### Adsorption procedure

Sorption capacities of poly (methacrylamide) cross-linked pregelled starch having different graft yields expressed as N % was determined by batch method as follows:

The polymer 0.25g was mixed with 4mL of a NaCl 0.1mol/L aqueous solution of the dye (100mg/L) in a tightly closed flask that was shaken for 24hour at room temperature. The residual concentration of the dye solute was determined by spectrophotometry.

The sorption capacity was then calculated and ex-

## Full Paper

pressed in percentage uptake (R in %), which represents the ration between the amount-adsorbed dye and the starting amount dye.

$$R\% = \frac{\text{amount of dye adsorped}}{\text{total amount of dye}} \times 100$$

### Preparation of cross-linking of pregelled starch

100g pregelled starch was slurred in 150mL 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 16 hrs at room temperature. The slurry now containing a highly 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.

### Polymerization procedure

The graft polymerization reaction was carried out in 100 mL 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 cross-linked pregelled starch and calculated amounts of sulphuric acid and ferrous sulphate were added and the reaction mixture was mixed thoroughly. To initiate the reaction a known amount of potassium monopersulphate solution was added. The contents were shaken occasionally during polymerization. After the desired reaction time, the flask contents were poured over 500mL of ethyl alcohol where a precipitate was formed that consisted of cross-linked pregelled starch graft copolymer and the homopolymer. The homopolymer, poly (methacrylamide), was removed by washing with 500 mL 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.

### 1. Evidence of grafting

This was done via measuring the nitrogen % of the grafted samples by a well-known Kjeldahal method<sup>[22]</sup> three times for each sample, as well as their standard deviation. On other words, both the nitrogen % and standard deviation for each sample were taken as an evidence of grafting onto cross-linked pregelled starch that is free from nitrogen groups as a starting substrate.

### 2. Characterization

The graft yield was traced by estimating the nitrogen content (%) and the graft yield was calculated as follows:

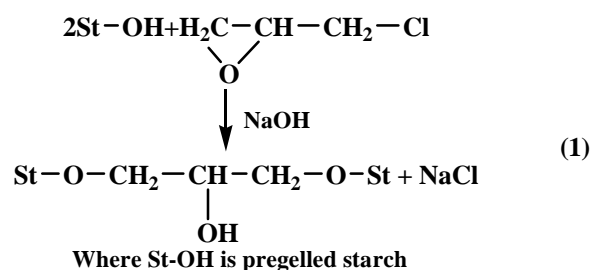
$$\text{Graft yield (\%)} = \frac{100(N\%), 6.07}{100 - (N\%), 6.07}$$

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

$$\text{G.R.E. (\%)} = \frac{\text{graft yield (\%)}}{\text{percent of monomer based on weight of starch (bows)}} \times 100$$

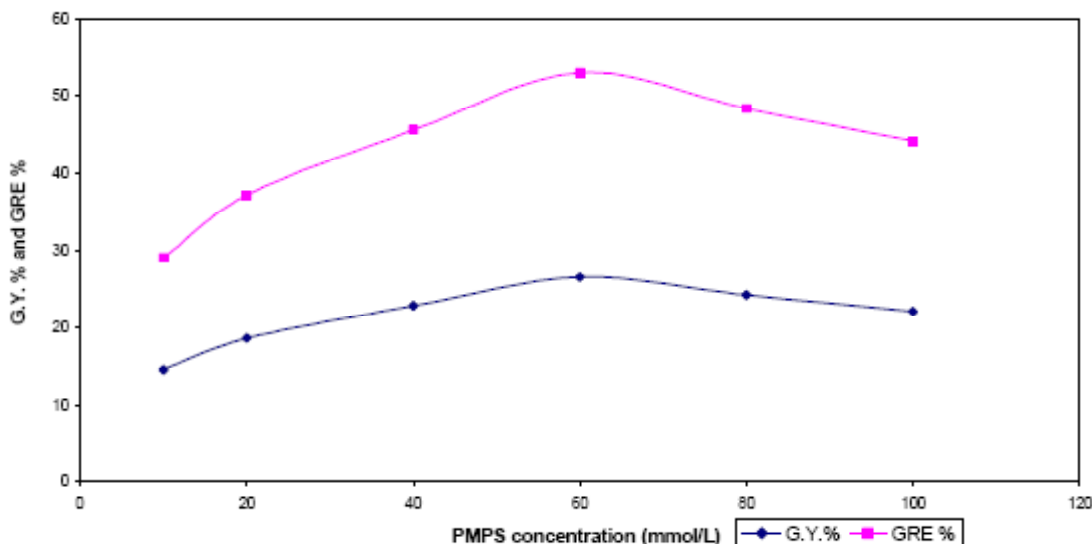
## RESULTS AND DISCUSSION

Pregelled starch was first cross-linked with epichlorohydrin in presence of sodium hydroxide to yield insoluble cross linked pregelled starch as follows:

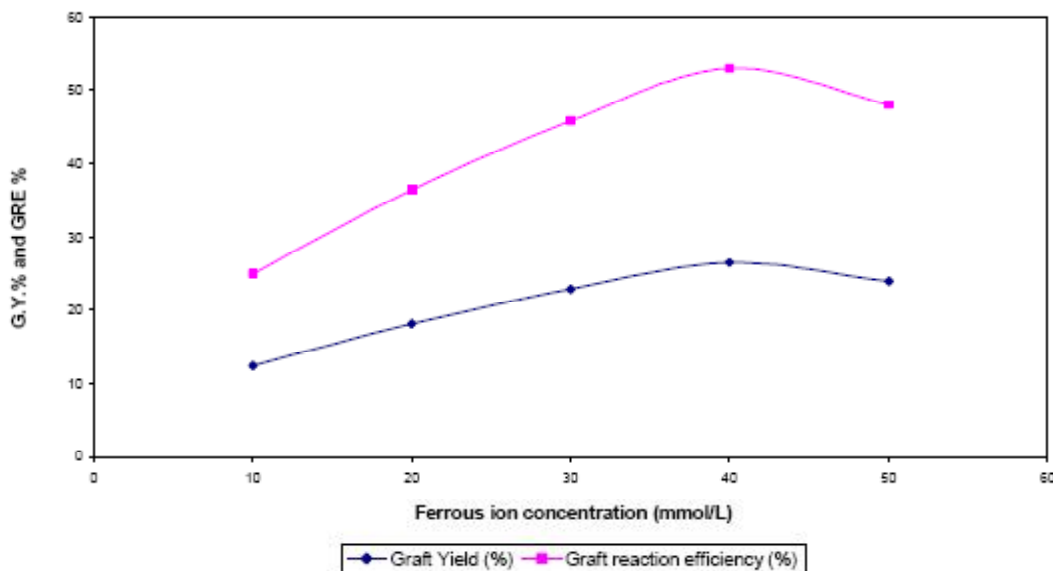


### 1. Potassium monopersulphate concentration (PMPS)

Figure 1 shows the effect of potassium monopersulphate (PMPS) concentration on the grafting parameters (graft yield and graft reaction efficiency %) of poly (MAAm)-crosslinked pregelled starch graft copolymers. Figure 1 shows that within the range studied, increasing PMPS concentration from 20 to 60mmol/L is accompanied by an increment in the graft yield, but beyond this concentration the graft yields decrease gradually. This is in agreement with the results of the graft



**Figure 1: Effect of PMPS concentration on GY % and GRE % of poly (MAAm)-cross linked pregelled starch graft copolymer; Reaction conditions: Cross linked pregelled starch, 3g;  $Fe^{2+}$ , 40 mmol/L; Sulphuric acid, 50mmol/L; Material to liquor ratio, 1:7.5, Methacrylamide, 50% based on weight of substrate; time, 60 min; temperature, 40°C**

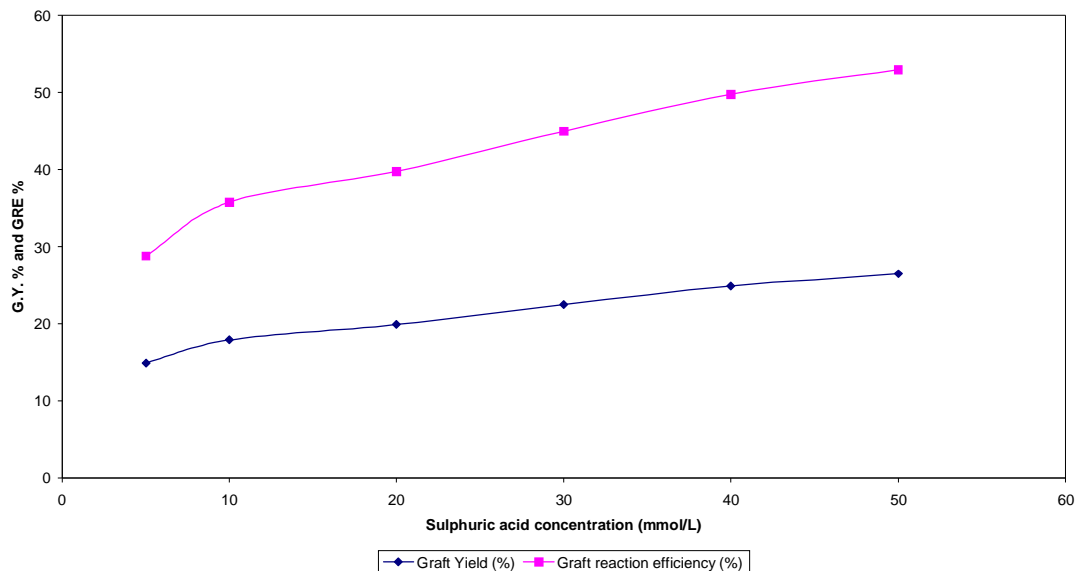


**Figure 2: Effect of ferrous ion concentration (mmol/L) on the G.Y. % and GRE % of poly (MAAm)-cross-linked pregelled starch graft copolymer; Reaction conditions: Cross-linked pregelled starch, 3g; PMPS, 60mmol/L; Sulphuric acid, 50mmol/L; Material to liquor ratio, 1:7.5, Methacrylamide, 50% based on weight of substrate; time, 60 min; temperature, 40°C**

reaction efficiency that shows a maximum value of about 52% at 60mmol/L potassium monopersuphate concentrations.

The increase in grafting parameter may be due to the progressive reduction of potassium monopersuphate by ferrous ion producing sulphate-ion radicals and hydroxyl free radicals that attack pregelled starch molecule creating more free radicals species that partici-

pate mainly in graft initiation. While on the other hand, the reduction in grafting parameter after 60mmol/L PMPS may be explained in terms of; (a) self-termination of growing grafted chain via presence of abundance of free radical species and (b) presence of excess of  $Fe^{3+}$  ions causes termination of grafted chain<sup>3</sup> due to it has been known as an ideal retarder of free radical polymerization<sup>[23-25]</sup>.



**Figure 3: Effect of sulphuric acid concentration on the G.Y.% and GRE% of poly (MAam)-cross linked pregelged starch graft copolymer;** Reaction conditions: Cross linked pregelged starch, 3g; PMPS, 60 mmol/L;  $\text{Fe}^{2+}$ , 40mmol/L; Material to liquor ratio, 1:7.5, Methacrylamide, 50% based on weight of substrate; time, 60min; temperature, 40°C

## 2. Ferrous ion concentration

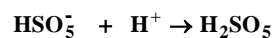
Figure 2 shows the effect of  $\text{Fe}^{2+}$  ion concentrations on the graft yield and graft reaction efficiency percent of poly (MAam)-cross-linked pregelged starch graft copolymers. Obviously increasing the  $\text{Fe}^{2+}$  concentrations from 10 to 40mmol/L is accompanied by an increase in the grafting parameters, after that the grafting parameters decrease.

The enhancement in grafting may be due to the increase in  $\text{KHSO}_5/\text{Fe}^{2+}$  concentration adduct which undergoes decomposition at pregelged starch surface resulting in generation of number of free radical species at faster rate at which addition of monomer takes place. While on the other hand, the decrease in grafting may be attributed to the excess of  $\text{Fe}^{3+}$  ion produced during disproportionation of  $\text{KHSO}_5/\text{Fe}^{2+}$  couple that retards the radical polymerization reaction<sup>[23-25]</sup>.

## 3. Effect of sulphuric acid concentration

Figure 3 shows the effect of sulphuric acid concentrations on the grafting parameters. It was found from the above figure that, the grafting parameters increase by increasing the concentration of an acid within the range studied. Increasing the grafting parameters with increasing the acid concentration may be due to increasing the concentration of the reactive species that result

in high production of primary free radical species as well as the ability of these radical species to react with other ingredient (s) rather than starch.

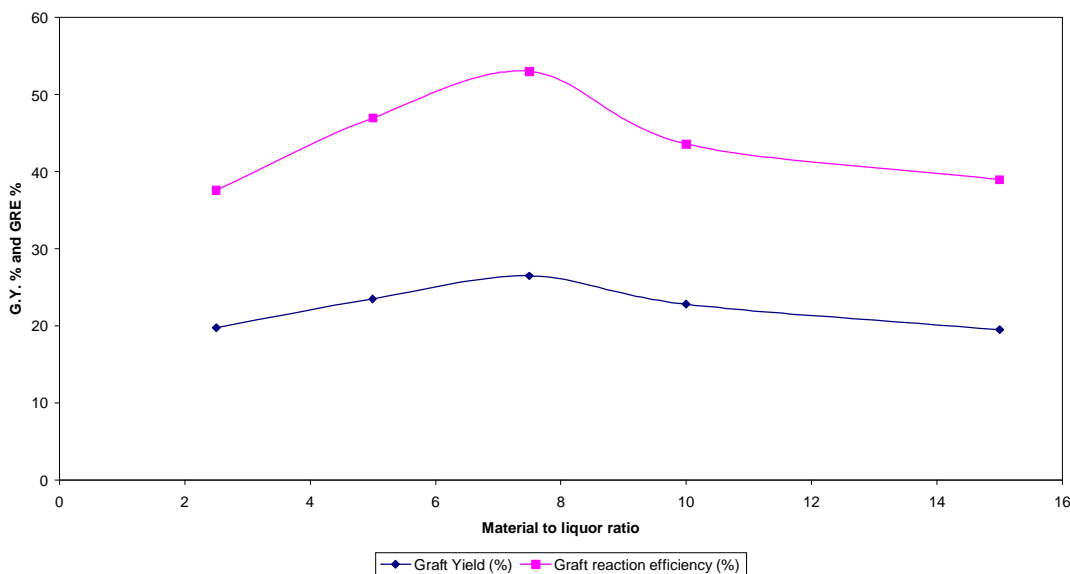


## 3. Material to liquor ratio

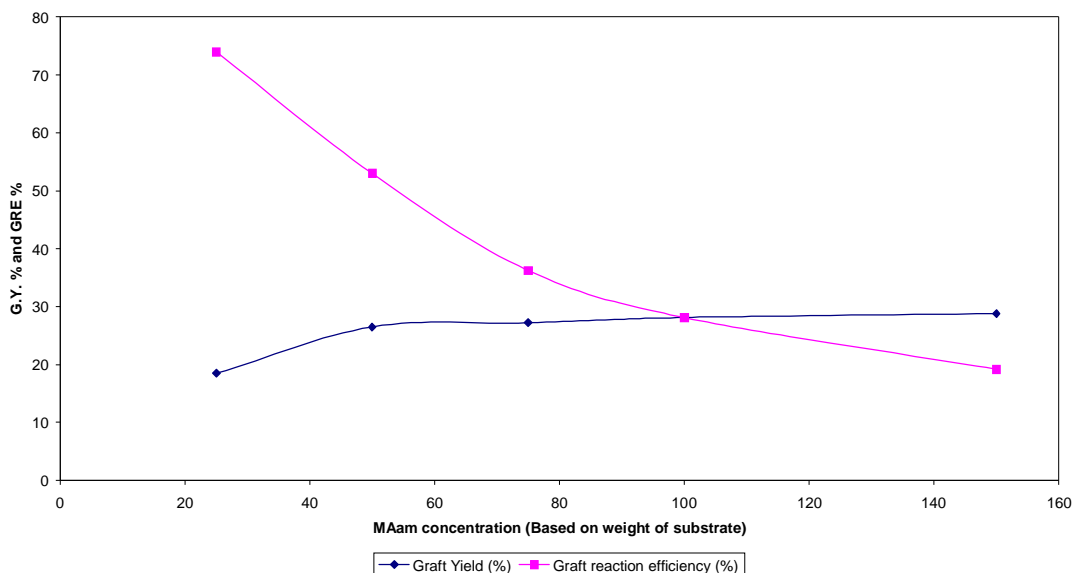
Figure 4 reveals the effect of changing the material to liquor ratio on the graft yield and graft reaction efficiency of poly (methacrylamide) - cross-linked pregelged starch graft copolymer. Figure-4 shows also that, increasing the material to liquor ratio up to 1:7.5 is accompanied by an increase in the grafting parameter, then decreases when the liquor ratio increases up to 1:15. So, it is logically to say that, of all liquor ratio studied, a material to liquor ratio 1:7.5 constitute the best ratio. 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 material to liquor ratio.

## 5. Effect of MAam concentration

Figure 5 shows the dependence of methacrylamide



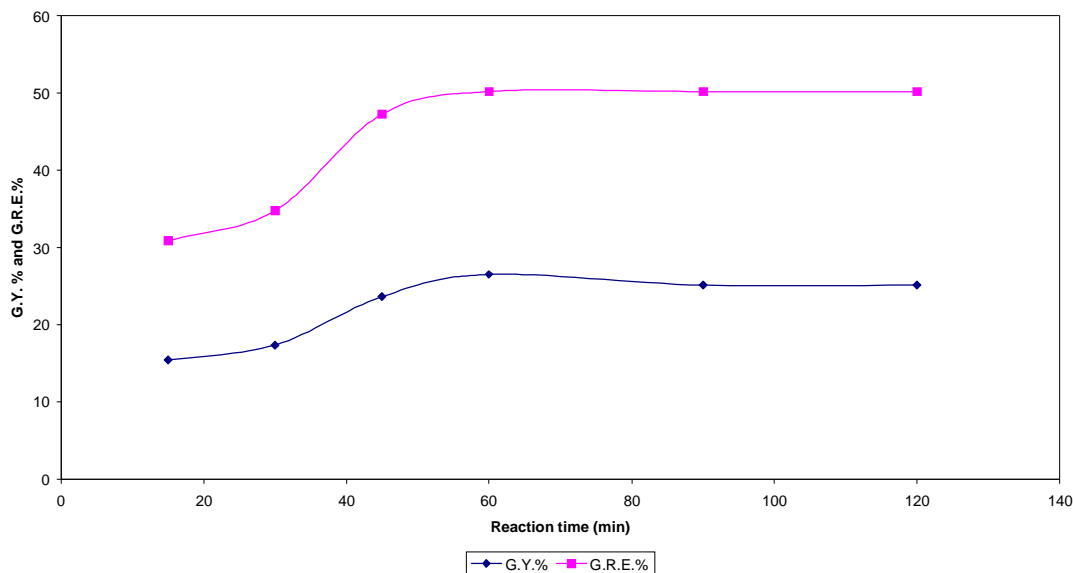
**Figure 4: Effect of material to liquor ratio on the G.Y.% and GRE% of poly (MAam)-cross linked pregelged starch graft copolymer; Reaction conditions: Cross linked pregelged starch, 3g; PMPS, 60mmol/L; Fe<sup>2+</sup>, 40mmol/L; sulphuric acid, 50mmol/L; Methacrylamide, 50% based on weight of substrate; time, 60 min; temperature, 40°C**



**Figure 5: Effect of MAam concentration on the G.Y. % and GRE % of poly (MAam)-cross linked pregelged starch graft copolymer; Reaction conditions: Cross linked pregelged starch, 3g; PMPS, 60mmol/L; Fe<sup>2+</sup>, 40mmol/L; sulphuric acid, 50mmol/L; Material to liquor ratio, 1:7.5, time, 60 min; temperature, 40°C**

concentration on the graft yield and graft reaction efficiency % of poly (MAam)-cross-linked pregelged starch graft copolymer. It is clear from the figure that, there is a direct relation between the graft yield and monomer concentration within the range studied. This is truly due to greater availability of the monomer molecules at higher methacrylamide concentration in the proximity of pregelged starch.

While on the other hand, with respect to G.R.E., 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 homo polymerization reaction. Since the grafting reaction competes with the homopolymerization and since the con-



**Figure 6: Effect of polymerization time on the G.Y. % and GRE % of poly (MAam)-cross linked pregelled starch graft copolymer; Reaction conditions: Cross linked pregelled starch, 3g; PMPS, 60mmol/L;  $Fe^{2+}$ , 40mmol/L; sulphuric acid, 50mmol/L; Material to liquor ratio, 1:7.5; Methacrylamide, 50% based on weight of substrate; temperature, 40°C**

centration of methacrylamide acts more in favor of the latter, and the observed decrement in G.R.E. by increasing methacrylamide concentration can be explained.

### 6. Effect of polymerization time

Figure 6 shows the effect of reaction time (period) on the grafting parameters by changing the time of reaction from 15 to 120 min. It is seen from figure-5 that, there is an increase in the graft yield and graft reaction efficiency percent as the reaction time increased from 15 to 60 min. then leveled off by increasing the reaction time to 120 min. Increasing the grafting parameter from 15 to 60 min. 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 may also be likely that, during the course of grafting, pregelled 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.

### 7. Effect of polymerization temperature

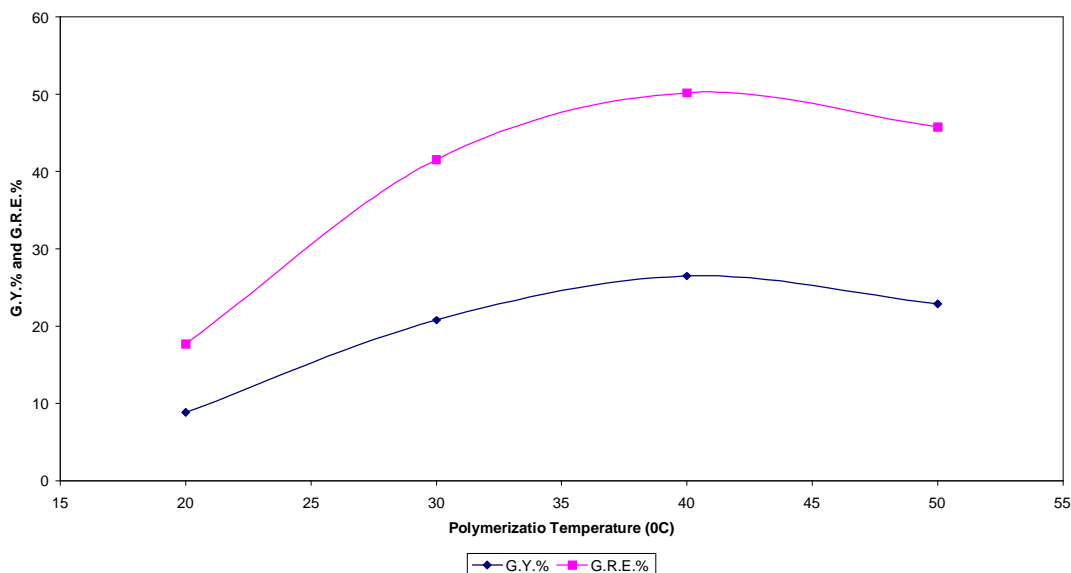
The effect of polymerization temperature on the graft yield and graft reaction efficiency percent of poly

(MAam)-pregelled 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 20°C to 40°C then decreases by raising the polymerization temperature to 50°C. Results of grafting reaction efficiency are in accordance with those of grafting reaction.

This behavior may be explained on the basis of the fact that with increase in temperature, the rate of production of primary free radicals species increase which generate the grafting sites at greater rate thereby increasing grafting. Beside the favorable effect of temperature (up to 40°C) on grafting could be ascribed to:

1. Better decomposition of the redox system, giving rise to more free radicals,
2. Increased mobility of methacrylamide molecules;
3. Greater swell ability of the pregelled starch;
4. Higher diffusion of MAN onto the pregelled starch structure, and;
5. Higher rate of initiation and propagation of the grafted chain.

While on the other hand, the lower grafting is observed at 50°C, perhaps, due to faster termination rate. 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

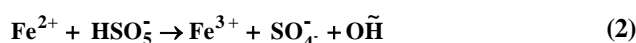
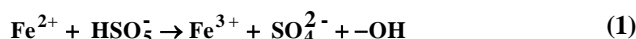


**Figure 7: Effect of polymerization temperature on the G.Y. % and GRE % of poly (MAAm)-cross linked pregelled starch graft copolymer; Reaction conditions: Cross linked pregelled starch, 3g; PMPS, 60mmol/L; Fe<sup>2+</sup>, 40mmol/L; sulphuric acid, 50mmol/L; Material to liquor ratio, 1:7.5; Methacrylamide, 50% based on weight of substrate; Time, 60min**

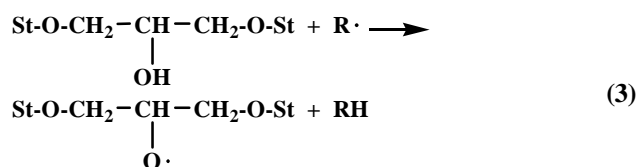
graft reaction efficiency % cannot be ruled out.

### Tentative mechanism for grafting

The presence of ferrous ion (Fe<sup>2+</sup>) in the polymerization medium with potassium monopersulphate (KHSO<sub>5</sub>) produces sulphate and hydroxyl ions free radicals species (R·), which occur most probably according to the mechanism, suggested by equations. (1) and (2):



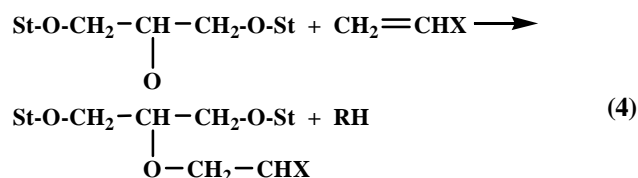
Once the free radical species (R·) are formed, they produce cross-linked pregelled starch macro radical St-O· via direct abstracting of hydrogen atoms from hydroxyl group. This reaction may be represented as follows:



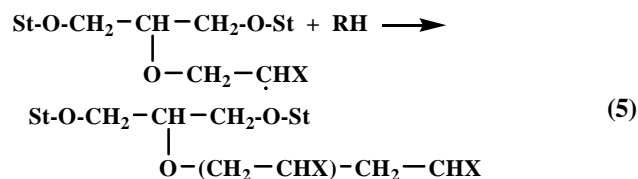
Where  $\begin{array}{c} \text{St-O-CH}_2-\text{CH}-\text{CH}_2\text{-O-St} \\ | \\ \text{OH} \end{array}$  represents the cross-linked pregelled starch molecule.

In the presence of synthetic vinyl monomer the cross

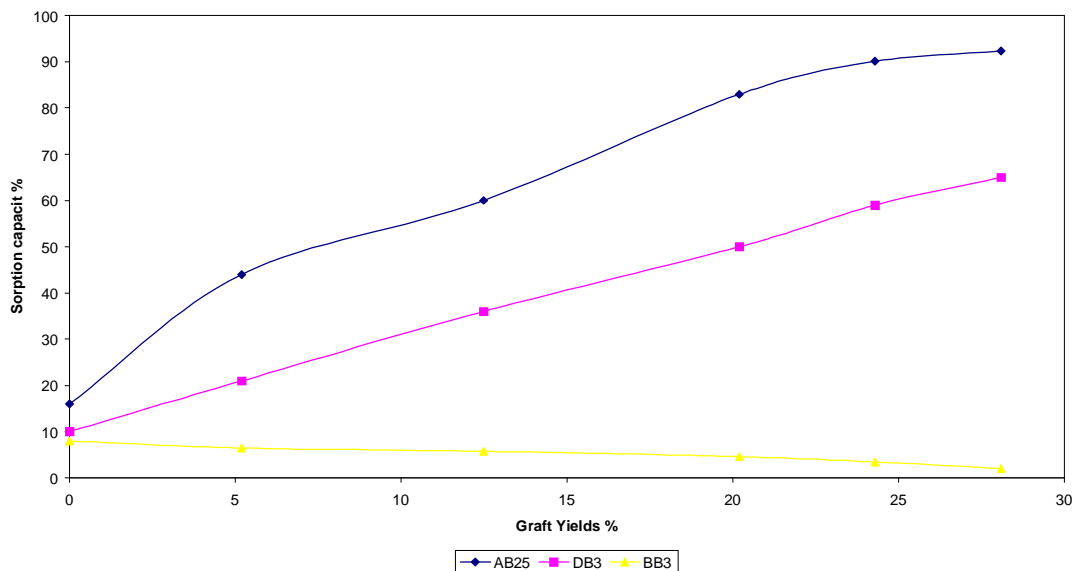
linked pregelled starch is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and pregelled starch with creation of a free radical on the monomer, i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting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



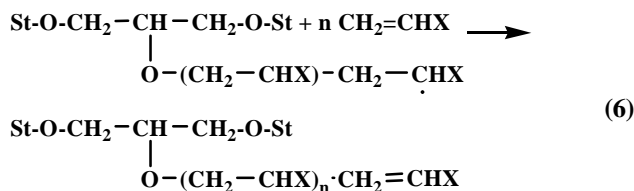
Subsequent addition of monomer molecules to the initiated chain leads ultimately to the cross-linking pregelled starch graft copolymer. The proposed interaction scheme of propagation and termination of grafting may be presented as follows:







**Figure 8:** Effect of varying graft yield of poly (MAam)-cross linked pregelged starch graft copolymers on the sorption capacity of the aforementioned dyes; Reaction conditions: 0.25g polymer; 4mL NaCl 0.1mol/L; 100mg/L Dye; contact Time; 24 hour at room temperature



### Characterization of the prepared copolymer in dyes removal

It is well known that the adsorption on a solid takes place in three stages: (a) external diffusion where the mass transfer by diffusion of the adsorbate molecules from the bulk fluid phase through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid; (b) internal diffusion where the transfer of the adsorbate to the interior of the particle by the migration of the adsorbate molecules from the relative small external surface of the adsorbent to the surface of the pores within each particles; and (c) the diffusion of the adsorbate molecules through the pores molecules.

The sorption capacity (dye uptake R%) is investigated using three types of dyes having anionic dye like acidic dye group (C.I. Acid blue 25), cationic dye like basic dye group (C.I. Basic blue 3) as well as nonionic dye like disperse dye (C.I. Disperse blue 3) as shown in dye structures. This was done under the optimized

experimental conditions as shown in the experimental part.

On the other hand, to evaluate the influence of the variation of the graft yield of the prepared copolymer on the sorption capacity, different tests were carried out using five copolymers having different graft yield in addition to crosslinked pregelged starch as a blank substrate having zero amide groups prior to grafting just for comparison.

Figure 8 shows the sorption capacity (expressed as percentage uptake) of acid, disperse and basic dyes on poly (methacrylamide) cross-linked pregelged starch having different amide groups and the blank one.

It is seen from figures 8 that, at any graft yield, the sorption capacity follows the order:

**Acid Dye (AB25) > Disperse Dye (DB3) > Basic dye (BB3)**

While by increasing the graft yields of the prepared copolymers, the sorption capacities for both acid and disperse dyes increases. In other words, the acid dye (AB25) displays the best interaction or sorption capacity with the polymers in question containing varying amide groups (i.e. interaction between amide groups on the copolymer and sulfonic acid groups in the acid dye). This was confirmed by the higher sorption capacities of the prepared copolymers that reach a maximum at 92.3% at higher graft yield. In addition to hy-

drogen bonding between amide groups of the polymer network and the function groups present in the dye. On the other hand, the sorption capacity of the copolymer with basic blue dye (BB3) shows a little or no interaction due to the presence of cationic functions groups that are not efficient for dye-polymer interaction. Furthermore, by increasing the graft yield in case basic dye sorption, the sorption capacity decreases, this may be attributed to the higher amount of the amide groups, which are not efficient for dye polymer interaction as shown above. While, on the other hand, disperse dye sorption lies in between and follows the same trend with acid dye but with lesser extent.

### CONCLUSIONS

Poly (methacrylamide)-cross linked pregelled starch having different graft yields are synthesized and characterized by measuring the nitrogen % for proves grafting. These copolymers are effective adsorbents for the removal of acid dyes from aqueous solutions and follow the order: Acid dye (AB25)>Disperse dye (DB3)>Basic dye (BB3). It would be interesting to use these copolymers as sorbent for the economic treatment of effluent containing acids.

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