

# Removal of Basic Dyes from Aqueous Medium Using Novel Poly(MAA)-Cross Linked Pregelled Starch Graft Copolymer

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**ABSTRACT:** Wastewater from textile industries may contain a variety of dyes that have to be removed before their discharge into waterways. For this purpose, pregelled starch (PG) as one of the most abundant biodegradable carbohydrate polymer was first cross linked with epichlorohydrin to obtain insoluble cross-linked pregelled starch (CPS). The latter was graft copolymerized 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/100 g starch) with increasing order and designated as (PMCPs 1 to PMCPs 6). The latter copolymers were used to remove basic dyes namely (safranin T, methylene blue, crystal violet) from their solution and filtered to form polymer–dyes complex. Major factors affecting the

dyes removal such as dye concentration, pH, polymer dose, treatment time, agitation speed, and extent of grafting were studied in detail. It was found from the obtained results that; the % dye removal increased by (a) increasing the dye concentration and pH within the range studied; (b) increasing the agitation speed until  $\geq 40$  rpm then leveled off thereafter; (c) increasing the polymer dosage from 0.25 to 3.0 g/L then leveled off thereafter; (d) increasing the time of the reaction up to 60 minute then leveled off after that; and (e) increasing the extent of grafting of PMCPs i.e., from PMCPs 1 to PMCPs 6. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2728–2735, 2010

**Key words:** pregelled starch; epichlorohydrin; cross-linking; methacrylic acid; grafted starch; activated carbon; dyes removal

## INTRODUCTION

It is well-known that, dyes, organic compounds and heavy metal ions remain a serious environmental problem facing the world for water pollution, as a result of their numerous industrial applications. Several dyes make their presence strikingly visible as their impart color to the water bodies. Color in water bodies' effect aquatic diversity by blocking the passage of sun light. Further, a color in water bodies has an adverse aesthetic effect. 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.<sup>1</sup> Therefore, their presence in water should be controlled. Different methods such as precipitation, ion-exchange, reverse osmosis, sol-

vent extraction, electro dialysis techniques,<sup>2,3</sup> biological treatments,<sup>4,5</sup> membrane process,<sup>6,7</sup> advanced oxidation process,<sup>8</sup> chemical and electrochemical techniques<sup>9</sup> and adsorption procedure<sup>10–13</sup> have been developed for the removal and recovery of dyes, 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 nonbiodegradability and high cost of the adsorbent resins were reported. Among these, polysaccharides, such as chitin and chitosan,<sup>14</sup> cyclodextrin<sup>15</sup> as well as starch derivatives<sup>16–18</sup> deserve particular attention with respect to their ability to remove dyes and heavy metal ions from aqueous solutions.

In this work, our research team attempt to explore the efficiency of basic dyes removal 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 PMCPs were prepared

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**TABLE I**  
**Preparation of Poly(MAA)-Cross Linked 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)
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;  $K_2S_2O_8$ , 40 mmol/L; material to liquor ratio, 1 : 7.5; Time, 2 hr; and temperature, 60°C.

N.B.

Blank: Cross linked pregelled starch before 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.

by grafting different amount of MAA onto cross linked PG using potassium persulfate as initiator and evaluated toward dyes removal from their solutions. For this purpose, major factors affecting the dye removal of basic dyes onto PMCPS, such as dye concentration, pH, contact time, polymer dose, agitation time, and extent of grafting were studied in detail.

## MATERIALS AND METHODS

### Materials

PG 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 mmHg. It was stored at -100°C until used. Epichlorohydrin, sodium chloride, potassium persulphate, hydrochloric acid, Nitric acid, sodium hydroxide were reagent grade chemicals. The basic dyes used were safranin T (ST), methylene blue (MB), and crystal violet (CV) (Sigma-Aldrich). The molecular structure of each dye has been clarified in "Basic dyes structures" section.

### Preparation of cross-linked PG

One-hundred gram of PG was slurred in 150 mL water containing 1.5 g sodium chloride and 8 mL epichlorohydrin. To this slurry, 6 g sodium hydroxide in 40 mL water was added slowly over 30 min. The mixture was stirred for 16 h at room temperature. The slurry now containing cross linked PG,

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 PG graft copolymer having different graft yields

Six levels of poly(MAA)-cross linked PG graft copolymers with different graft yields (expressed as meq COOH/100 g starch), used for basic dyes removal 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 cross-linked PG (10 g) and (40 mmol/L)  $K_2S_2O_8$  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 PG 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 PG/poly(methacrylic), by estimating carboxyl content of the mixture after each wash until constant value.

### Determination of carboxyl content<sup>19</sup>

To 0.5 g of grafted cross linked PG, 25 mL 0.1 N 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 0.1 N NaOH solutions with phenolphthalein as indicator. A blank test was also performed with cross linked PG before grafting.

Carboxyl content was calculated as follows:

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

### 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 for grafting MAA onto cross-linked PG that is free from carboxyl groups as a starting substrate.

### Dyes removal

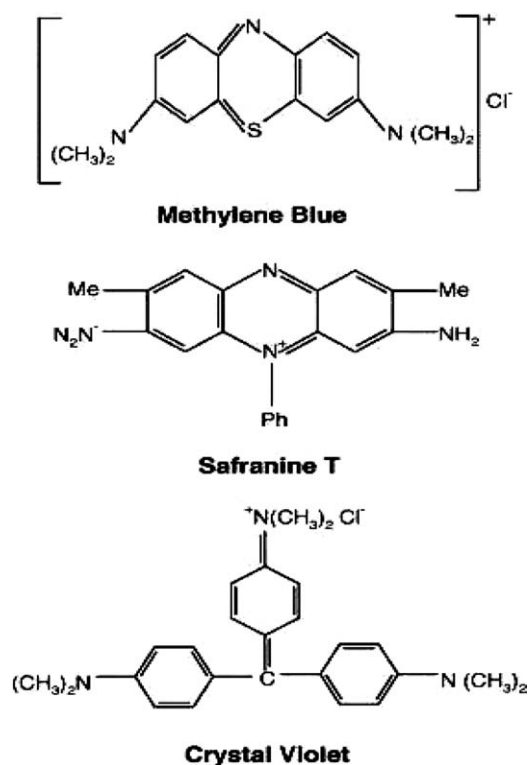
Accurate weight of poly(MAA)-cross linked PG graft copolymer (0.2–3 g) and 100 mL of different dye concentration (10–120 mg/L) were placed in 125 glass-stoppered flasks at specific pH and automatically agitated with different speeds ranged from (10–100 rpm) for certain time period (15–180 min.) at (26°C ± 1°C). Then, 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.

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

### Basic dyes structures

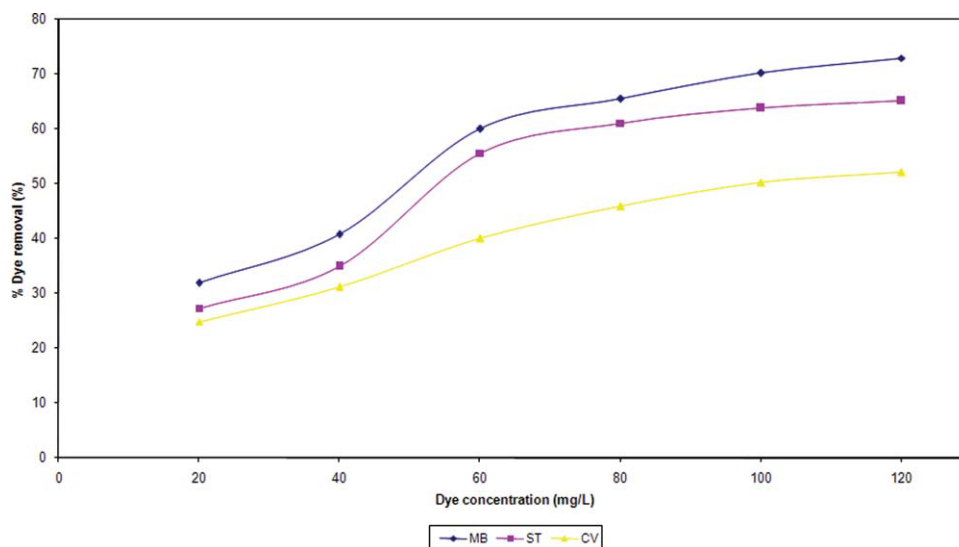
The molecular structure of each dye has been clarified in Chart 1.



## RESULTS AND DISCUSSIONS

### Effect of initial concentration of dye

Figure 1 declares the effect of dye concentration on the % dyes removal namely ST, MB, and CV onto the prepared copolymer at fixed carboxyl content i.e., 198.2 meq. COOH /100 g starch. It is seen Figure 1 that, the % dyes removal increased with the increase in initial dye concentration within the studied range. For dyes in questions the % dye removal increased from 31.9 to 73% for MB and from 27.3 to 65.1% for ST and from 24.9 to 52.1 for CV respectively, when the initial dye concentration was increased from 20–120 mg/L. This was observed when all other variables such as adsorbent dose,

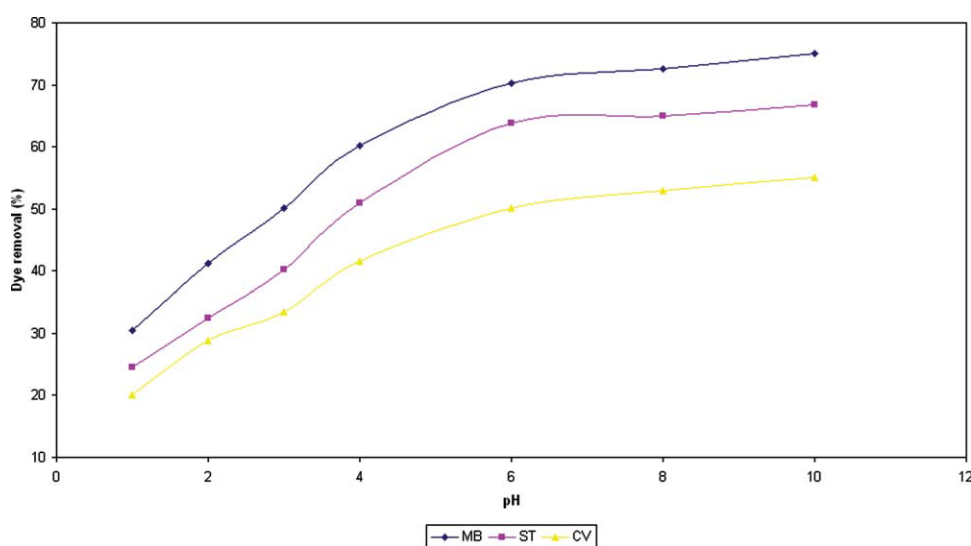


**Figure 1** Effect of dye concentration on the % dye removal of the prepared copolymer reaction conditions: PMPCS, 1 g; pH, 6; time, 60 min.; agitation speed, 40 rpm; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

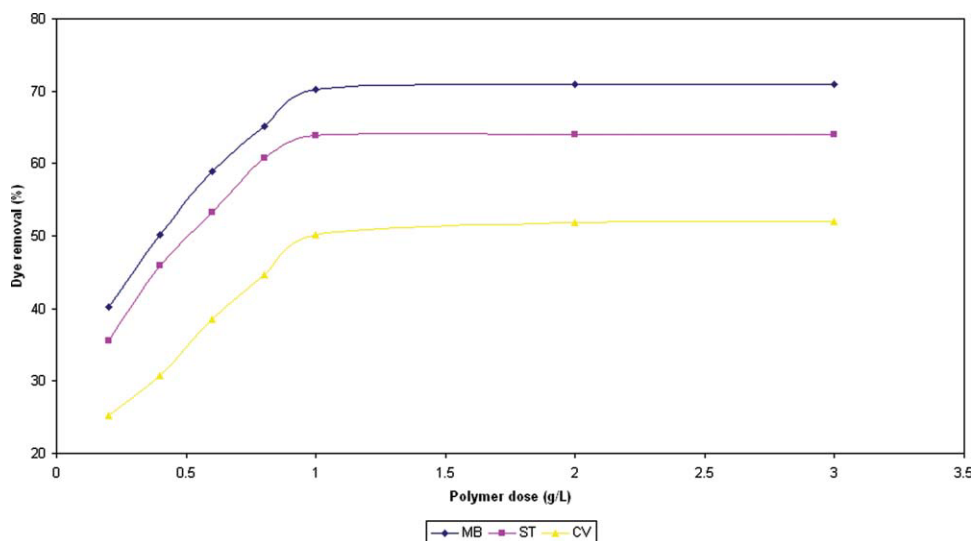
pH, agitation speed, contact time and extent of grafting were the same for different experimental runs. It is clear also that the efficiency of dye removal depends on the initial dye concentration, and the amount of dye adsorbed increased with increase in dye concentration. This is due to the dyes concentration affected the diffusion of dye molecules through the solution to the surface of the adsorbent. Higher concentration of dyes resulted in higher driving force for the concentration gradient. This driving force accelerated the diffusion of dyes from the solution into the adsorbent<sup>20</sup> and follows the order: MB < ST < CV.

### Effect of pH

Figure 2 represents the effect of changing pH on the % dye removal from its solution on poly(MAA)-cross linked PG graft copolymer (expressed as meq-COOH group/100 g starch) at fixed carboxyl content i.e., 198.2 meq COOH/100 g starch. It is seen Figure 2 that, at low pH value, the carboxyl groups on the surface of the polymer that are responsible for binding with basic dyes in questions are predominantly protonated ( $-\text{COOH}$ ), hence incapable of binding basic dyes. As the pH increased, sorption became favorable due to the deprotonation of the carboxyl groups ( $-\text{COO}^-$ ), resulting in sorption sites that



**Figure 2** Effect of pH on the % dye removal of the prepared copolymer. Reaction conditions: PMPCS, 1 g; dye concentration, 100 mg/L; time, 60 min.; agitation speed, 40 rpm; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** Effect of polymer dose on the % dye removal of the prepared copolymer. Reaction conditions: dye concentration, 100 mg/L; pH, 6; time, 60 min.; agitation speed, 40 rpm; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

were available for binding with basic dyes. Furthermore, with increasing pH, the number of positively charged sites decreased and the number of negatively charged sites increased. This phenomenon favors the sorption of positively charged dye due to electrostatic attraction.<sup>21</sup>

#### Effect of polymer dose

PMCPs exhibits the ability to remove color from dye containing aqueous solution with various efficiencies. Figure 3 presents the effect of dose of PMCPs on the % dye removal of the three basic dyes in question. The color removal increases gradually with increasing dose of PMCPs in all the cases up to certain value then leveled off after that. This corresponds to an increase in copolymers active sites as well as saturation occurred at 1.0 g/L at which further increase in polymer dosage had little or no effect on dyes removal. A point should be useful for establishing the optimum economical dose of PMCPs in dye removal.

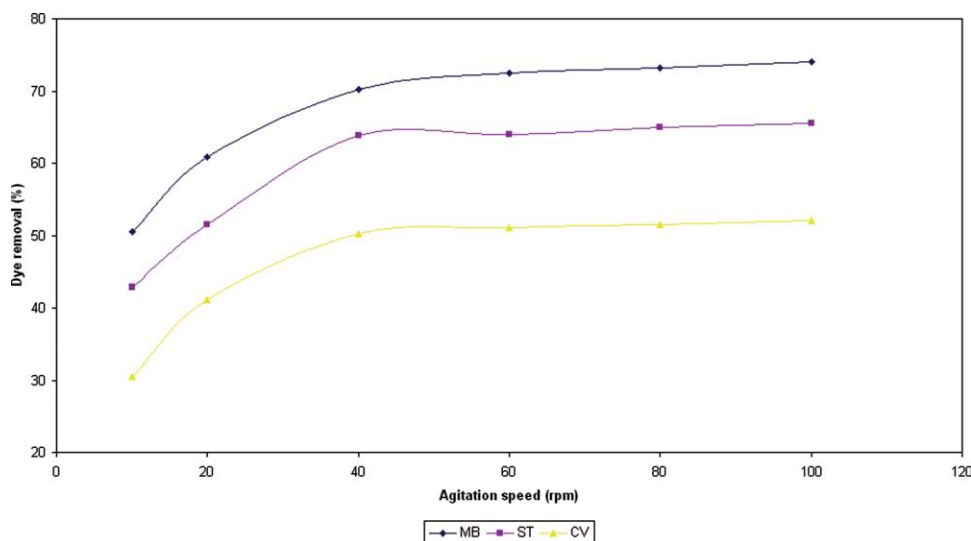
#### Effect of agitation speed of PMCPs

Figure 4 represents the effect of changing of agitation speed on basic dyes removal using poly(MAA)-cross linked PG graft copolymer (expressed as meq-COOH group/100 g starch) at fixed carboxyl content i.e., 198.2 meq COOH /100 g starch. The % dye removal on PMCPs was found to be affected by the speed of agitation. An agitation speed of  $\geq 40$  rpm at the optimum conditions examined before i.e., pH 6.0  $\pm$  0.5 and dye conc. 100 mg/L contact time 2 hr,

198.2 meq. COOH/100 g sample at  $26^{\circ}\text{C} \pm 0.5$ ) resulted in decolorization up to 70.2% from aqueous solution of MB, 63.8% for ST and 50.2% for CV. On the other hand, below 40 rpm, the efficiency of color removal decreased to 50.5% for MB, 42.9% for ST and 30.5% for CV respectively at 10 rpm and 60.9% for MB, 51.5% for ST and 41.2% for CV respectively at 20 rpm. This can be explained in the manner of increasing agitation rate (speed) at the optimum value  $\geq$  decrease the film resistance to mass transfer surrounding the sorbent particles thus increasing sorption of the dye molecules onto the polymer.

#### Effect of contact time

The influence of contact time on the removal of dyes using PMCPs is depicted in Figure 5. The uptake of the dye species is faster during the first 15 min of contact time which may be due to chemisorption of the adsorbate molecules. The functional groups on the surface of the adsorbent i.e., the carboxylic groups may have participated in the chemisorption. Thereafter, it becomes slower which may be due to utilization of more active sites in the mesopore regions and the process of gradual diffusion of the dyes before the equilibrium is attained. The swelling and adsorption are in dynamic equilibrium till the saturation-swelling regime is attained in PMCPs and the two phenomena can be correlated.<sup>22</sup> Moreover, a large number of surface sites are available for the adsorption in initial stages. However, the remaining surface sites may be difficult to be occupied due to steric repulsion among the dye molecules on the surface and incoming dye molecules.

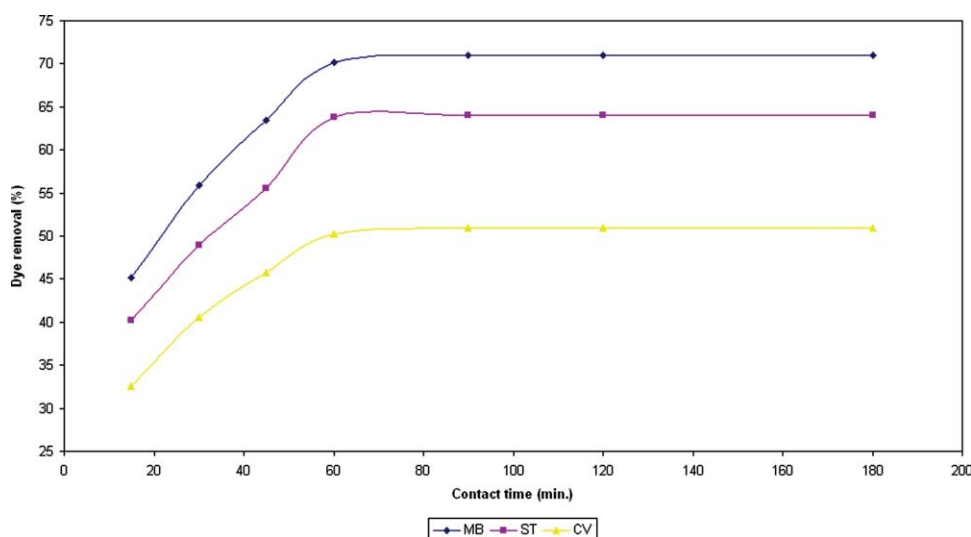


**Figure 4** Effect of agitation speed on the % dye removal of the prepared copolymer. Reaction conditions: PMCPS, 1 g; dye concentration, 100 mg/L; pH, 6; time, 60 min.; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

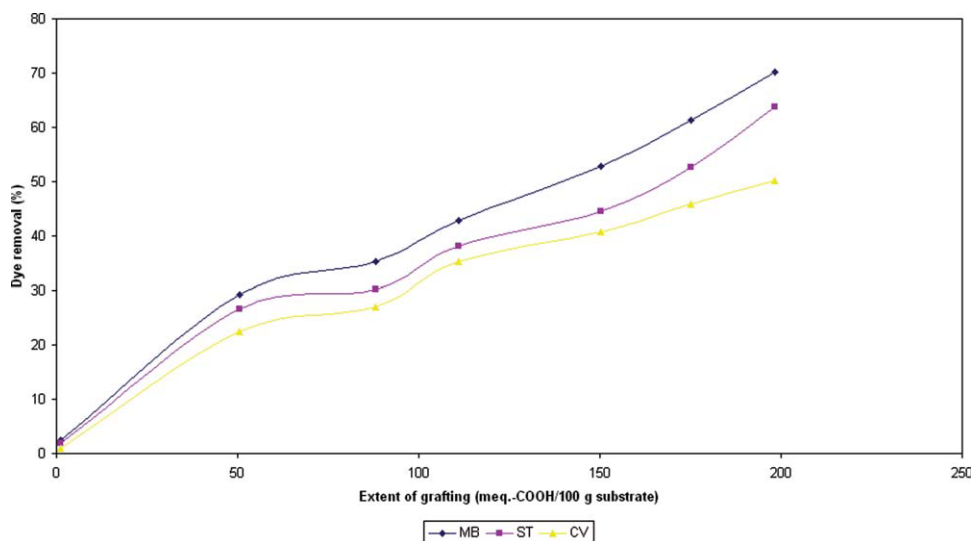
#### Effect of extent of grafting on dyes removal

The sorption capacity of dyes was investigated using the aforementioned dyes. 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 ( $-\text{COOH}$ ) 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 1.01 meq- carboxyl groups/100 g starch just for comparison. It seen from Figure

6 that, at any graft yield, the capacity of dyes removal follows the order:  $\text{MB} > \text{ST} > \text{CV}$ . 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 cationic 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 MB, 63.8 for ST and 50.2 for CV at higher carboxyl contents i.e., 198.2



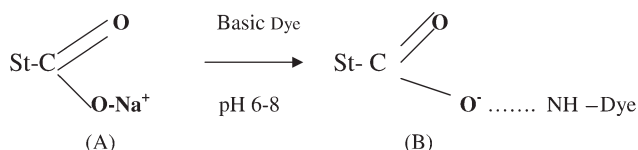
**Figure 5** Effect of contact time on the % dye removal of the prepared copolymer. Reaction conditions: PMCPS, 1 g; dye concentration, 100 mg/L; pH, 6; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Effect extent of grafting (meq. COOH/100 g starch) on the % dye removal of the prepared copolymer. Reaction conditions: PMCPs, 1 g; dye concentration, 100 mg/L; pH, 6; time, 60 min.; temperature,  $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; carboxyl content, 198.2 meq COOH/100 g starch; total volume, 100 mL. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

meq COOH/100 g starch. Moreover, basicity, molecular size and stereochemistry of the dyes appeared to influence the amount of dye adsorbed on PMCPs beside the carboxylic function groups.

Tentative mechanism for Dye/Polymer interaction:



where St- = Cross-linked PG substrate.

It is well-known that, activated adsorption is considered as electrostatic process governed by charged surface of adsorbent and ionic adsorbate species.<sup>23</sup> This is influenced by many physico-chemical factors like dye sorbent interaction; sorbent surface area, particle size, pH atomic size; temperature and contact time.<sup>24</sup> Furthermore, according to,<sup>25</sup> basic dyes in questions are mostly removed via ion-exchange process; i.e., A particular adsorbent is applicable to a particular class of dye e.g., negatively charged adsorbent has a high adsorption capacity for cationic dyes.<sup>26</sup>

## CONCLUSION

By cross linking followed by grafting with MAA, PG could be used to remove basic dyes from their aqueous solutions. Basicity, molecular size and stereochemistry of the dyes appeared to influence adsorption on PMCPs. Basic dyes were removed through adsorption exchange mechanism involving carbox-

ylic acid groups of the polymer and cationic basic function groups on the dye. Beside, at low carboxyl content 50.2 of the copolymer, valuable amount of these dyes could be effectively removed from water by dispersing  $1.0 \text{ mg L}^{-1}$  of the copolymer for (60 min.) at pH 6.5 and subsequent filtering the polymer-dye complex. For effective dye removal, the dye solution should not to be acidic. By raising the levels of grafting, dye scavenging activity of the copolymer could be increased up to the level required for industrial application and follows the order: MB > ST > CV.

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