

# SYNTHESIS AND PROPERTIES OF TREATED WASTE CELLULOSE AND GMA GRAFTED COMPOSITE TO REMOVE DIFFERENT ACID DYES FROM AQUEOUS SOLUTIONS

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The present study investigated the alkali treatment of waste cellulose (Cell) and its grafting with glycidyl methacrylate monomer (GMA) using gamma rays of  $\text{Co}^{60}$  source and a solvent mixture of methanol/ $\text{H}_2\text{O}$ . The obtained Cell/GMA composite was assessed as to its efficiency as a sorbent for the removal of acid dye contaminants from wastewater. Various concentrations of GMA and irradiation doses were used to determine the optimum grafting conditions of the composite. The characterization the Cell/GMA composite was done by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and infrared spectrometer analysis (FTIR). The ability of the composite to absorb water was studied as a function of GMA concentration, irradiation dose and pH of the medium. The efficiency of Cell/GMA in removing several acid dyes (such as acid fast yellow,  $\lambda = 404$  nm, acid methyl blue,  $\lambda = 620$  nm, and acid methyl green,  $\lambda = 597$  nm) from aqueous solutions was investigated. The effect of parameters such as medium pH and GMA monomer content in the grafted composite on the dye removal efficiency was studied. The adsorption isotherm was well described by the Freundlich equation and the empirical constants  $n$  and  $k$  were calculated. It was found that the adsorption capacity of Cell/GMA was high at relatively low temperature, which means the adsorption is exothermic in nature and the heat change ( $\Delta H$ ) of adsorption was calculated using the Arrhenius equation. These results show that the Cell/GMA composite can be used as a sorbent for the removal of acid dye contaminants from wastewater and can be successfully employed in wastewater treatment.

**Keywords:** gamma-irradiation, composite, waste cellulose, grafting, dye adsorption

## INTRODUCTION

Cellulose is one of the most abundant and renewable biopolymers in nature. It is a carbohydrate homopolymer consisting of  $\beta$ -glucopyranose units joined together by  $\beta$ -1,4-glycosidic linkages.<sup>1</sup> Cellulose includes crystalline and amorphous regions, while its mercerization makes the hydroxyl groups of the macromolecules more accessible, decreasing the crystalline content and increasing both the tensile strength and modulus.<sup>2-5</sup>

Many efforts have been made to isolate cellulose from various biomass sources.<sup>6,7</sup> Delignification can significantly facilitate the extraction of the hemicelluloses during alkali treatment, therefore, highly pure cellulosic polymer residue is obtained.<sup>8-10</sup>

Radiation-induced grafting offers unique advantages over the conventional grafting methods: no additive is needed for initiation and homogeneous and temperature-independent initiation is achieved.<sup>11</sup> As cellulose belongs to the class of radiation degradable polymers, this technique has been used to improve the fabrication of cellulose-based adsorbents for water purification.<sup>12</sup> Radiation-induced radical reactions in the polymers may lead to cross-linking or chain scission.<sup>13-15</sup> In the macromolecules of cellulose, the radiation-induced reactions are initiated through rapid localization of the absorbed energy within the molecules to produce highly reactive intermediates, long- and short-lived free radicals, ions, and excited

states.<sup>16-18</sup> The radicals are formed with localized unpaired electrons mainly in positions 1 and 4 of the pyranose ring. The most probable process is the dehydration of the radicals with double bond formation in the pyranose ring yielding allyl type radical.<sup>19-21</sup> Interactions of high-energy radiation with cellulose result in dehydration, oxidative degradation by cleavage of glycosidic bonds, and destruction of the basic monomer unit.<sup>22-24</sup> In the presence of oxygen, the carboxyl and carbonyl content increase with increasing the absorbed dose and a slight modification in the mechanical properties is achieved.<sup>25</sup> The radicals produced in amorphous regions decay quickly, while others that are trapped in the crystalline and semi-crystalline regions decay more slowly.

Many studies have been performed to obtain low-cost adsorbents with greater adsorption capacities to remove dyes from waste effluents. For this purpose, a variety of agricultural wastes have been tested due to their unique advantages, such as nontoxicity, biocompatibility, biodegradability, low cost and high availability.<sup>26,27</sup> Moreover, cellulose-based composites present even more advantages. For example, C.-S. Wu reported to have obtained a composite from treated cellulose acetate (t-CA) and acrylic acid-grafted poly(hydroxyalkanoate) (PHA-g-AA/t-CA), exhibited noticeably superior mechanical properties compared with the PHA/CA composite, due to the greater compatibility between the two components.<sup>28</sup>

In this study, treated waste cellulose (Cell) was grafted by GMA monomer by free radicals polymerization reaction using gamma irradiation. The optimum GMA concentration and irradiation dose were determined and various characterizations of the grafted

composite were carried out. The efficiency of the grafted composite was assessed in the removal of acid dyes from aqueous solution.

## EXPERIMENTAL

### Materials

The cellulose waste (Cell) collected from an Egyptian field. Glycidyl methacrylate (GMA) of 99% purity was purchased from Aldrich, Germany (Scheme 1). All other chemicals were of analytical grade (Merck) and were used as received. The pH of the solution was adjusted with acetate and phosphate buffer solutions. Three types of acid dyes were used: acid fast yellow,  $\lambda = 404$  nm, acid blue,  $\lambda = 620$  nm, and acid methyl green,  $\lambda = 597$  nm (Scheme 1).

### Chemical treatment of waste cellulose

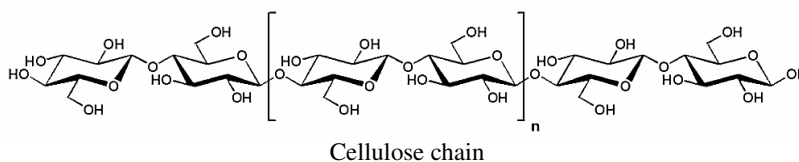
Flax wastes were subjected to alkali treatment using 24% KOH and 2% boric acid at 20 °C for 2 h, resulting in 41.8-43.0% of cellulose, which was then bleached with peracetic acid.<sup>26,27</sup> The obtained purified flax waste was used as a starting material for the preparation of the hydrogel.

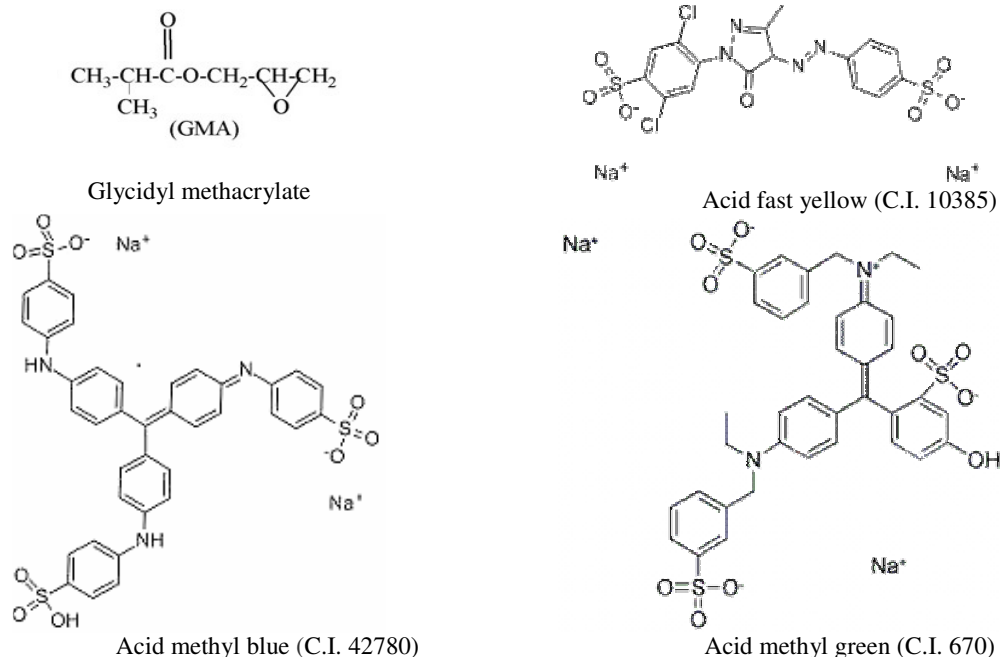
### Preparation of Cell/GMA grafted composite

A known weight of the Cell was placed in a round bottom flask, and an appropriate amount of GMA was dissolved in a methanol/water mixture (60/40, v/v). The polymerization reaction was allowed to proceed using a <sup>60</sup>Co gamma source with different radiation doses between 5 to 20 kGy at a fixed dose rate of 1.2 Gy/s. The copolymer composite obtained was purified under extraction by a Soxhlet apparatus, using methanol/distilled water in a 60/40 volume ratio at 80 °C for 5 hours to remove the unreacted GMA monomer and the homopolymers that may have been formed during the irradiation process. Then it was dried in a vacuum oven at 60 °C and stored for later evaluations. The grafting percent of the poly(Cell/GMA) composite was measured according to the following equation:

$$\text{The grafting percent (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where  $W_0$  and  $W_g$  represent the weights of the initial sample and of the grafted one, respectively.





Scheme 1: Chemical structure of cellulose, glycidyl methacrylate and dyes

### Instrumental techniques

#### UV-Visible analysis

The concentrations of different dyes were determined by a UV-Visible spectroscopic instrument. Optical density measurements were carried out against blanks of individual solvents at room temperature (25 °C) using a Perkin-Elmer 601 single beam UV-VIS spectrophotometer and quartz cell of 1 cm optical length.

#### FTIR measurements

Fourier-transform infrared (FTIR) spectra were recorded over the range 400-4000  $\text{cm}^{-1}$ , in a Mattson 1000 Unicomp infrared spectrophotometer (Cambridge, England).

#### Thermogravimetric analysis (TGA)

A Shimadzu TGA system type TGA-50 was used for TGA measurement. Nitrogen gas flow at a constant rate of about 50 ml/min was used to prevent thermal oxidation processes of the polymer samples. The heating rate was 10 °C/min from the ambient temperature up to 600 °C.

#### Scanning Electron Microscopy (SEM)

A scanning electron microscope Joel SEM-25 was used to observe the surface morphology of the copolymer.

#### Water absorbency

Approximately 0.5 g of dried sample was dispersed in 20 ml of de-ionized water at a desirable pH. The weight of the sample containing absorbed water was

measured after a suitable time, and the water absorbency was calculated according to the following equation:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where  $W_d$  and  $W_s$  are the weights of the dry and swollen samples, respectively.

### Adsorption studies

#### Equilibrium adsorption isotherm

Batch adsorption experiments were carried out at 20 °C. Exactly 20 ml of the dye solution of a known initial concentration was shaken at a certain agitation speed (200 rpm) with 0.5 g of the adsorbent. The pH of the solution was adjusted to the required value by acetate and phosphate buffers. After the desired contact time, the mixture was centrifuged and the remaining concentration of the dye was measured. The concentration of the dye at equilibrium  $C_e$  was determined using a UV-visible spectrometer at  $\lambda_{\text{max}} = 404, 620$  and  $597$  nm for acid fast yellow, acid methyl blue and acid methyl green dyes, respectively. The calibration curve was determined by UV absorption intensity measurements for dye solution concentrations ranging from 10-100 mg/L. Therefore,  $q_e$  values were calculated from the following equation:

$$q_e = \frac{x}{m} = (C_i - C_e) \times V \quad (3)$$

where  $q_e$  is the weight  $x$  in (mg) of the dye adsorbed per gram (g) of dry adsorbent,  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of dye adsorbate solution in mg/L, while  $V$  is the volume of acid dye

solution in (L).

The Freundlich equation was employed to describe the adsorption data for each acid dye adsorbed as follows:

$$q_e = k C_e^{1/n} \quad (4)$$

$$\log q_e = \log k + 1/n \log C_e \quad (5)$$

where k and n are the Freundlich empirical constants.

**Thermodynamic of adsorption isotherm**

The effect of temperature on the acid dye adsorption was investigated at different acid dye concentrations, ranging from 10 up to 100 mg/L at 20, 30 and 40 °C. To determine the thermodynamic parameters, the adsorption experiments were repeated at a constant concentration (100 mg/L) at temperatures of 25 and 35 °C. The apparent enthalpy change (adsorption heats) ( $\Delta H$ ) was calculated using the following thermodynamic function:

$$\ln(C_{e_1} - C_{e_2}) = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

where  $C_{e_1}$  and  $C_{e_2}$  are the free dye concentrations at absolute temperatures  $T_1$  and  $T_2$ , respectively; R is the universal gas constant and  $\Delta H$  is the heat of adsorption.

**RESULTS AND DISCUSSION**

**Preparation of Cell/GMA grafted composite**

The effect of the irradiation dose on the grafting yield of GMA onto Cell is given in Fig. 1. It can be seen that the grafting percent increases with the increase in irradiation dose up to 15 kGy, and then a decrease occurs. This increment may be attributed to the increased number of free radicals formed on both the polymer backbone and monomer. Above 15 kGy, chain scission may occur during grafting.<sup>7</sup> Figure 2 shows the effect of the GMA content on the grafting percent of Cell/GMA at an irradiation dose of 10 kGy. It is obvious that increasing GMA concentration results in increasing grafting

yield, reaching a maximum value at 10%. Further increase in the monomer content with respect to solvent leads to a decrease in the grafting yield. At GMA content lower than 10%, a great number of molecules are available to react with the free radicals on the backbones of the polymer chains. Alternatively, a large number of growing chains are produced, resulting in higher grafting yield. At higher GMA content, the monomer solution becomes more viscous as a result of homopolymer formation, thus, the diffusivity through the polymer matrix is reduced.

**Characterization of the adsorbent**

**FTIR spectroscopic analysis**

The IR spectra of the pure Cell and Cell/GMA grafted composite are shown in Fig. 3. The IR spectrum of Cell shows absorption bands at 2983  $\text{cm}^{-1}$  and 1187  $\text{cm}^{-1}$  due to the stretching bands of C–H and C–O groups, respectively. A strong absorption band can be seen at 3223  $\text{cm}^{-1}$  due to O–H stretching of the non-substituted hydroxyl groups of cellulose. The appearance of a broad band at 3495  $\text{cm}^{-1}$  is attributed to the presence of intra-molecular hydrogen bonding in the cellulose sodium salt molecules. The IR spectra of the Cell/GMA grafting composite cross-linked by gamma irradiation indicate the disappearance of some absorption bands and the appearance of others, as shown in Fig. 3. A very broad absorption band is observed between 3050 and 3570  $\text{cm}^{-1}$ . This may be explained by the formation of hydrogen bonding between the amine groups and the non-substituted hydroxyl groups of the cellulose molecule. A series of bands are noted in the range between 3100 and 3600  $\text{cm}^{-1}$ , which may be due to O–H stretching of H-bonded hydroxyl groups.

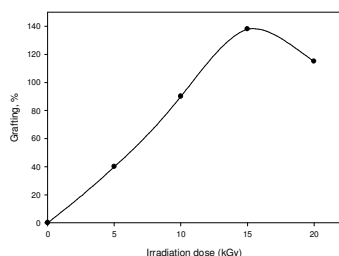


Figure 1: Effect of gamma irradiation dose on the grafting percent of Cell/GMA grafting composite at 15% GMA content

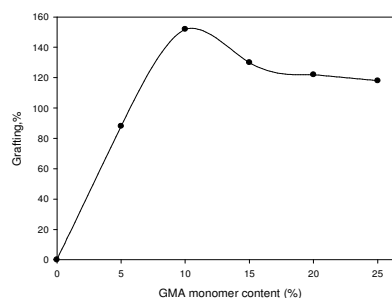


Figure 2: Effect of GMA monomer content on the grafting percent of Cell/GMA grafting composite at an irradiation dose of 15kGy

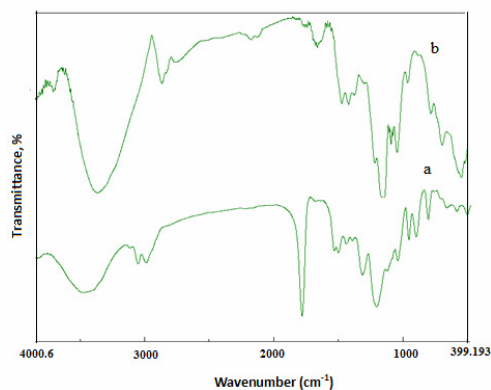


Figure 3: FTIR spectra of Cell (a) and Cell/GMA (b)

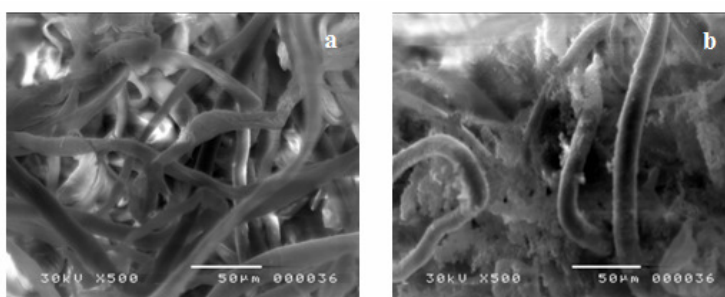


Figure 4: SEM of Cell (a) and Cell/GMA (b)

### Scanning Electron Microscopy (SEM)

The surface morphology of Cell and Cell/GMA grafted composite was analysed by scanning electron microscopy (Fig. 4). As seen in Fig. 4a, the natural (Cell) fibers are constituted by elementary fibers, consisting of helical spirals, which generally contain non-cellulosic polysaccharides. For the Cell/GMA grafted composite (Fig. 4b), a large middle lamella (ml) is observed as a result of grafting and can be recognized as a thin layer between two adjacent elementary cellulose fibers. It can be concluded that the Cell/GMA grafted composite shows a larger pore structure than the ungrafted cellulose.

### Thermal analysis

The thermal behavior of Cell and Cell/GMA grafted composite was investigated by thermogravimetric analysis (TGA) in a nitrogen atmosphere (Fig. 5). Figure 5 indicates characteristic three-step decomposition for both Cell and Cell/GMA. The first decomposition step within the temperature range of 50-230 °C caused weight losses of about 8% and 20% for Cell and Cell/GMA grafted composite, respectively. This may be due to the evaporation of some water and

CO<sub>2</sub> molecules. The major weight loss (57%) occurred in the second step in the temperature range of 230-350 °C, which may be attributed to the degradation of the crosslinked cellulosic chains to small polysaccharide structures. Above this temperature (third step), the weight loss of Cell and Cell/GMA grafted composite increased with raising the temperature from 400 °C to about 450 °C, and is referred to as complete decomposition (weight loss of about 98% for both materials and about 2% carbon residue was left). It is clear that the thermal stability of Cell/GMA is higher than that of Cell. This means that the addition of GMA to cellulose increased the thermal stability of the Cell/GMA composite. It can be concluded that Cell presented higher weight loss than the Cell/GMA grafted composite. Thus, grafting of Cell with GMA enhanced the thermal stability of the cellulosic backbone.

### Water uptake

#### Effect of GMA content

The influence of the GMA content in the Cell/GMA composite on equilibrium swelling was investigated (Fig. 6). As can be seen, the swelling capability increased with increased

cellulose content in the composite, due to its different types of hydrophilic functional groups. The increasing cellulose content in the initial feed mixture thus results in higher swelling of the grafted composite. In other words, the equilibrium swelling decreased with increasing GMA content in the feed mixtures. This can be explained by the fact that increasing GMA content in the feed mixture enhances the cross-linking formation by intra-molecular hydrogen bonding between the GMA chains in the network structure, which results in a decrease of the swelling behavior.

*Effect of irradiation dose*

The influence of the irradiation dose on the equilibrium swelling of the prepared grafted composite is illustrated in Fig. 7. It can be seen that the equilibrium swelling decreases by increasing the irradiation dose. This may be attributed to the enhancement of the cross-linking process at high irradiation doses. As a consequence, the diffusion and swelling properties are hindered by the network structure formation.

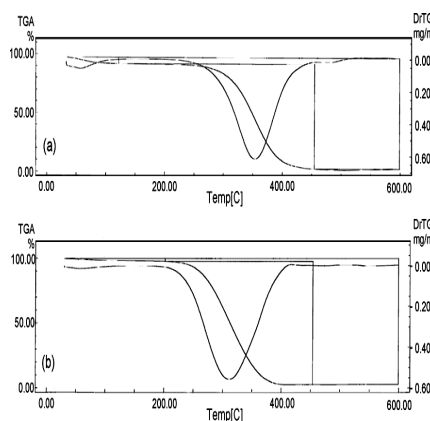


Figure 5: TGA of Cell (a) and Cell/GMA (b)

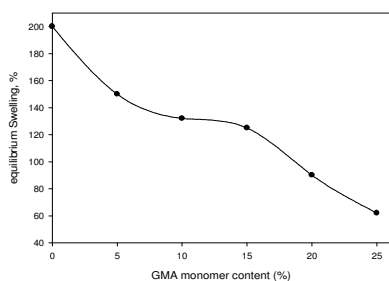


Figure 6: Effect of GMA monomer content on the equilibrium swelling of Cell/GMA grafting composite

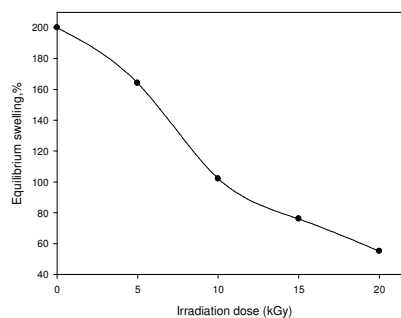


Figure 7: Effect of irradiation dose on equilibrium swelling of Cell/GMA grafting composite

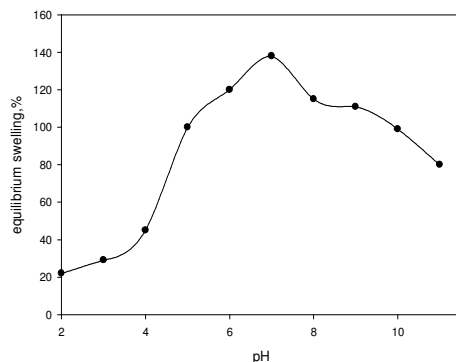


Figure 8: Effect of pH on the equilibrium swelling of Cell/GMA grafting composite

### *Effect of medium pH*

Both Cell and its composite Cell/GMA are natural polyelectrolytes, which have many carboxylic groups in their molecular chains. The dissociation degree of the carboxyl groups is closely related to the pH value of the medium. The influence of medium pH on the equilibrium swelling of Cell/GMA is shown in Fig. 8. It can be seen that the equilibrium swelling of Cell/GMA continuously increases with increasing the pH values. At low pH values, below the pKa of carboxylic groups, approximately 4.6, the carboxylic groups in Cell are protonated and hydrogen bonds between  $-\text{COOH}$  and  $-\text{OH}$  groups may be formed, which results in a decrease of the swelling percent. The lower the pH value of the medium, the stronger the formed hydrogen bonds, and thus a decrease in the swelling percent of the grafted composite occurs. When the pH value is increased above 4.6, the carboxylic groups become ionized and electrostatic repulsion between the molecular chains predominates, which leads to expanding the network and increasing the swelling capacity up to pH 7. Beyond this value, a screening effect of the counter ions, i.e.,  $\text{Na}^+$ , shields the carboxylate anions charge and prevents an efficient repulsion. As a result, a remarkable decrease in equilibrium swelling is observed.<sup>8</sup>

### *Adsorption of dyes*

#### *Effect of pH on the adsorption process*

The pH value of the solution is a controlling parameter in the adsorption process, which affects both the surface charge of the adsorbent and the degree of speciation of the adsorbate. Figure 9 illustrates the effect of medium pH on the adsorption of the investigated dyes onto the Cell/GMA composite. The adsorption capacity diminished slowly from pH 1.5 through 5 and decreased sharply from pH 5 to 12. At a low pH value, an electrostatic attraction exists between the positive charge on the chains of the copolymer sites and the negatively charged dyes.<sup>29</sup> As the pH of the system increases, the adsorbent surface appears negatively charged, which does not favor the anionic dye adsorption due to the electrostatic repulsion between the negatively charged surface and the acidic dye anions. Also, the lower dye adsorption at higher pH is caused by the abundance of  $\text{OH}^-$  ions, which compete with the anionic acid dye molecules for the adsorption sites.

### *Effect of GMA monomer content*

The effect of different Cell/GMA compositions on the adsorption of the acid dyes investigated is illustrated in Fig. 10. For all the dyes under study, the adsorption increased with decreasing GMA content in the Cell/GMA composite. Cellulose-rich compositions possess high dye uptake and a high degree of swelling, which increases the diffusion of dyes inside the Cell/GMA composite. Such Cell/GMA compositions contain a large number of hydroxyl groups, which can form intermolecular hydrogen bonds between the sulfonate groups of the dyes and the polymer. Also, there is a special aqueous solution interaction involving the aromatic rings on the anionic dye molecules and the methane or methylene groups of the cross-linked polymer chains. The structure of the investigated dyes is flat and planar, hence the adsorption capacities are higher.<sup>30</sup> The Cell/GMA composite exhibits approximately the same sorption capacity trends toward all the investigated acidic dyes. Some changes in the adsorption capacity of the composites result from the relatively different physico-chemical structure of the dyes. The adsorption capacities towards the acid dyes under study were demonstrated in the order of: acid green B > acid fast yellow > acid methyl blue.

### *Equilibrium adsorption isotherm*

The Freundlich isotherm is an empirical equation used for the description of heterogeneous systems (heterogeneous surface adsorption) with a uniform energy distribution and reversible adsorption. The model also predicts that the dye concentration on the material will increase as long as there is an increase of the dye concentration in the solution. The adsorption isotherm of the Cell/GMA grafted composite for all investigated dyes was analyzed by the Freundlich equation (Eq. 8). The linear plot of  $\ln q_e$  versus  $\ln C_e$  under the given experimental conditions provided the values of  $n$  and  $k_f$  from the slope and intercept, respectively. The Freundlich empirical constants  $k_f$  and  $n$  represent the Freundlich constant and affinity of the adsorbate solution, respectively. The Freundlich isotherm constants and  $R^2$  values for different solutions are summarized in Table 1. The equilibrium isotherm results were found to fit well with the Freundlich isotherm model. It can be noted that the variation in  $n$  and  $K_f$  reflects the influence of the physico-chemical characteristics of the dyes on the adsorption process and their

affinity to adsorption. Consequently, the adsorption parameters ( $K_f$  and  $n$ ) describe the adsorption process on a quantitative basis, when

the Freundlich constant  $n > 1$  indicates favorability of adsorption.<sup>31,32</sup>

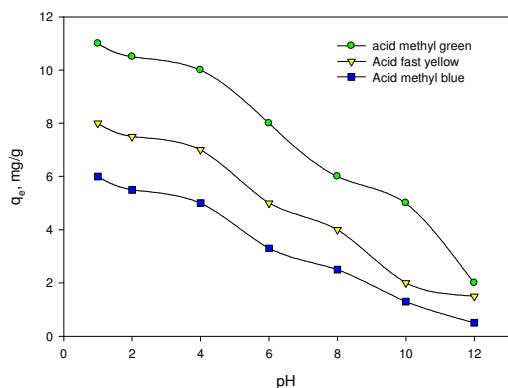


Figure 9: Effect of pH on the dye adsorption of Cell/GMA grafting composite

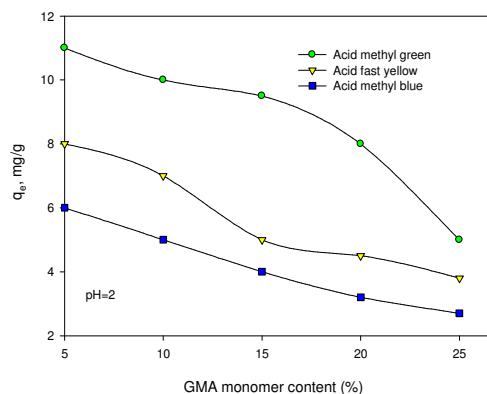


Figure 10: Effect of GMA content on the dye adsorption of Cell/GMA grafting composite

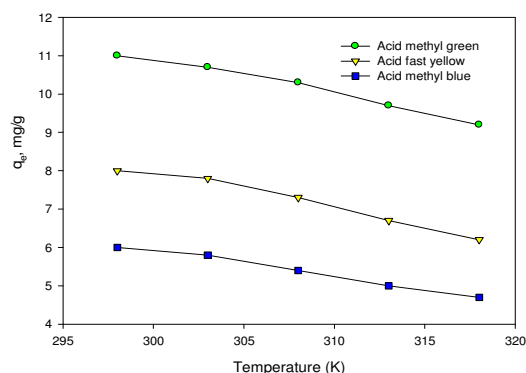


Figure 11: Effect of temperature on the dye adsorption of Cell/GMA grafting composite

Table 1  
Freundlich and thermodynamic parameters for dye adsorption

Dye	$\Delta H$ (kJ/mol)	$K_f$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
Acid methyl green	38.81	0.2780	0.9590	0.9973
Acid methyl blue	34.77	0.1958	0.8718	0.9431
Acid fast yellow	27.65	0.2970	1.0314	0.9851

### Thermodynamics of adsorption

The effect of temperature on the adsorption of the dyes (acid methyl green, acid fast yellow and acid methyl blue) onto Cell/GMA is shown in Fig. 11. The adsorption capacity of the Cell/GMA grafted composite is higher at a relatively low temperature, which suggests the adsorption is exothermic in nature. In order to gain an insight into the adsorption mechanism involved in the

adsorption process, the thermodynamic parameters for the present system were calculated by plotting  $\ln C_e$  versus  $1/T$  (Eq. 12), which should give a linear relationship; the slopes of these graphs give  $\Delta H/R$  values. The calculated  $\Delta H$ 's are listed in Table 1. The variation of energy ( $\Delta H$ ) for the physical adsorption is generally smaller than that of chemical adsorption. Typically,  $\Delta H$  for physical adsorption ranges from



0 to 40 kJ/mol, compared to that of chemical adsorption ranging from 40 to 80 kJ/mol.<sup>31</sup> As shown in Table 1, the values of  $\Delta H$  for acid methyl blue and acid fast yellow adsorption are 34.77 and 27.65 kJ/mol, respectively, which corresponds to physical adsorption. However, for acid methyl green the  $\Delta H$  value is 38.81 kJ/mol, which also corresponds to physical adsorption, but is close to the lowest limit value of chemical adsorption. This suggests that the adsorption process might be considered as physical in nature, but chemical sorption may also be involved in the dye adsorption of the Cell/GMA hydrogel.

## CONCLUSIONS

The synthesis of a grafted composite has been achieved by radiation-induced graft polymerization of GMA onto treated waste cellulose (Cell). The optimum conditions for the preparation of the Cell/GMA grafted composite were determined to be: monomer concentration of 10% in methanol/water mixture (60/40, v/v) at an irradiation dose of 15 kGy and fixed dose rate of 1.2 Gy/s. The grafting was demonstrated by TGA and FTIR of the prepared material. The swelling behavior was studied and equilibrium swelling was found to increase with increasing pH value of the external solution from 2 to 7. Glycidyl methacrylate monomer grafted cellulose showed a good sorption ability towards different acid dyes in the following order: acid methyl green > acid fast yellow > acid methyl blue. The equilibrium isotherm results were found to be fitted well by the Freundlich isotherm model and variation in  $n$  and  $K_f$  reflected the influence of the physico-chemical characteristics of the dyes on the adsorption. The values of  $\Delta H$  for acid methyl blue, acid fast yellow and acid methyl green were of 34.77, 27.65 and 38.81 kJ/mol, respectively, and the adsorption was found to be exothermic in nature.

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