Separation of copper(II) ions using sulfonated poly(glycidyl methacrylate) grafted cellulose films: kinetic, isotherm, and thermodynamic studies

M.A. Abu-Saied, E.A. Soliman, E.A. Hassan, M.S. Mohy-Eldin*

*Corresponding author.

1. Introduction

The accelerated growth of the world population creates massive stress on the consumption of fresh water. Limited fresh water sources and industrial development all over the world produce thousands of pollutants every year charged at the environmental water system raising seriously the challenge of wastewater treatment. Among the most hazardous contaminants, heavy metals contamination has been a critical and accumulated problem in the environment. Direct impacts, such as soil and water pollution, caused by many toxic heavy metals lead in the medium and long term to indirect impact on human health and the global economy. The continuous straggling to explore different techniques and technologies to treat wastewater is a world concern. Among many materials developed for the treatment process of wastewater, natural materials have a massive contribution due to many advantages including,
but not limited to, eco-friendly characteristics and abundance. Cellulose is the most abundant and renewable natural polymer in the universe. A wide variety of cellulose derivatives have been prepared through different techniques and applied in a wide range of applications including environmental ones. Cellulose graft copolymers having ion-exchange properties find applications for the removal of heavy metal ions from aqueous solutions [1–10]. Hydroxamic acid functionalized grafted cellulosic copolymers have a recognized contribution in the removal of different heavy metal ions from aqueous solutions. Haron et al. [11] removed Cu(II) ions using hydroxamic acid-functionalized PMMA-oil palm empty fruit bunch. Jiao et al. [12] removed Cu2+, Zn2+, Pb2+, and Cr3+ using a new poly(amidoxime-hydroxamic acid) cellulose derivative obtained by grafting ethyl(ethoxymethylene) cyanoacetate onto cellulose followed by reaction with hydroxylamine hydrochloride. Rahman et al. [13] reported a lot of work in this direction using cellulose from different sources grafted by poly(methyl acrylate) and treated with hydroxylamine hydrochloride to remove different metals including Cu2+, Fe3+, Mn2+, Co2+, Cr3+, Ni2+, and Zn2+.

Chauhan et al. [14] established the optimum grafting of methyl methacrylate onto cellulose and used it to co-graft with its co-monomers such as acrylamide, acrylic acid, and acrylonitrile. The metal ion sorption performance was a reflection of the structure of the co-polymers. The metal ion sorption performance was a reflection of the structure of the copolymers. The sorption of ferrous (Fe2+) ions was decidedly high compared to Cu2+ and Cr3+. Sharma and Chauhan [15] developed cellulose graft copolymers by grafting 2-hydroxy methacrylate alone and with comonomers acrylic acid, acrylamide, and acrylonitrile by benzoyl peroxide initiation. The sorption of Fe2+, Cu2+, and Cr3+ ions on graft copolymers was investigated to define their end-uses in separation technologies. The sorption of Fe2+ ions was greater than that of Cu2+ or Cr3+. Ekebafe et al. [16] developed graft copolymers of cassava starch and acrylonitrile. The grafted copolymer and the hydrolyzed graft copolymer (hydrogel) were used as sorbent for the uptake of nickel, copper, and lead. The capacity values for the sorbent of the grafted copolymer: 54 mg·Pb/g, 64.5 mg·Cu/g, and 71.1 mg·Ni/g, and for the hydrogel: 72 mg·Pb/g, 76.6 mg·Cu/g and 86.5 mg·Ni/g. Hajeeth et al. [17] grafted extracted cellulose with acrylic acid and used as adsorbent for the removal of Cr(VI) from the aqueous solution. The monolayer’s maximum adsorption capacity according to Langmuir is other was found 305 mg/g. Assem et al. [18] synthesized poly(acrylic acid-co-methyl methacrylate) grafted cellulose via raft polymerization and applied it as an adsorbent for Ca2+, Cu2+, and Pb2+ ions. The grafted cellulose showed good adsorption performance for Ca2+ and Pb2+ ions than Cu2+ ions. The aim of this work is the application of the sulfonated poly(glycidyl methacrylate) grafted cellulose ions exchanger films (SPGMA-g-C) for the separation of metal ions from aqueous solution. Copper ions were selected as a model for this study. The kinetics and isothermals of the adsorption process were monitored for a better understanding of the separation process. Moreover, the thermodynamic parameters of the adsorption process have been calculated.

2. Materials and methods

2.1. Materials

Glycidyl methacrylate (GMA) (purity 97%) is obtained from Sigma-Aldrich Chemicals, (Switzerland). Potassium persulfate (KPS) (purity 99%, M.wt. 270.31), sulfuric acid (purity 95%–97%), 2-propanol (purity 99.8%), ethyl alcohol absolute (purity 99.9%), sodium sulfite anhydrous (purity 95%), copper sulfate (purity 98%, M.wt. 249.68), cellulose sheets type, uncoated; dimensions, 80 cm × 117 cm; cellulose content, 80% (W%) regenerated cellulose; additives content, 20% (glycerol and Na2SiO3) is obtained from Misr Rayon Co. Kafr El-Dawar, (Egypt). The additives were removed by extraction with hot distilled water, and then the films were cut with dimensions 5 cm × 5 cm.

2.2. Methods

2.2.1. Preparation of sulfonated poly(glycidyl methacrylate) grafted cellulose films

Cellulose films were first grafted with glycidyl methacrylate dissolved in KPS ethanol/water solution. The grafting process was conducted in definite temperature in a water bath for definite time. The epoxy groups of the PGMA chains were reacted with sodium sulfite (Na2SO3) dissolved in alcohol and water at definite temperature and for definite time. The details of the preparation conditions were mentioned elsewhere [9]. The used PGMA-g-cellulose films in this study have 40.0% grafting percentage.

2.2.2. Infrared spectroscopic analysis

Analysis by infrared spectroscopic investing the un-grafted cellulose, the PGMA grafted cellulose, the sulfonated PGMA grafted cellulose (SPGMA-g-C), and the Cu-sulfonated grafted cellulose films (Cu2+-SPGMA-g-C) was carried out using Fourier-transform infrared spectrophotometer (Shimadzu FTIR-8400S, Japan).

2.2.3. Thermal gravimetric analysis

Analysis by thermogravimetric analysis (TGA) of the un-grafted cellulose and the PGMA grafted cellulose films were carried out using Thermogravimetric Analyzer (Shimadzu TGA-50, Japan).

2.2.4. Scanning electron microscope and energy dispersive analysis X-ray

The morphology changes resulted from the grafting process have been monitored. In addition, the chemical structure changes of the PGMA grafted cellulose films and the sulfonated PGMA grafted cellulose films (SPGMA-g-C) before and after the separation of the Cu(II) ions have been followed by performing elemental analysis using energy dispersive analysis X-ray (Jeol, JSM-6360LA, Japan).

2.2.5. Separation of Cu(II) ions process and regeneration of the adsorbed Cu(II) ions

The sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) were tested to separate copper...
ions from CuSO₄ solution (317.5–3,175 mg/L) and shaken at 150 rpm for definite time (5–120 min) at selected temperature (30°C–80°C). The films were sequentially washed with DI water to remove the unbounded or weakly linked copper ions. The films turned to blue color as an indicator of copper ions adsorption. The amount of copper adsorbed and eluted was determined by using atomic absorption spectrophotometer (Analysis T300, PerkinElmer, U.S.A.). The adsorption capacity of the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) were calculated using Eq. (I).

\[
\text{Adsorption capacity} \left( \text{mg/m}^2 \right) = \frac{V(C_0 - C_e)}{A}
\]  

where \( C_0 \) and \( C_e \) are the copper ions' initial and final concentrations at definite adsorption time, \( V \) is the volume of the copper ions solution (L), and \( A \) (m²) is the area of the sulfonated poly(glycidyl methacrylate) grafted cellulose film, (SPGMA-g-C).

The regeneration of the adsorbed Cu(II) ions after completion of the separation process from the sulfonated poly(glycidyl methacrylate) grafted cellulose film, (Cu²⁺-SPGMA-g-C), was carried by immersed in 50 mL 0.1 N HCl solution. The amount of copper released in the solution was determined using an atomic absorption spectrophotometer (Analysis T300, PerkinElmer, U.S.A.). The regeneration efficiency was determined by dividing the amount of released Cu(II) ions by the amount of adsorbed Cu(II) ions for the individual membrane.

3. Results and discussion

3.1. Effect of copper ions concentration

The effect of variation of the copper ions solution concentration on the adsorption capacity of the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) were investigated in Fig. 1. From Fig. 1 it is clear that an increase in the copper ions concentration in the solution has a positive effect on the adsorption capacity of the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C). The capacity was found to be increased linearly within the studied range of copper ions solution concentrations (317.5–3,175 mg/L) from 260 to 2,550 mg/m². No slowing down of the adsorption capacity has been detected which is a good indication of the existence of remaining excess free adsorption sites superior to the number of available dissolved Cu(II) ions in the liquid phase. The progressive linear increase of the dissolved Cu(II) ions in the solution kept the concentration gradient between the Cu(II) ions' liquid phase and the SPGMA-g-C adsorbent solid phase constant which is the main driving force controlling the movement of the Cu(II) ions from the liquid phase to the SPGMA-g-C adsorbent solid phase. The progressive adsorption of Cu(II) ions onto the SPGMA-g-C adsorbent solid phase increases its swelling which co-ordinately facilitates the diffusion of the Cu(II) ions from the film surface to the interior pores surface. Our results are agreed with previously published results by Ekebafe et al. [16] where graft copolymers of cassava starch and acrylonitrile were developed for the separation of nickel, copper, and lead. Jiao et al. [12] reported a similar behavior with different metal ions, Cu²⁺, Zn²⁺, Pb²⁺, and Cr⁶⁺, using a new poly(amidoxime-hydroxamic acid) cellulose derivative obtained by grafting of ethyl(ethoxyethylene) cyanoacetae onto cellulose followed by reaction with hydroxyl amine hydrochloride.

3.1.1. Adsorption isotherm models

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among solid and liquid phases and are thus important from the chemical design point of view. The results obtained on the adsorption of Cu²⁺ ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) were analyzed by the well-known models given by Freundlich, Langmuir, Temkin, and Harkins–Jura. The sorption data obtained for equilibrium conditions have been analyzed by using the linear forms of these kinds of isotherms. The Freundlich isotherm is a widely used equilibrium isotherm model but provides no information on the monolayer sorption capacity, in contrast to the Langmuir model [19,20]. The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known empirical equation and is shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces [21].

\[
\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e
\]  

where \( K_f \) is the Freundlich constant depicts adsorption capacity and \( n_f \) is a constant indicating adsorption intensity. With plotting \( \ln q_e \) against \( \ln C_e \), a straight line with slope \( 1/n_f \) and intercept \( \ln K_f \) is obtained. The intercept of the line, \( K_f' \), indicates roughly of the adsorption capacity with slope, \( n_f \), as an indicator of adsorption effectiveness. For the adsorption isotherms, the initial Cu²⁺ ions concentration was varied while the pH and temperature of the solution, the agitation
speed, and the adsorbent weight in each sample were held constant. Linear fits of sorption data of the Cu\(^{2+}\) ions are given in Fig. 2. According to the correlation coefficient \(R^2\) value (0.9962), it was demonstrated that the removal of Cu\(^{2+}\) ions using sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) obeyed the Freundlich isotherm. The values of Freundlich constants \(n_f\) and \(K_F\) that were estimated from the slope and intercept of the linear plot were 1.042 and 5.39. From the estimated value of \(n_f\), it was found that \(n_f > 1\) indicated favorable adsorption for Cu\(^{2+}\) ions using sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) [22].

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules is given by Eq. (3) [23]:

\[
\frac{C_e}{q_e} = \frac{1}{q_mK} + \frac{C_e}{q_m}
\]  

(3)

where \(q_e\) is the amount adsorbed (mg/g), \(C_e\) is the equilibrium concentration of the adsorbate ions (mg/L), and \(q_m\) and \(K\) are Langmuir constants related to maximum adsorption capacity (monolayer capacity) (mg/g) and energy of adsorption (L/mg). Plotting of \(C_e/q_e\) vs. \(C_e\) indicates a straight line with a \(1/q_m\) slope and an intercept of \(1/q_mK\). Fig. 3 illustrates the linear plot of the Langmuir equation for the Cu\(^{2+}\) ions removal using sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) at various initial Cu\(^{2+}\) ions concentrations. The value of the correlation coefficient \(R^2\) is considered an indicator of the goodness-of-fit of experimental data on the isotherm’s model. The \(R^2\) value was 0.5601 indicating a non-good mathematical fit of the adsorption date. Langmuir parameters for Cu\(^{2+}\) ions removal, \(q_m\) and \(K\), were calculated from the slope and intercept of Fig. 3. It was found from the calculated values of \(q_m\) equal to 20,000 mg/m\(^2\) and \(K\) equal to 4312 L/mg, indicating that the sulfonated poly(glycidyl methacrylate) grafted cellulose

![Fig. 2. Equilibrium Freundlich isotherm for the adsorption of the Cu(II) ions onto sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).](image)

![Fig. 3. Equilibrium Langmuir isotherm for the adsorption of the Cu(II) ions onto sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).](image)

\[ R_L = \frac{1}{1 + K_C} \]  

(4)

Values of \(R_L\) (Table 1) for the Cu\(^{2+}\) ions removal fall between zero and one showing favorable adsorption [25] which confirmed that the adsorption of the Cu\(^{2+}\) ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) under the conditions used in this study was favorable by Langmuir isotherm.

<table>
<thead>
<tr>
<th>(C_0) (mg/L)</th>
<th>(R_L)</th>
</tr>
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<tr>
<td>317.5</td>
<td>7.30·10(^{-7})</td>
</tr>
<tr>
<td>635</td>
<td>3.65·10(^{-7})</td>
</tr>
<tr>
<td>1,270</td>
<td>1.82·10(^{-7})</td>
</tr>
<tr>
<td>1,905</td>
<td>1.22·10(^{-7})</td>
</tr>
<tr>
<td>3,175</td>
<td>7.30·10(^{-6})</td>
</tr>
</tbody>
</table>
intercept. From Fig. 4 the calculated $K_T$ is equal to 0.0175 L/g, which represents the equilibrium binding constant corresponding to the maximum binding energy; however, the constant $B_T$ that is equal to 932.04 J/mol is related to the heat of adsorption.

Finally, the Harkins–Jura adsorption isotherm can be expressed as [28].

$$\frac{1}{q_e} = \left(\frac{B_T}{A_H} - \left(\frac{1}{A_H}\right)\right) \log C_e$$

(6)

The Harkins–Jura adsorption isotherm accounts for multilayer adsorption and can be explained by the existence of heterogeneous pore distribution. The value of $1/q_e^2$ was plotted against log$C_e$. where $B_H$ (intercept/slope; mg/L) and $A_H$ (1/slope; g/L) is the isotherm constants; Fig. 5. The Harkins–Jura isotherm is analogous to the Freundlich model in addition to considering the existence of a heterogeneous pore's distribution. The model shows the $R^2$ value is 0.7541. The obtained result confirmed the formation of a multilayer of adsorption.

In conclusion, the Freundlich isotherm model gave the highest $R^2$ value (0.9962), showing that the Cu$^{2+}$ ions sorption on the synthesized polymers was best described by this model. This suggested that the formation of multilayers of adsorption [28].

3.2. Effect of the adsorption time

The effect of varying the adsorption time from 5 min to 120 min on the adsorption capacity of the Cu$^{2+}$ ions on the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) was explored in Fig. 6. Fig. 6 illustrates that the adsorption capacity is linearly increased with adsorption time up to 15 min. Beyond 15 min, the adsorption capacity increment has been slower and tended to level off after 60 min. An equilibrium state has been reached at 120 min. The corresponding removal percentage has the same behavior which increased from 18% to 69% at equilibrium. Our results are in agreement with the obtained results by Zafar et al. [29] which report the adsorptive discharge of copper ion (Cu(II)) from wastewater by using rice husk (RH) at ambient temperature. They explained their findings by the existence of a maximum number of empty sites onto RH and interaction was developed between adsorption sites and Cu(II). After that, the removal of Cu(II) was not fast. Then the equilibrium was achieved and no significant increase in adsorption occurred with contact time. Due to the movement of Cu(II) into the interior pores of RH, it was slowed down when all empty sites were covered. The reduction of dissolved copper ions concentration in the solution with time corresponding with an increase of the adsorbent amount.
on the SPGMA-g-C adsorbent surface strongly reduces the copper ions concentration gradient, the main driving force for the adsorption process. This consequently leads to reaching the equilibrium state shortly.

### 3.2.1. Adsorption kinetic models

Adsorption is a physiochemical process that involves the mass transfer of a solute (adsorbate) from the liquid phase to the adsorbent surface. A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for an efficient process. The most common models used to fit the kinetic sorption experiments are Lagergren’s pseudo-first-order model [Eq. (7)] [26], pseudo-second-order model [Eq. (8)] [27], and Elovich model [Eq. (9)] [30].

\[
\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{7}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}
\]

\[
q_t = \alpha + \beta \ln t \tag{9}
\]

where \(q_e\) (mg/g) and \(q_t\) (mg/g) are the amount of dye adsorbed at equilibrium and at time \(t\), respectively. \(k_1\) (min\(^{-1}\)) and \(k_2\) (g/mg·min) are the Pseudo-First-Order and Pseudo-Second-Order adsorption rate constants, respectively. The Elovich constants are \(\alpha\) (mg/g·min), the initial sorption rate, and \(\beta\) (g/mg); the extent of surface coverage and activation energy for chemisorption.

#### Pseudo-first-order model

The Pseudo-First-Order kinetic model was the earliest model about the adsorption rate based on the adsorption capacity. The value of the pseudo-first-order constant \((k_1; 0.0721)\) and correlation coefficient \((R^2; 0.9546)\) was obtained from the slope of the plot \(\ln(q_e - q_t)\) vs. time in Fig. 7. The value of the first-order rate constant \(k_1\) and correlation coefficient \(R^2\) obtained from the slope of the plot \(\ln(q_e - q_t)\) vs. time (Fig. 7) are reported in Table 2. It is indicated that the correlation coefficients are good enough. However, the estimated value of \(q_e\) calculated from the equation; 2,035.3 (mg/m\(^2\)) has a close value from the experimental one, 2,553 (mg/m\(^2\)).

#### Pseudo-second-order model

The experimental kinetic data were further analyzed using the Pseudo-Second-Order model. By plotting \(t/q_t\) against \(t\) for Cu\(^{2+}\) ions, a straight line was obtained and the second-order rate constant \((k_2; 0.0009)\) and \(q_e\) value \((166,667 \text{ mg/m}^2)\) were determined from the slope and intercept of the plot, Fig. 8. The values of the correlation coefficients \((R^2; 0.3003)\) were found very low. Accordingly, the kinetics of the Cu\(^{2+}\) ions adsorption can’t be described by a
second-order equation. This suggests that the rate-limiting step in these sorption processes is not the chemisorption.

**Elovich model**

The simple Elovich model is one of the most useful models for describing the kinetics of the chemisorption of gas onto solid systems. However recently it has also been applied to describe the adsorption process of pollutants from aqueous solutions. Fig. 9 illustrates the plot of $q_t$ against $\ln t$ for the sorption of the Cu$^{2+}$ ions onto the sulfonated poly(glycidyl methacrylate) grafted films (SPGMA-g-C). From the slope and intercept of the linearization of the simple Elovich equation, the estimated Elovich equation parameters were obtained. The value of $\beta$ is indicative of the number of sites available for adsorption (611.41) while $\alpha$ value (6.1639) is the adsorption quantity when $\ln t$ is equal to zero, that is, the adsorption quantity when $t$ is 1 min. This value helps us understand the adsorption behavior of the first step [31].

### 3.3. Adsorption mechanism models

Following the adsorption mechanism of any ions onto a solid from the aqueous phase is going through a multi-step process. Initially, two steps are recognized in the liquid phase. The first step is the transport of the ions from the aqueous phase to the surface of the solid particles which is known as bulk diffusion. This step is followed by diffusion of the ions via the boundary layer to the surface of the solid particles (film diffusion). The last step, consequently, happened in the solid phase where the ions transport from the solid particle surfaces to its interior pores, known as pore diffusion or intraparticle diffusion. This step is likely to be slow and therefore, it may be considered as the rate-determining step. Adsorption of an ion at an active site on the solid phase surface could also occur through a chemical reaction such as ion exchange, complexation, and chelation. The diffusion rate equations inside the particulate of Dumwald-Wagner and intraparticle models were used to calculate the diffusion rate of the Cu$^{2+}$ ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C). On the other hand, concerning the external mass transfer, the Boyd model was examined to determine the actual rate-controlling step for the Cu$^{2+}$ ions removal. Usually, the adsorption process is controlled by either the intraparticle (pore diffusion) or the liquid-phase mass transport rates (film diffusion) [32]. Experimenting in a batch system with rapid stirring left the possibility that intraparticle diffusion is the rate-determining step [33]. Weber and Morris [34] explored the possibility of affecting the adsorption process via intraparticle diffusion resistance using the intraparticle diffusion model described in Eq. (10):

$$q_t = k_{id}t^{1/2} + I$$

where $k_{id}$ is the intraparticle diffusion rate constant. Kannan et al. [35] have figured out the thickness of the boundary layer from the values of $I$. A greater boundary layer effect was noticed with a larger intercept [35]. The plot of $q_t$ vs. $t^{0.5}$ is presented in Fig. 10. Two separate linear portions that represent each line can be observed in the figure. These two linear portions in the intraparticle model suggest that the removal process consists of both surface removal and intraparticle diffusion. While the initial linear portion of the plot is the indicator of the existence of the boundary layer effect, the second linear portion is due to intraparticle diffusion [36]. The intraparticle diffusion rate ($k_{id}$), 23.411 (mg/m²·min), calculated from the slope of the second linear portion and the values of C (2309), the intercept, provides an idea about the thickness of the boundary layer. The larger the intercept, the greater the boundary layer effect [35]. In the case of involving the intraparticle diffusion in the sorption process, then a linear relationship would result from the plot of $q_t$ vs. $t^{1/2}$, and the intraparticle diffusion would

**Fig. 9.** Elovich kinetic rate model for the adsorption of the Cu(II) ions onto sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).

**Fig. 10.** Intraparticle diffusion model for the adsorption of the Cu(II) ions onto sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).
be the controlling step if this line passed through the origin [32]. Fig. 10 confirms straight lines not passed through the origin. The difference between the rate of mass transfer in the initial and final steps of the sorption process may cause the deviation of straight lines from the origin. Accordingly, it can be concluded that pore diffusion is not the sole rate-controlling step [37]. Additional processes, such as the adsorption on the boundary layer, may also be involved in the control of the adsorption rate.

The diffusion rate equation inside particulate of Dumwald–Wagner can be expressed as [38]:

$$\log(1 - F^2) = -\left(\frac{K}{2.303}\right)t$$  \hspace{1cm} (11)

where \(K\) is the diffusion rate constant and the removal \(F\), \(F\) is calculated by \((q_t/q_e)\). The very good linear plot of \(\log(1 - F^2)\) vs. \(t\) indicates \((R^2; 0.9702)\) the applicability of this kinetic model (Fig. 11). The diffusion rate constant \(K\) for the Cu\(^{2+}\) ions into the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) was found to be \(-0.65\ \text{min}^{-1}\).

The adsorption data were further analyzed by the kinetic expression becomes:

$$B_t = -0.4978 \ln \left(1 - \frac{q_t}{q_a}\right)$$  \hspace{1cm} (14)

Thus, the value of \(B_t\) can be calculated for each value of \(“F”\) using Eq. (14). The calculated \(B_t\) values were plotted against time as shown in Fig. 12. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle-transport controlled rates of sorption \((R^2; 0.9547)\). Fig. 12 shows the plot of \(B_t\) vs. \(t\) which is a straight line that does not pass through the origin, indicating that film diffusion governs the rate-limiting process [40].

### 3.4. Effect of the adsorption temperature

The temperature is one of the critical factors that influence the adsorption of the Cu\(^{2+}\) ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C). It can change several characteristics of the adsorption process, for example, the swelling capacity of the adsorbent, and the equilibrium position concerning the endothermic or exothermicity of the adsorption phenomenon [41]. So, the effect of temperature on the stability of the Cu\(^{2+}\) ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) was investigated in the temperature range of 30°C–80°C. Fig. 13 displays a linear increment of the adsorption capacity by raising the temperature in the studied range from 30°C to 60°C. This phenomenon can be explained by increasing the kinetic energy of the Cu\(^{2+}\) ions at a higher temperature. Consequently, increase in the collision of the Cu\(^{2+}\) ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) active adsorption sites [42]. Parallel with that, the swelling of the
sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) increased with temperature elevation which facilitates the diffusion of the copper dissolved ions to the interior pores surface area reaching the bulk adsorption active sites. The synergetic effect of both factors helps keep the concentration gradient of the copper-dissolved ions enough to drive them toward the adsorbent film. Further increase of the adsorption temperature to 80°C increased the adsorption capacity but at a slower rate and the curve turned to level off due to the reduction of the adsorption active sites available for interaction with dissolved copper ions and combined with the reduction of the copper ions concentration gradient between the metal ions liquid phase and the solid adsorbent phase which the main driving force for the adsorption process.

### 3.4.1. Adsorption thermodynamic studies

The effect of variation adsorption temperature is illustrated previously in Fig. 13. A positive impact of elevating the adsorption temperature of the Cu²⁺ ions has been observed. Such finding is an indication of the endothermic nature of the Cu²⁺ ions adsorption process on the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C). From engineering aspects, the values of thermodynamic parameters such as the enthalpy change (ΔH°), the free energy change (ΔG°), and the entropy change (ΔS°) should be taken into consideration to conclude the spontaneity of the adsorption process. A spontaneous system will display a decrease in ΔG° and ΔH° values with increasing the temperature. All the thermodynamic parameters are calculated from Eqs. (15)–(19) [43]:

\[
\ln K_q = \frac{\Delta S}{R} - \frac{\Delta H}{RT} 
\]  

(15)

\[
[\text{Where: } K_q = \frac{q_d}{C_i}] 
\]  

(16)

\[
\Delta G = -RT \ln K_q 
\]  

(17)

\[
\Delta H = -R \times \text{Slope} 
\]  

(18)

\[
\Delta S = R \times \text{Intercept} 
\]  

(19)

where R is the gas constant (8.314 J/mol·K), and T is the temperature in K. Table 3 lists down the values for the thermodynamic parameters (Fig. 14). The positive value for the ΔH° (7.88 kJ/mol), indicates the endothermic nature of the process, which explains the increase of the Cu²⁺ ions adsorption efficiency as the temperature increased. As informed by Khan et al. [43], the enthalpy change values as a result of the chemisorption are between 40 and 120 kJ/mol, which are larger than that caused by the physisorption. Consequently, the lower value of the heat of adsorption acquired in this study indicates that the adsorption of the Cu²⁺ ions is probably attributable to the physisorption. The positive value for the entropy change, ΔS° (34.965 J/mol·K) illustrating the disorderliness at the solid/liquid interface during the adsorption of the Cu²⁺ ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C). The ΔG° values reflect the feasibility of the process.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-2.711</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-2.964</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-3.505</td>
<td>7.88125</td>
<td>34.965</td>
</tr>
<tr>
<td>60</td>
<td>-3.909</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>-4.367</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 13. Effect of the adsorption temperature on the adsorption capacity of the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).

Fig. 14. Van’t Hoff plot of the adsorption of the Cu(II) ions onto the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C).
3.5. Regeneration of the Cu$^{2+}$-sulfonated poly(glycidyl methacrylate) grafted cellulose films (Cu$^{2+}$-SPGMA-g-C)

The regeneration of the Cu$^{2+}$-sulfonated poly(glycidyl methacrylate) grafted cellulose films (Cu$^{2+}$-SPGMA-g-C) obtained under different separation conditions namely copper ions concentration, adsorption time, and adsorption temperature has been performed and the obtained results are presented in Tables 4–6. The data showed excellent regeneration efficiency with a minimum of 93.48% and a maximum of 99.88%.

3.6. Adsorption capacity comparative study

Table 7 provides an interesting comparison of adsorption capacity of copper ions for different adsorbents. The table shows the superiority of the developed sulfonated poly(glycidyl methacrylate) grafted cellulose films over other adsorbents.

3.7. Grafting and functionalization evidences

3.7.1. FTIR analysis

Fig. 15 illustrates the FTIR spectra for un-grafted, grafted, and sulfonated cellulose films. The IR-spectrum shows the absorption bands at 1,724 cm$^{-1}$, characteristic for $-C=O$ stretching as well as three bands at 1,238–1,255, 840 and 750 cm$^{-1}$ attributed to the epoxy ring, Curve (B), which confirmed the grafting process. The occurrence of the sulfonation process has been confirmed through the appearance of the characteristic absorption bands of the sulfonated groups at 1,150, 1,050 and 670 cm$^{-1}$; Curve (C). The remaining of the characteristic absorption bands of the epoxy groups could be attributed to the uncompleted conversion to sulfonated groups and part of the epoxy rings may have taken part in the formation of cross-linking structure during the grafting reaction [1].

3.7.2. TGA analysis

Thermal analysis for the un-grafted and PGMA-grafted cellulose films was performed by thermogravimetric analyzer

Table 5

Regeneration efficiency of the Cu$^{2+}$-sulfonated poly(glycidyl methacrylate) grafted cellulose films (Cu$^{2+}$-SPGMA-g-C) obtained under different adsorption temperature

<table>
<thead>
<tr>
<th>Adsorption temperature (°C)</th>
<th>Regeneration efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>93.48</td>
</tr>
<tr>
<td>40</td>
<td>99.08</td>
</tr>
<tr>
<td>50</td>
<td>99.43</td>
</tr>
<tr>
<td>60</td>
<td>98.61</td>
</tr>
<tr>
<td>70</td>
<td>99.26</td>
</tr>
<tr>
<td>80</td>
<td>99.46</td>
</tr>
</tbody>
</table>

Table 6

Regeneration efficiency of the Cu$^{2+}$-sulfonated poly(glycidyl methacrylate) grafted cellulose films (Cu$^{2+}$-SPGMA-g-C) obtained under different adsorption time

<table>
<thead>
<tr>
<th>Adsorption time (min)</th>
<th>Regeneration efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>94.07</td>
</tr>
<tr>
<td>30</td>
<td>99.24</td>
</tr>
<tr>
<td>45</td>
<td>99.67</td>
</tr>
<tr>
<td>60</td>
<td>99.86</td>
</tr>
<tr>
<td>120</td>
<td>99.75</td>
</tr>
</tbody>
</table>

Table 7

Adsorption capacity of different adsorbents for copper ions

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Capacity (mg/g)</th>
<th>Capacity (mg/m²)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan–alginate beads</td>
<td>27.44</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Low-cost mineral</td>
<td>33.18</td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>AC Ceiba pentandra hulls</td>
<td>9.060</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>Dehydrated wheat bran</td>
<td>14.10</td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>Cone biomass</td>
<td>5.110</td>
<td></td>
<td>48</td>
</tr>
<tr>
<td>Rice husk</td>
<td>53.123</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>Chitosan/sisal/banana fiber composite</td>
<td>1.885</td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>Poly(methacrylic acid) grafted cellophane ion exchanger membranes</td>
<td>4.016</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Sulfonated poly(glycidyl methacrylate) grafted cellulose films</td>
<td>67 (mg/g)</td>
<td>2,550 (mg/m²)</td>
<td>This work</td>
</tr>
</tbody>
</table>

This work
in nitrogen atmosphere at heating rate 20°C/min. It is clear from Fig. 15 that the weight-loss in case of the un-grafted cellulose film occurs at a relatively high rate between 280°C and 350°C where the cellulose film lost about 50% of its original weight. Above this temperature, the rate of weight loss becomes lower. On the other hand, the PGMA grafted cellulose film shows different behavior probably due to the gained thermal stability as compared with the un-grafted cellulose one. The weight loss at 350°C has been reduced to reach 22% as compare with 68% in case of the un-grafted cellulose film. The temperature needed to loss 50% of the film original weight, T_{50}, has been recognized at 350°C for the un-grafted cellulose film while shifted to higher temperature, 390°C, for the PGMA grafted cellulose film. This behavior could
be attributed to the formation of graft copolymer between PGMA and the cellulose backbone. The possibility of including homo-polymers purse has been eliminated depending on the absence of characteristic thermal beaks of PGMA [1].

3.7.3. Scanning electron microscope analysis

Fig. 17 displays scanning electron microscopy pictures for the un-grafted cellulose film (a), and the PGMA grafted cellulose film (b).

![Fig. 16. Thermogravimetric analysis thermographs of the un-grafted cellulose film (A), and PGMA grafted cellulose film (B).](image)

![Fig. 17. Scanning electron micrographs of the un-grafted cellulose film (a), and PGMA grafted cellulose film (b).](image)

Table 8
Energy-dispersive X-ray spectroscopy analysis the cellulose, PGMA grafted cellulose, and Cu²⁺-sulfonated PGMA grafted cellulose films

<table>
<thead>
<tr>
<th>Cellulose film type</th>
<th>C</th>
<th>O</th>
<th>S:Cu</th>
<th>Sulfonyc groups (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose film</td>
<td>48.68</td>
<td>51.32</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>PGMA grafted cellulose film</td>
<td>50.54</td>
<td>49.46</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cu²⁺-sulfonated PGMA grafted cellulose film</td>
<td>NA</td>
<td>NA</td>
<td>65.35</td>
<td>1.9</td>
</tr>
</tbody>
</table>
cellulose film (b). It is clear from the pictures that no phase separation has been observed as a result of the grafting process. Furthermore, the changes in the chemical structure as a result of the grafting process and subsequent sulphonation and copper ions adsorption processes have been proved by energy-dispersive X-ray spectroscopy analysis (Table 8). From the table it is demonstrate the changes in C:O ratio as a result of the grafting process. The results indicate that C:O ratio has been changed in the favour of C as a result of PGMA grafted branches add-on. On the other hand, the S:Cu ratio of the Cu²⁺-sulfonated PGMA grafted cellulose film proved the adsorption process.

4. Conclusion

Sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) were successfully developed and used in the separation of copper(II) ions from synthetic solution. The adsorption capacity of the sulfonated poly(glycidyl methacrylate) grafted cellulose films (SPGMA-g-C) increased linearly from 260 to 2,550 mg/m² with increase of the copper(II) ions concentration from 317.5 to 3,175 mg/L. The adsorption data were found fitted well with Freundlich isotherm model indicated of the multilayers nature of the adsorption process. Adsorption was found linearly increased within the first 15 min. Slower rate of adsorption was observed with increase the adsorption time from 30 min up to 120 min when equilibrium was achieved. The kinetic of the adsorption process was found followed the Pseudo-First-Order model. Different diffusion models were tested to understand the diffusion mechanism of the copper(II) ions adsorption process. The thermodynamic parameters of the adsorption process indicate that the adsorption process is endothermic one. The Cu²⁺-sulfonated poly(glycidyl methacrylate) grafted cellulose films (Cu²⁺-SPGMA-g-C) show an excellent regeneration efficiency where a minimum of 94% of adsorbed copper ions was recovered reaching to almost 100% in most of the Cu²⁺-SPGMA-g-C films. The adsorption capacity compared with other adsorbent shows the superiority of the developed sulfonated poly(glycidyl methacrylate) grafted cellulose films adsorbent over other adsorbents. Many characteristics nominate him as a convenient candidate adsorbent material for continuous membrane separation process of soluble metals ions such as:

1. Commercial availability,
2. Low cost,
3. Green biodegradable,
4. Film forming physical form,
5. Good mechanical properties,
6. Excellent regeneration properties.

Moreover, the Fourier transforms infrared analysis and thermal gravimetric analysis provided evidences of the grafting and the adsorption processes.

References


