*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2020.24947

178 (2020) 182–192
February

# Poly (methacrylic acid) grafted regenerated cellulose ions exchangers membranes for Cu(II) ion adsorption: kinetic, isotherm, and thermodynamic studies

G.F. El Fawal[a], R.E. Khalifa[a], S. Abdel Rahman[b,#], M.S. Mohy Eldin[a,*]

*[a]Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, Scientific Research and Technological Applications City, New Borg El-Arab City 21934, Alexandria, Egypt, emails: mohyeldinmohamed@gmail.com (M.S. Mohy Eldin), gom_fawal@yahoo.com (G.F. El Fawal), randaghonim@yahoo.com (R.E. Khalifa)*
*[b]Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt, email: somaya.abdelrahman@yahoo.com*
*Dedication: This publication to dedicate the memory of our wonderful colleague late Dr Somaya Abdel Rahman (S. Abdel Rahman), Professor of Chemistry, Department of Chemistry, Zagazig University, Zagazig, Egypt.*

Received 5 January 2019; Accepted 24 September 2019

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## ABSTRACT

Poly (methacrylic acid) grafted cellophane ions exchanger membranes have been developed for $Cu^{2+}$ ions separation from synthetic metal solutions in this study. Factors affecting the adsorption process, namely the copper ions concentration, the adsorption time, the adsorption temperature, and the grafting percentage have been studied. It was found that the $Cu^{2+}$ uptakes increase by increasing $Cu^{2+}$ ions concentration and the grafting percentage. Equilibrium has been obtained after 30 min of adsorption while the temperature is found to be of neglectable effect. Moreover, the kinetics, isotherms and thermodynamics of the adsorption process have been monitored. Adsorption behavior was kinetically considered using the pseudo-first-order and the pseudo-second-order models. The experimental data mostly correlated with the pseudo-second-order model. Moreover, the diffusion mechanism of the Cu(II) ions through the adsorption process has been studied. Various kinetic models namely; intraparticle diffusion model, D-W diffusion model, and Boyd diffusion model used. The actual rate-controlling step for Cu(II) ions removal determined. The adsorption equilibrium was assessed by using the Langmuir and the Freundlich isotherm equations where the Freundlich model had greater constancy with the equilibrium data. Also, the maximum monolayer adsorption capacity based on the Langmuir isotherm was 4.016 mg/g. Thermodynamic parameters as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$), and entropy change ($\Delta S°$) also were calculated. It is revealed that the adsorption of $Cu^{2+}$ ions is spontaneous, favorable, and exothermic. Fourier transforms infrared analysis, thermal gravimetric analysis, and energy dispersive X-ray analysis provided pieces of evidence of the grafting and the adsorption processes. Morphological changes have been followed using a scanning electron microscope. The membranes show excellent reusability. Minor reduction of the adsorption and regeneration processes has been detected after 10 cycles.

*Keywords:* Cellulose; Graft copolymers; Ions exchanger; Copper ions; Adsorption; Kinetics; Isotherms; Thermodynamics

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## 1. Introduction

A severe impact on both the environment and consequently the human health has been realized as a result of the heavy metals wastewater generation. Even minor concentrations of heavy metals are capable of producing toxicity [1]. Copper is one among the most discharged and toxic heavy metals [2]. A broad spectrum of health drawbacks have been observed upon uptake of large doses of copper [3]. Discharge of copper arises from mining, brass manufacture,

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* Corresponding author.

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electroplating, fertilizers, pulp and paper, and petroleum industries. Intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression, severe gastrointestinal irritation, and necrotic changes in the liver and kidney [3]. The WHO has defined 2 ppm as the limits allowed of copper ions in drinking water. Accordingly, ensuring the removal of copper ions from wastewater before discharging becomes a must. To achieve this goal, continuous research to have adequate techniques and materials for treatment of the heavy metals contaminated effluents is going on worldwide.

Generally, many different methods have been studied by a more substantial number of researchers to remove copper ions from industrial wastewater. These treatment methods can be classified as chemical, physical, and biological. They are often selected based on many advantages such as high selective separation, simplicity in control, and lower space requirement. Physico-chemical treatments can be considered as the most suitable treatment methods for the removal of copper ions from industrial wastewater. However, they still suffer from high operating cost due to the high price associated with the chemicals used and high energy consumption. Since metal-contaminated wastewater may contain some inorganic and organic matters, photocatalysis is a promising method for the removal of organic and inorganic contaminants together. Overall, each treatment method has its advantages and limitations. The main advantages and disadvantages of the different physico-chemical treatments have been discussed in the published review by Al-Saydeh et al. [4].

Adsorption attracts much attention in this direction due to the availability of different adsorbents of high efficiency, reasonable handling, reusability, and above that, the reduced cost [5]. The efficient adsorbent recognized by its high adsorption centres availability, which reflects on the fast adsorption process. Cellulose is the most abundant and renewable natural polymer in the universe. A wide variety of the cellulose derivatives have been prepared through different techniques and applied in a wide range of applications including the environmental ones. Cellulose-based graft copolymers having ion-exchange property find requests for removal of heavy metal ions from aqueous solutions [6–11]. Different grafting techniques were used to develop functional polymers using different cellulose origin matrices [12–17]. Accordingly, a wide range of ions exchangers for adsorption applications of charged molecules and ions was developed. Carboxylated PAM-g-coconut husk was developed and used for Hg ions removal with an adsorption capacity up to $7 \times 10^{-4}$ mol/g [12]. Composites of PMAA graft cellulose copolymers with bentonite and $TiO_2$ were developed to increase the surface area and the adsorption capacity for BSA and copper ions [13,14]. Ferdous Khan [15] developed methacrylic acid-g-natural lignocellulose (jute) fiber using 1-hydroxycyclohexyl-phenyl ketone as a photoinitiator. Abdel-Halim and Alhoqbani [16] developed polyacrylic acid grafted cellulose using chemical initiation system for lead removal, which obtained 250 mg/g as a maximum monolayer adsorption capacity. Awadallah and Sobhy [17] developed cellulose triacetate–graft–polymethacrylic acid films for dyes removal. They obtained 26 and 14 mg/g as a maximum monolayer adsorption capacity for ethyl violet (EV) and phenol red (PR) dyes. It can be seen that a wide range of adsorbents has been developed and investigated for the removal of heavy metals and dyes contaminants. The aim of this work is the development of poly (methacrylic acid) grafted cellophane ions exchanger films for Cu(II) ions separation from synthetic metal solutions. Factors affecting the adsorption process, namely copper ions concentration, adsorption time, adsorption temperature, and grafting percentage, have been studied. Furthermore, the kinetics, isotherms, and thermodynamics of the adsorption process have been monitored. Finally, the reusability of the developed adsorbent was evaluated. Pieces of evidence of the PMAA grafting process and the Cu(II) ions adsorption have been provided by performing FT-IR, thermal gravimetric analysis (TGA), and SEM-Energy dispersive X-ray analysis (EDAX) analysis.

## 2. Experimental

### 2.1. Materials

Cellophane sheets, kindly supplied by Misr Rayon Co. Kafr Eldawar (Egypt), were used after extraction with hot distilled water to remove the surface additives (20% glycerol and $Na_2SO_3$). Potassium Persulfate (KPS; purity 99%, M.wt. 270.31), sodium bisulfite (SBS) (purity 98%, M.wt. 190.11), and methacrylic acid (MAA) (purity 98 %) obtained from Sigma-Aldrich (Germany). Copper sulfate (purity 98%, M.wt. 249.68) obtained from El-Naser Pharmaceutical Co. for Chemicals, Egypt.

### 2.2. Methods

#### 2.2.1. Grafting of MAA onto regenerated cellulose films (Cellophane)

All the polymerization reactions were carried out in air atmosphere [18–20]. Grafting per cent (GP %) calculated as mentioned elsewhere [21]. A redox initiator aqueous system (KPS: SBS) used for performing the grafting process by solution polymerization technique. The details of the grafting process were mentioned in a previous publication [22].

#### 2.2.2. FT-IR analysis

FT-IR spectra of the un-grafted cellophane, PMMA-grafted cellophane and Cu(II)-PMMA–grafted cellophane membranes recorded on a Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400S, Japan).

#### 2.2.3. Thermal gravimetric analysis

TGA [23] is a technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specific atmosphere, is programmed. TGA was carried out using a Shimadzu Thermal Analyzer 50 (Japan).

#### 2.2.4. Morphological characterization using SEM and energy dispersive X-ray analysis

SEM micrographs for the un-grafted, PMAA grafted and Cu(II)-PMMA–grafted cellophane membranes were obtained using analytical scanning electron microscope (JEOL JSM 6360LA, Japan). To verify the modification process of the un-grafted cellophane membrane with PMAA and the adsorption of Cu(II) ions, the composition (weight ratios) of the un-grafted, PMAA grafted, and Cu(II)-PMAA-grafted cellophane membranes were examined by EDAX analysis using scanning electron microscopy.

### *2.2.5. Adsorption and desorption processes*

The PMAA-grafted cellulose membranes (25 g/1 $m^2$) were tested to remove copper ions from 1 L $CuSO_4$ solution (10–80 mg/L) and shaken at 150 rpm for a definite time (15–90 min) at a selected temperature (30°C–70°C) unless other stated. The membranes were sequentially washed with DI water to remove the unbounded or weakly linked copper ions. The membranes turned to blue color as an indicator of copper ions adsorption. For regeneration of the $Cu^{2+}$-PMAA-grafted cellulose membranes, the elution process was successfully performed for 30 min using 0.1 N HCl at 30°C at 150 rpm. The amount of copper adsorbed and eluted was determined by using atomic absorption spectrophotometer (Analysis T300, PerkinElmer, USA).

## 3. Results and discussion

### *3.1. Adsorption and recovery of $Cu^{2+}$ ions*

Different operational conditions affecting the adsorption process of $Cu^{2+}$ ions, namely copper ions concentration, adsorption time and temperature, and the grafting percentage were investigated. The detailed results were discussed as follows.

### *3.1.1. Effect of the copper ions concentration*

The impact of varying the $Cu^{2+}$ ions concentration on the removal percentage and the adsorption capacity of the $Cu^{2+}$ ions is shown in Fig. 1. From the figure, the adsorption capacity increases linearly with increasing of the $Cu^{2+}$ ions concentration up to 40 mg/L. Further increase of the $Cu^{2+}$ ions concentration to 60 mg/L found of less effect and leveled off at 80 mg/L. This behavior may be due to the consumption of most of the available exchange centers with $Cu^{2+}$ ions using 60 mg/L. On the other hand, the removal percentage has a different behavior where increases linearly to reach 100% with 30 mg/L and then starts to decrease reaching to 59.5% with 80 mg/L. The obtained result is following the results obtained by other authors [5,17]. Tian et al. [5] developed cellulose acetate (CA) nonwoven membrane for heavy metal ion adsorption by electrospinning and modified its surface with PMAA. The adsorption of $Cu^{2+}$heavy metal ions on this membrane was found linearly increased with the initial concentration up to 20 ppm [5]. Awadallah and Sobhy [17] grafted cellulose triacetate (CTA) with PMAA and exploited in adsorption of ethyl violet (EV) and phenol red (PR) dyes. They noticed that the adsorption capacity of CTA–g–PMAc either for EV or PR dyes increased by increasing agitation time, initial dye concentration and temperature as well [17].

We found that the adsorbed $Cu^{2+}$ ions have been recovered (desorbed) almost completely from membranes using 0.1 N HCl. The desorbed percentage ranged between 97.5% and 99%. This character indicates the capability of reusing the membranes.

### *3.1.2. Effect of the adsorption time*

Fig. 2 shows the effect of increasing the adsorption's time on the uptake of the $Cu^{2+}$ ions from 150 ppm initial concentration. We noticed a rapid adsorption rate at the first 30 min. With the prolongation of the adsorption time, the equilibrium reached after 45 min only where the removal percentage reached 18.72% and then leveled off. Anirudhan et al. [13] reported that the uptake of $Cu^{2+}$ ions by poly (methacrylic acid)-grafted $TiO_2$-densified cellulose was faster in the first 15 min then became slow. That is due to the availability of a large number of adsorption sites initially for adsorption [13]. The desorbed percentage of the adsorbed $Cu^{2+}$ ions is ranged between 96% and 99%.

### *3.1.3. Effect of the adsorption temperature*

In contrary to the results obtained by Haron et al. [24], no significant impact of the adsorption temperature increment

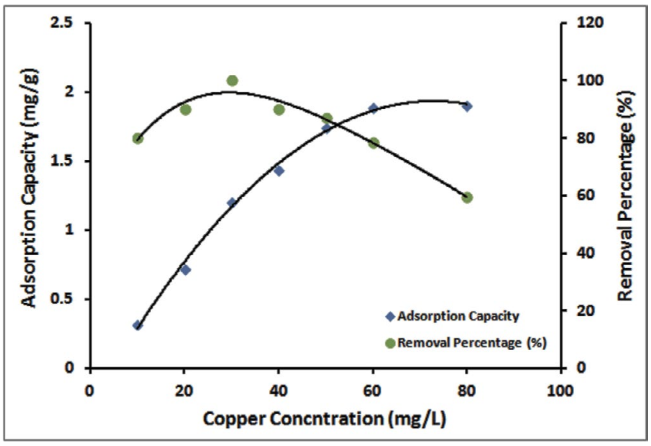

Fig. 1. Effect of the Cu(II) ions concentration on the adsorption capacity and the removal percentage (%).

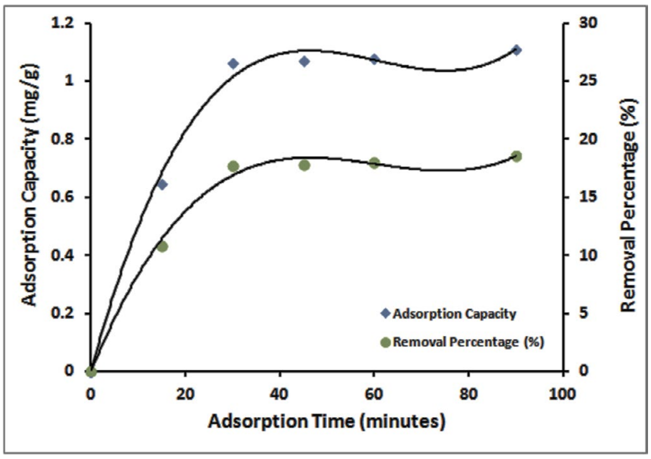

Fig. 2. Effect of the adsorption time on the Cu(II) ions adsorption capacity and the removal percentage (%).

was observed on the amount of adsorbed $Cu^{2+}$ ions (Fig. 3). The removal percentage has the same trend. The occurrence of the adsorption process on the PMAA-g-cellophane membranes surfaces mainly causes crosslinking between the PMAA graft branches and as a result, two things happen simultaneously. The first thing is creating a high concentration of immobilized $Cu^{2+}$ ions on the membranes' surface. That acts to reduce the concentration gradient of the $Cu^{2+}$ ions between the PMAA-g-cellophane membranes and the bulk solution and after with reduces the travelling of the $Cu^{2+}$ ions to the PMAA-g-cellophane membranes surface. The second is an increase of the graft copolymer compactness and thus minimizes the surface area and the pore size and as a result reducing the diffusion of the $Cu^{2+}$ ions from the bulk solution to the graft copolymer interior [16]. The desorbed percentage of the adsorbed $Cu^{2+}$ ions is ranged between 96% and 98.3%.

### 3.1.4. Effect of the grafting percentage

Logic increment of the adsorbed $Cu^{2+}$ ions has been observed with increasing of the PMAA grafting percentage due to its impact on the number of the carboxylic groups' centers bearded on the membranes (Fig. 4). Similar findings have been found by other authors [16,25]. Abdel-Halim and Alhoqbani [16] developed PAA cellulose adsorbent for the removal of lead ions. They found that the removal percentage of the lead ions increased linearly with the increase of the grafting percentage until it reached 100% removal with 40% grafting percentage.

## 3.2. Adsorption kinetic studies

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 essential for an efficient process. The most common models used to fit the kinetic sorption experiments are Lagergren's pseudo-first-order model and pseudo-second-order model [26,27], which are expressed as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where $q_t$ and $q_e$ are the amount of Cu(II) ions adsorbed (mg/g) at time $t$ (min), equilibrium, $k_1$ (min$^{-1}$) and $k_2$ (m$^2$/mg min) is the rates constant of the pseudo-first and pseudo-second-order models.

Furthermore, the initial adsorption rate as $t \to 0$ can be regarded as:

$$h = k_2 q_e^2 \tag{3}$$

The correlation coefficients ($R^2$) and the kinetic rate constants obtained from the straight-line plots of ln ($q_e - q_t$) against $t$ and $t/q_t$ vs. $t$ (Figs. 5a and b). The value of $q_{e,\,\mathrm{cal}}$ calculated from the intercept of the linear plot and shown in Fig. 1a is different from the experimental ones ($q_{e,\,\mathrm{exp}}$) (Table 1), suggesting that this model is not appropriate to predict the adsorption kinetics of the Cu(II) ions onto the polymethacrylic acid-g-cellophane membrane for the whole adsorption period. A similar trend previously was observed by many researchers [28,29].

Table 1 demonstrates that the calculated $q_{e,\mathrm{cal}}$ value obtained from the pseudo-second-order model agreed reasonably with the experimental value with a regression coefficient, $R^2 = 0.987$. It is showing that this model can be applied for the adsorption process and confirms the chemisorption of Cu(II) ions onto the prepared adsorbent. That finding is consistent with other reported studies [30,31].

## 3.3. Adsorption mechanism

The description of the diffusion process of the Cu(II) ions from the liquid phase (solution) to the solid phase (adsorbent) was performed using three kinetic models. The intraparticle and Dumwald–Wagner models described liquid film diffusion or intraparticle diffusion. The external mass transfer was examined by Boyd model.

The intraparticle diffusion model [32] is described as:

$$q_t = K_p t^{0.5} + C \tag{4}$$

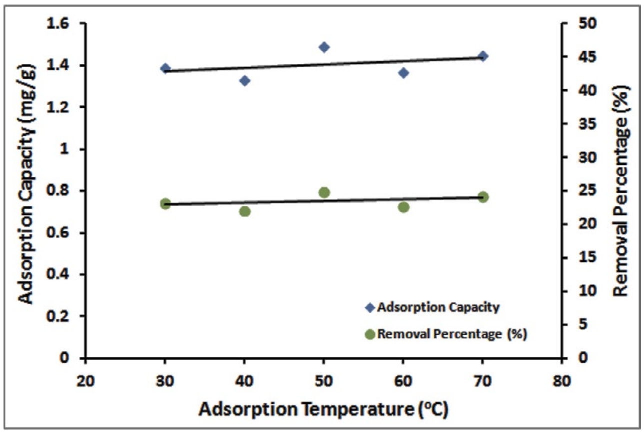

Fig. 3. Effect of the adsorption temperature on the Cu(II) ions adsorption capacity and the removal percentage (%).

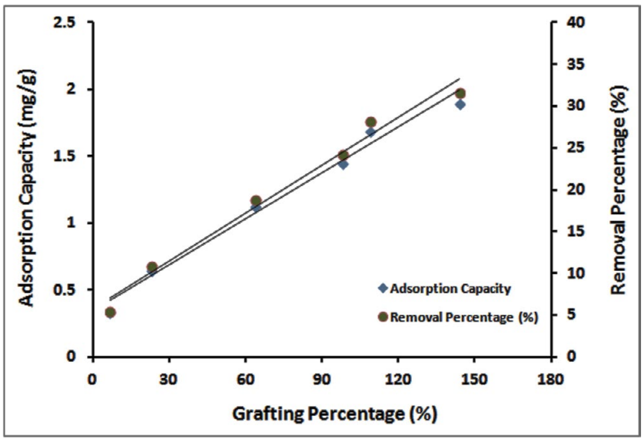

Fig. 4. Effect of the PMAA grafting percentage on the Cu(II) ions adsorption capacity and the removal percentage (%).

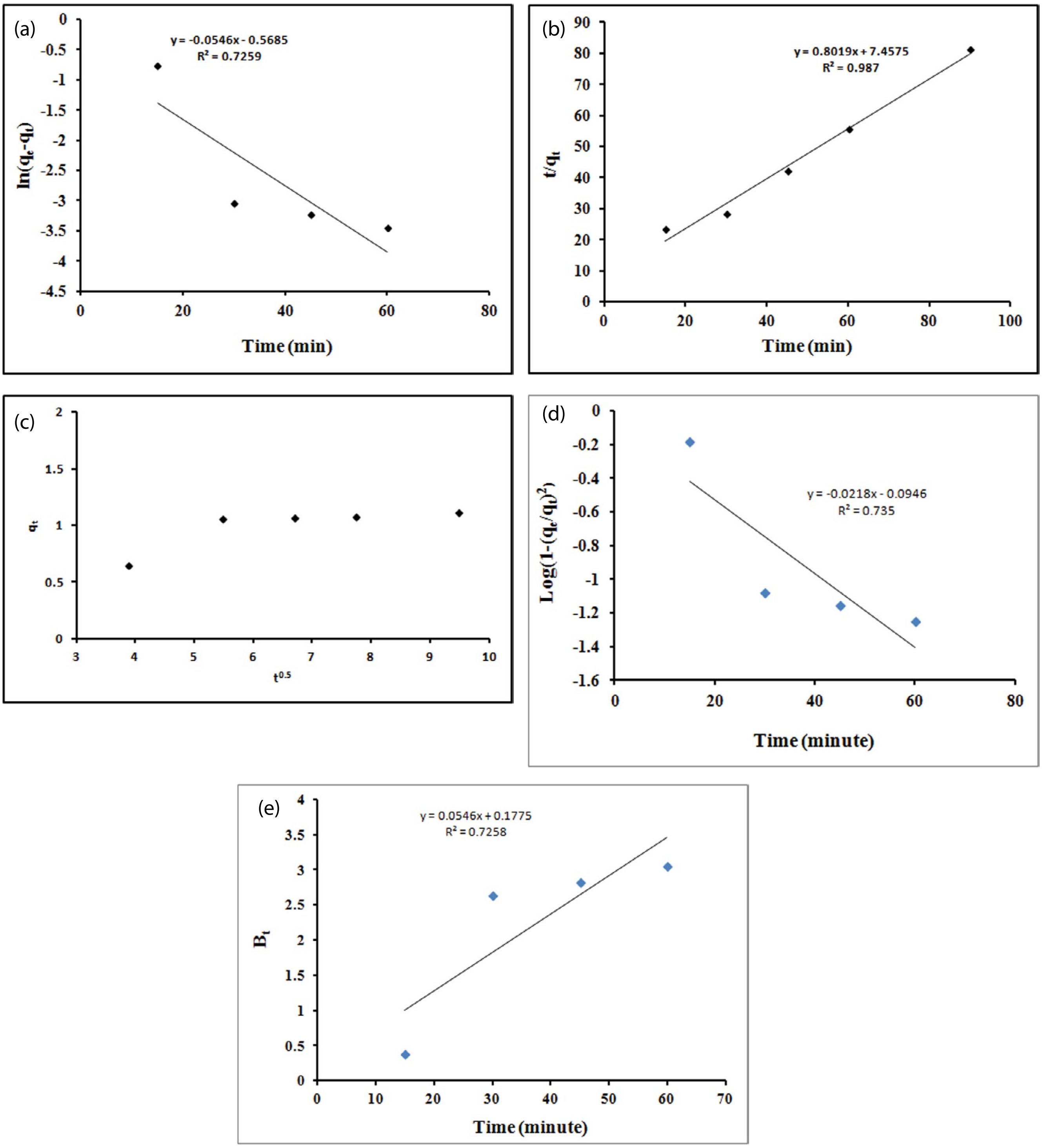

Fig. 5. Kinetic rate models for the adsorption of Cu(II) ions onto the PMAA-grafted cellophane membrane; (a) the pseudo-first order and (b) the pseudo-second order, (c) the intraparticle diffusion model, (d) Dumwald–Wagner diffusion model, and (e) Boyd diffusion model.

where $K_p$ (mg g$^{-1}$ min$^{-1/2}$) is the intraparticle rate constant, which can be obtained from the slope of the second portion of the straight line of the plot $q_t$ vs. $t^{0.5}$ as mentioned in Table 2, three different stages organized the adsorption of Cu(II) ions (Fig. 5c). The first rapid exterior surface adsorption, the gradual adsorption where the intraparticle-diffusion is the rate-controlling factor, and finally the equilibrium stage due to the lower Cu(II) concentration in the liquid phase in addition to the lack in the available active sites. Thus, it is observable that the intraparticle diffusion is not the individual

Table 1
Adsorption parameters of the pseudo-first and the pseudo-second order kinetic models

| Pseudo-first-order | | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|
| $q_{e,\exp,}$(mg g$^{-1}$) | $q_{e,\mathrm{cal}}$,(mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | $q_{e,\mathrm{cal}}$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
| 1.112 | 0.5664 | –0.0546 | 0.7259 | 1.247 | 7.4575 | 0.987 |

Table 2
Adsorption parameters of the intraparticle diffusion model, Dumwald–Wagner diffusion model, and Boyd diffusion model

| Intraparticle diffusion model | | | D-W diffusion model | | Boyd diffusion model | |
|---|---|---|---|---|---|---|
| $K_{p,\,1-3}$,(mg/g.min) | $C$ | $R^2$ | $K$ | $R^2$ | Intercept | $R^2$ |
| 0.0148 | 0.9698 | 0.9649 | 0.05021 | 0.735 | 0.1775 | 0.7258 |

rate-limiting step as the second portions of the plot shown did not have a zero intercept [33].

The linear form equation determined the diffusion rate inside particulate using the Dumwald–Wagner model [34] presented in Eq. (5). $k$ is the diffusion rate constant and the removal percentage, $F$ is calculated by ($q_t/q_e$).

$$\log\left(1-F^2\right) = -\left(\frac{k}{2.030}\right)t \tag{5}$$

Fig. 5d presents fitting of the adsorption data using the Dumwald–Wagner model. From the figure it is clear that the Dumwald–Wagner did not fit the adsorption data very well ($R^2 = 0.735$), and the diffusion rate constant $K$ was found to be 0.05021 min$^{-1}$.

The actual rate-controlling step involved in the Cu(II) ions adsorption process was determined by further analyzing the sorption data by the Boyd kinetic model as follows [35]:

$$F = 1-\left(\frac{6}{\pi^2}\right)e^{\left(-B_t\right)} \tag{6}$$

$$F = \left(\frac{q}{q_\alpha}\right) \tag{7}$$

$$B_t = -0.4978 - \ln\left(1-\left(\frac{q}{q_\alpha}\right)\right) \tag{8}$$

$q$ and $q_\alpha$ represent the amount sorbed (mg/g) at any time $t$ and at an infinite time (in the present study 30 min). $F$ is the fraction of Cu(II) ions adsorbed at different time $t$ given by Eq. (7) and $B_t$ is a mathematical function of $F$. With substituting Eq. (6) into Eq. (7), we obtained the kinetic expression presented in Eq. (8).

According to Eq. (8), the data fitted in Fig. 5e and useful information can be extracted to distinguish between external transport and intraparticle transport controlled rates of sorption. From the linearity of this plot, which did not pass through the origin, we concluded that the film diffusion governs the rate-limiting process [36].

### 3.4. Adsorption isotherms studies

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among solid and liquid phases and are thus crucial from the chemical design point of view. The distribution of metal ions between the liquid and the solid phase commonly designated by the Langmuir [37] and the Freundlich [38] isotherm models. The applicability of these models to the adsorption process was evaluated by judging the correlation coefficients values. The following equations represent the linear forms of the Langmuir and the Freundlich isotherms:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \tag{9}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{10}$$

where $C_e$ is the equilibrium Cu(II) ion concentration (mg/L), $q_e$ is the amount of Cu(II) ion adsorbed at equilibrium (mg/g). $q_{\max}$ is the maximum monolayer adsorption capacity (mg/g). $K_L$ is the Langmuir constant (L mg$^{-1}$) related to the adsorption energy, which quantitatively reveals the empathy between the adsorbent and adsorbate. $K_F$ is the maximum multilayer adsorption capacity (mg/g), and $n$ is correlated to the adsorption intensity. The maximum adsorption capacity obtained from the slope of the plot of $C_e/q_e$ vs. $C_e$ (Fig. 6a) was found to be 4.016 mg/g (Table 3).

It is also significant to compare the value of $q_{\max}$ obtained from this study with values of other stated adsorbents (Table 4) [39–44].

A dimensionless equilibrium parameter $R_L$ is calculated from Eq. (11) specifying that the equilibrium adsorption was favorable as $R_L$ values lie between 0.0 and 1.0 for the initial Cu(II) concentration range from 10 to 80 mg L$^{-1}$. However, the $R^2$ value is 0.4126 verifying that the adsorption data not fitted to the Langmuir model.

$$R_L = \frac{1}{1+K_L C_0} \tag{11}$$

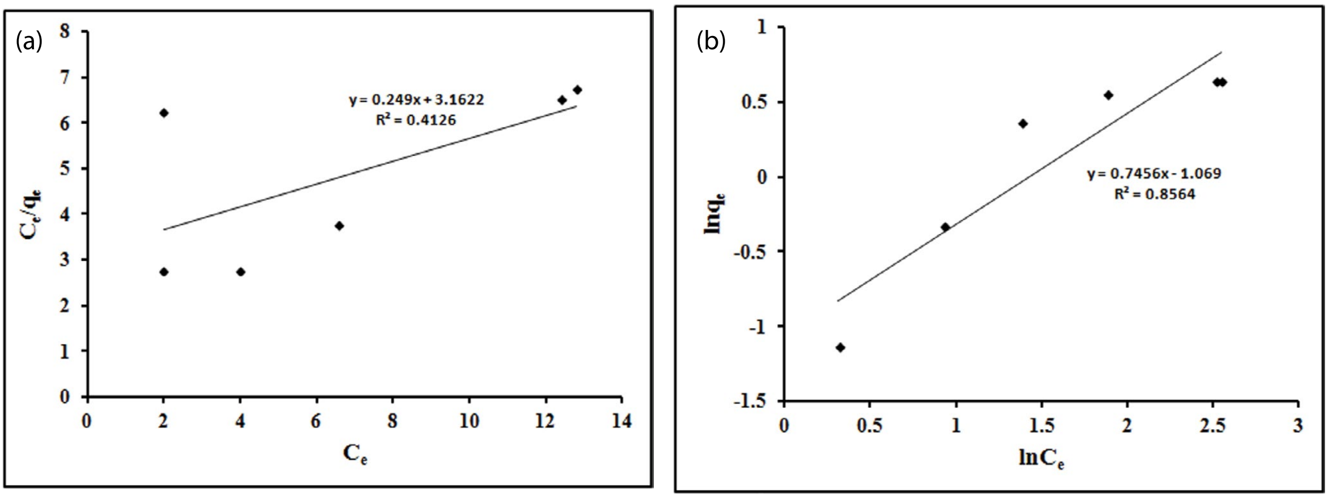

Fig. 6. Equilibrium isotherm for the adsorption of Cu(II) ions onto the PMAA-grafted cellophane membrane; (a) the Langmuir and (b) the Freundlich isotherm.

Table 3
Parameters and the correlation coefficients of the Langmuir and the Freundlich isotherm

| Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|
| $q_{\max}$,(mg. g$^{-1}$) | $K_L$ (L.mg$^{-1}$) | $R^2$ | $K_f$ (mg.g$^{-1}$) | $N$ | $R^2$ |
| 4.016 | 12.7 | 0.4126 | 0.343 | 1.34 | 0.8564 |

On the other hand, the value of *n* determined from the Freundlich plot (Fig. 6b) was 1.34 (Table 3). The obtained value is demonstrating that the metal ions are favorably adsorbed on the adsorbent surface, as stated by Mohanty et al. [45]. As well, the adsorption follows the Freundlich isotherm according to the correlation coefficient value.

### 3.5. Adsorption thermodynamic studies

From engineering aspects, the values of thermodynamic parameters such as the enthalpy change ($\Delta H°$), the free energy change ($\Delta G°$), and the entropy change ($\Delta S°$) should be considered to conclude the spontaneity of the adsorption process. A spontaneous system will display a decrease in $\Delta G°$ and $\Delta H°$ values with increasing the temperature. All the thermodynamic parameters were calculated from the following equations [46,47]:

$$\ln K_0 = \frac{\Delta S}{\Delta R} - \frac{\Delta H}{RT} \tag{12}$$

where

$$K_0 = \frac{q_e}{C_0} \tag{13}$$

$$\Delta G = \Delta S - RT \ln K_0 \tag{14}$$

where $R$ is the gas constant (8.314 J/mol K), and $T$ is the temperature in Kelvin. Table 5 lists down the thermodynamic parameters values (Fig. 7). The negative value for the $\Delta H°$

Table 4
A comparison of the maximum adsorption capacity for the adsorption of Cu(II) ions by PMAA-g-cellophane membrane and other adsorbents

| Adsorbent type | Maximum adsorption capacity | Reference |
|---|---|---|
| Chitosan beads | 33.44 mg/g | 12 |
| Chitosan/PVA beads | 47.85 mg/g | 12 |
| Chitosan-coated sand | 8.76 mg/g | 13 |
| Epichlorohydrin cross-linked chitosan microspheres | 39.31 mg/g | 14 |
| Chitosan–heparin polyelectrolyte complex microspheres | 81.04 mg/g | 14 |
| Polyaniline graft chitosan beads | 100 mg/g | 15 |
| Cross-linked chitosan–cellulose beads | 53.2 mg/g | 16 |
| Methacrylic acid-grafted poly(ethylene terephthalate) fibers | 8.85 mmol/g | 17 |
| Polymethacrylic acid-g-cellophane | 4.016 mg/g | This study |

Table 5
Thermodynamic parameters for the adsorption of Cu(II) ions by PMAA-g-cellophane membrane

| $T$ (K) | $\Delta G°$, (kJ mol$^{-1}$) | $\Delta H°$, (kJ mol$^{-1}$) | $\Delta S°$,(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| 313 | 11.638 | –3.698 | –25.2654 |
| 333 | 12.039 | | |
| 343 | 12.429 | | |

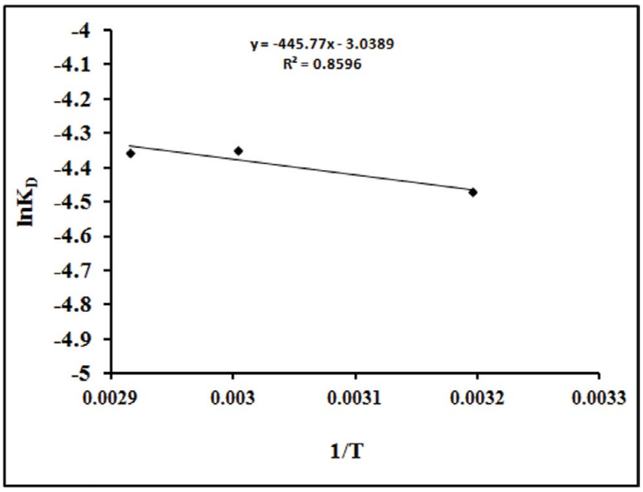

Fig. 7. Van't Hoff plot of the adsorption of Cu(II) ions onto PMAA-grafted cellophane membrane.

(3.698 kJ/mol) indicates the exothermic nature of the process, which explains the decrease of Cu(II) adsorption efficiency as the temperature increased. As informed by Alkan et al. [48], the enthalpy values change as a result of the chemisorption are between 40 and 120 kJ mol$^{-1}$, 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 metal ions is probably attributable to the physisorption. Conversely, in the kinetics study, it was described that the adsorption is chemisorption. Thus, it is evident from the lower $\Delta H°$ value that the physisorption also takes part in the adsorption process in which the metal ions adhere to the adsorbent surface only through weak intermolecular interactions. The positive value for the entropy change, $\Delta S°$ (25.2654 J/mol K) illustrating the disorderliness at the solid/liquid interface during the adsorption of Cu(II) ions onto the polymethacrylic acid-g-cellophane membrane. The $\Delta G°$ values reflect the feasibility of the process.

### 3.6. Reusability

Due to the importance of the reusability from cost-effectiveness, adsorption and regeneration cycles have been conducted. Minor reduction of the adsorption capacity and regeneration processes efficiency has been detected after 10 cycles. The adsorption capacity has been reduced from 1.904 to 1.86 mg/g, while the recovery percentage decreased from 99% to 97.8%.

### 3.7. Membranes characterization

It is well known that the grafting copolymerization of vinyl monomers onto cellulosic materials was initiated by many kinds of oxidizing agents resulting in the formation of covalent bonds between monomers and cellulose backbone. The formed graft copolymers are new materials of modified properties relative to the original cellulose. Monitoring of chemical structure changes by FT-IR analysis and thermal properties changes by TGA is the primary evidence of occurring grafting process [18,21,49,50] in addition to verifying of the adsorption process. Furthermore, morphological changes have been followed by a scanning electron microscope.

#### 3.7.1. FT-IR

Fig. 8 illustrates the FT-IR spectra of the un-grafted, grafted membranes and immobilized $Cu^{2+}$ ions grafted membranes. From the figure, the IR-spectrum shows that absorption bands between 3,250 and 3,500 cm$^{-1}$ arising from hydroxyl groups located on the un-grafted membranes; Fig. 9a. The IR spectra of the polymethacrylic acid grafted cellophane showed a characteristic band at 1,731 cm$^{-1}$, which is peculiar to the carbonyl group of acid stretching vibrations indicating the formation of PMAA-grafted cellulose [51] (Fig. 9b). Adsorption of the $Cu^{2+}$ ions on the PMAA-grafted membranes noticeably masked this band. That confirms the interaction between $Cu^{2+}$ ions and the carboxylic groups of the PMAA graft branches (Fig. 9c).

#### 3.7.2. TGA

Thermal analysis of the un-grafted, PMAA-grafted and Cu-PMAA-grafted cellophane membranes was carried out by thermo gravimetric analyzer in a nitrogen atmosphere at a heating rate 20°C/min. From Fig. 10 it can be observed a relatively high rate weight loss of the ungrafted cellophane membrane at a temperature ranged between 288°C and 375°C. The membrane lost about 53% of its original weight. Above this temperature, the rate of weight loss became lower (Fig. 10a). On the other hand, the PMAA-grafted membrane show a different behavior and gained thermal stability compared with the ungrafted one where weight loss at 375°C was reduced to reach 21% (Fig. 10b).

Additional thermal stability of the $Cu^{2+}$ ions immobilized grafted membrane was observed through the reduction of the weight loss at the same temperature range; 16.5% (Fig. 10c). That could refer to the contribution of the complexation action of the $Cu^{2+}$ ions between the carboxylate grafted chains. That conclusion has been confirmed in the higher temperature, 600°C, where the ungrafted, grafted and $Cu^{2+}$ ions immobilized grafted membranes lost 90%, 80% and 69%, respectively, of their weights. In conclusion, the obtained thermograms verified the formation of the graft copolymers and the immobilization of $Cu^{2+}$ ions.

#### 3.7.3. Energy dispersive X-ray analysis

The elemental analysis of the un-grafted cellophane, PMAA-grafted cellophane, and $Cu^{2+}$ ions immobilized

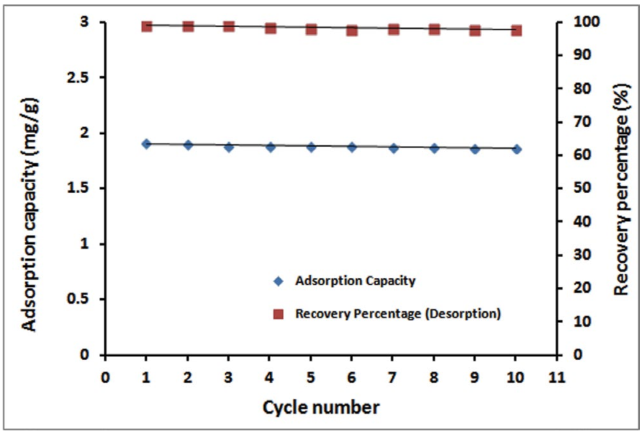

Fig. 8. Reusability of PMAA-grafted membrane in the adsorption of Cu II) ions.

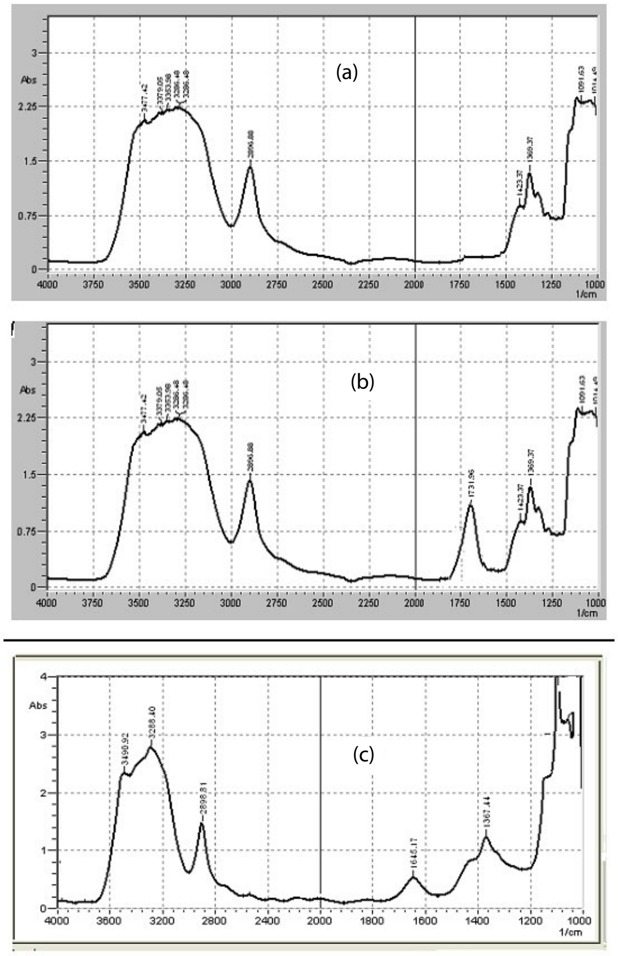

Fig. 9. FT-IR spectra of: (a) un-grafted cellophane membrane, (b) PMAA-grafted membrane (GP = 63%), and (c) $Cu^{+2}$-immobilized PMAA-grafted membrane.

PMAA-grafted cellophane membranes presented in Table 6. From the table, it is clear that the changes in the C, O, and Cu weight percentage due to the modification of the cellophane with PMAA. The increment of the C weight percentage on the benefits of the O weight percentage is referring

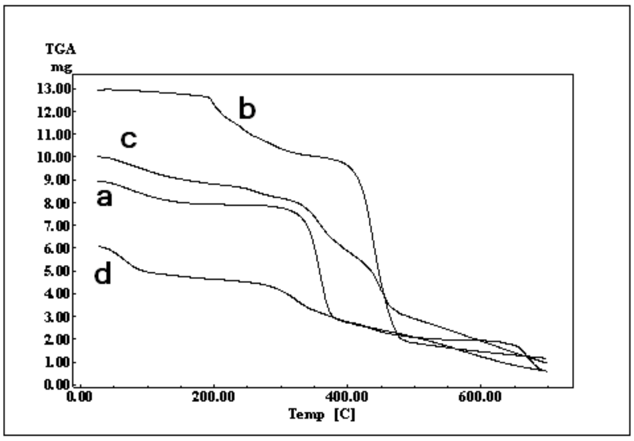

Fig. 10. TGA thermographs of: (a) un-grafted cellophane membrane, (b) PMAA-grafted cellophane membrane (GP = 63%), and (c) Cu-immobilized PMAA-grafted cellophane membrane.

to the grafting of the PMAA on the cellophane structure. The appearance of the Cu in the structure of the $Cu^{2+}$ ions adsorbed PMAA-grafted cellophane membranes evidenced of the adsorption process of the Cu(II) ions.

### 3.7.4. SEM micrographs

Fig. 11 shows the SEM micrograph (surface and cross-section) of the un-grafted, PMAA-grafted, and $Cu^{2+}$-PMAA-grafted cellophane membranes. The figure revealed that the surface of the un-grafted cellophane is rougher than both the PMAA-grafted cellophane, and the $Cu^{2+}$-PMAA-grafted cellophane membranes. It is appeared that the grafting process coated the surface, and the surface's smoothness increased. The adsorption of the Cu(II) ions further improved the surface smoothness. The cross-section micrographs of the un-grafted cellophane evidenced the porous structure. The PMAA-grafted cellophane show reduction of its porous structure and no phase separation has been noticed considering as a good indication of the grafting homogeneity. The inner membranes homogeneity further improved with adsorption of the Cu(II) ions and a noticeable increase of the grafted membranes thickness has been observed.

## 4. Conclusion

Poly (methacrylic acid) grafted cellophane ions exchanger membranes have been developed for the purpose of separation Cu(II) ions from synthetic metal solutions. Factors affecting the adsorption process, namely; the copper ions concentration, the adsorption time, the adsorption temperature, and the grafting percentage have been studied. The reported results showed that 25 g of the developed PMAA-g-cellophane is enough to reduce the Cu(II) ions concentration to the acceptable limit by the WHO (2 ppm) in 1 L of a contaminated water with 30 ppm Cu ions concentration at a reasonably short time; 90 min at RT. The developed PMAA-g-cellophane shows a distinguished reusability; it retained more than 98% of its efficiency after reuse for 10 successive adsorption–desorption cycles. The isotherm study indicates that the equilibrium adsorption data correlated well with the

Table 6
Elemental analysis of C, O, and Cu for un-grafted cellophane, PMAA-grafted cellophane and Cu(II)-PMAA-grafted cellophane membranes

| Matrix | C wt% | O wt% | Cu wt% |
|---|---|---|---|
| Un-grafted cellophane | 43.24 | 56.76 | NA |
| PMAA-grafted cellophane | 44.92 | 55.08 | NA |
| Cu(II)-PMAA-grafted cellophane | 44.80 | 55.00 | 0.20 |

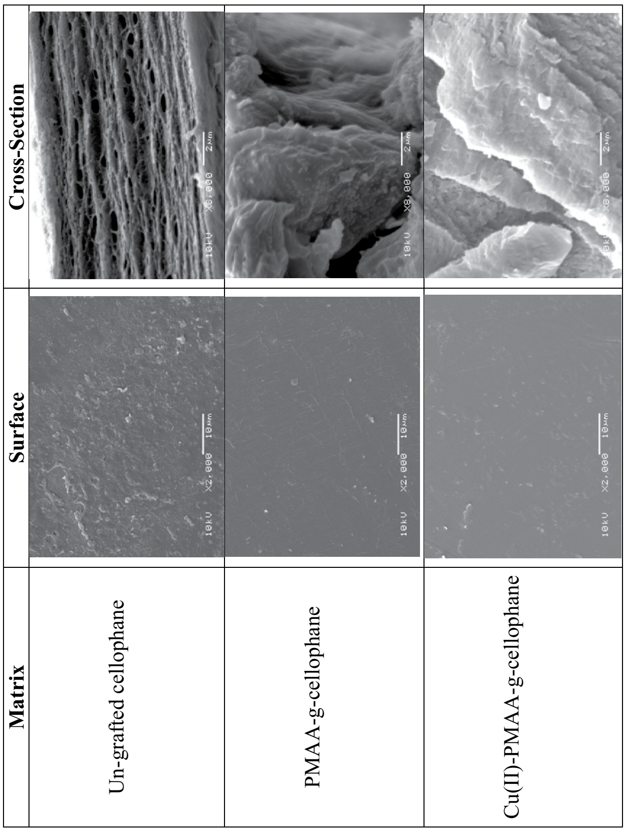

Fig. 11. SEM micrograph of: (a) un-grafted cellophane membrane, (b) PMAA-grafted cellophane membrane (GP = 63%), and (c) Cu-immobilized PMAA-grafted cellophane membrane.

Freundlich isotherm models. The kinetic data revealed that the pseudo-second-order kinetic model conformed better than the pseudo-first-order model. The adsorption mechanism models study showed that the film diffusion governs the rate-limiting process. The adsorption was also more favorable and spontaneous at a lower temperature.

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