35

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Separation of Cu (II) Ions by Hydroxamic Acid Functionalized Poly (Methyl Methacrylate) Grafted Cellophane Membranes

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Abstract

Hydroxamic acid functionalized Poly (methyl methacrylate) grafted cellophane ions exchanger membranes have been used 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. It was found that the Cu+2 uptakes increase by increasing the grafting percentage. The maximum uptake amount of Cu+2 ions obtained with membranes of grafting percentage 58%. However, the recovery of the adsorbed Cu+2 ions has not been affected by variation of the grafting percentage. Equilibrium has been obtained after 60 minutes of adsorption while the temperature was found of neglectable effect. Fourier transforms infrared analysis and thermal gravimetric analysis provided evidences of the adsorption processes. Moreover, the kinetics and isotherms of the adsorption process have been monitored. The membranes show a very good applicability and reusability where very slow reduction of the adsorption and regeneration processes has been detected after ten cycles.

Keywords: cellulose; graft copolymers; ions exchanger; copper ions; adsorption; kinetics; isotherms; thermodynamics

1. Introduction

Accelerated growth of the world population creates a massive stress on the consumption of the fresh water. A limited fresh water sources and the industrial development all over the world which produce thousands of pollutants every year charged at the environmental water system raising seriously the challenge of waste water treatment. Among the most hazard contaminants, heavy metals contamination has been a critical and accumulated problem in the environment. A direct impact, such as soil and water pollution, caused by many toxic heavy metals leads in the medium and long term to indirect impact on human health and the global economy.

Continuous straggling to explore different techniques and technologies to treat the waste water is a world concern. Among many materials developed for the treatment process of waste waters, natural materials have a massive contribution due to many advantages including, but not limited to, the eco-friendly characters and abundance.

Cellulose is the most abundant and renewable natural polymer in the universe[1]. A wide variety of the cellulose derivatives have been prepared through different techniques and applied in wide range of applications including the environmental ones [2,3]. Cellulose graft copolymers having ion-exchange property find applications for removal of heavy metal ions from aqueous solutions [4-14]. Hydroxamic acid functionalized grafted cellulose copolymers have a recognized contribution in the removal of different

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heavy metal ions from aqueous solutions. Haron et al [15] removed Cu (II) ions using hydroxamic acid functionalized PMMA-g-oil palm empty fruit bunch. Jiao et al [16] removed Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+} using a new poly(amidoximehydroxamic acid) cellulose derivative obtained by grafting of ethyl (ethoxymethylene) Cyanoacetate onto cellulose followed by reaction with Hydroxyl amine hydrochloride. Rahman et al reported a lot of work in this direction [17-19] using cellulose from different sources grafted by poly(methyl acrylate) and treated with Hydroxyl amine hydrochloride to remove different metals including Cu^{2+}, Fe^{3+}, Mn^{2+}, Co^{3+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}.

The aim of this work is the development of hydroxamic acid functionalized Poly (methyl methacrylate; PMMA) grafted cellophane ions exchanger membranes 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 better understanding of the separation process.

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 Na2SO3). Potassium persulphate (KPS) (purity 99%, M.wt. 270.31). Hydroxylamine hydrochloride (purity 99%) and methyl methacrylate (MMA) (purity 98 %) were obtained from Sigma-Aldrich (Germany). Copper sulfate (purity 98%, M.Wt. 249.68) was obtained from El-Naser Pharmaceutical Co. for Chemicals, Egypt.

2.2. Methods

2.2.1. Preparation of the hydroxamic acid functionalized PMMA grafted cellophane membranes

First, the cellophane membranes were grafted with PMMA under different polymerization conditions; monomer concentration (5-15%; v/v), initiator concentration KPS (0.01-0.1%; w/v), reaction temperature (60-80°C), reaction time (1-6h), solvent composition (Water-Ethanol; 1:1). All the grafting reactions were carried out in air atmosphere [20-22]. The grafting percent (GP %) was calculated as mentioned elsewhere which varied between 6% and 58% [23]. The PMMA grafted membranes under

specific conditions (0.05% KPS, and 10% MMA, time 3h, 60°C) with GP% 58 have been selected for performing the adsorption process where functionalized with hyroxamic acid through reaction with hydroxylamine under definite conditions; 0.5% hydroxyl amine hydrochloride solution, reaction temperature 40°C, and reaction time 30 minutes. The flow chart of the steps is presented in Figure 1.
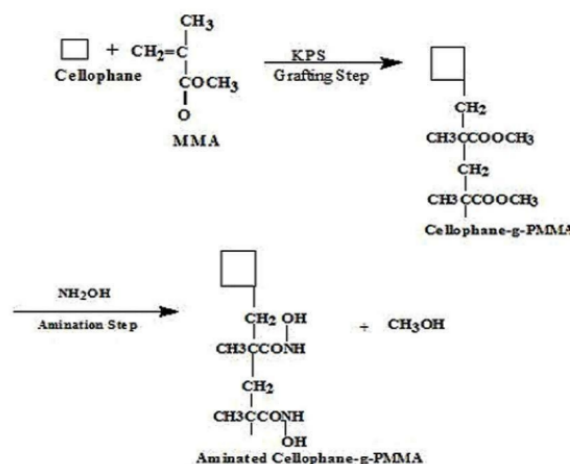

Figure 1: Schematic diagram of the amination process of the cellophane-g-PMMA membranes.

2.2.2. Adsorption process

The hydroxamic acid functionalized PMMA grafted membranes were tested to remove copper ions from $CuSO_4$ solution (10-60 mg/L) and shaken at 150 rpm for definite time (15-90 minutes) at selected temperature (30-70°C). 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 adsorbed Cu^{+2}-hydroxamic acid functionalized PMMA grafted cellophane membranes, the elution process was successfully performed for 30 min using 0.1N HCl in 30°C at 150 rpm. The amount of copper adsorbed and eluted was determined by using atomic absorption spectrophotometer (Analysis T300, Perkin Elmer, USA).

3. Characterization:

3.1. FT-IR analysis

FT-IR spectra, in the absorbance mode, of the native and the grafted cellophane membranes have been recorded using FT-IR spectrometer (Shimadzu FTIR- 8400 S, Japan), connected to a PC, and analysis the data by IR Solution software (Version 1.21). The spectra (128 scans at 2 cm^{-1} resolution)

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have been collected with the frequency range of 4000-400 cm^{-1}. The FTIR spectra were Fourier-deconvoluted with a resolution enhancement factor of 1.5 and a bandwidth of 15 cm^{-1}.

3.2. Thermo-gravimetric analysis

TGA analyses were carried out using a Shimadzu Thermal Analyzer 50. (Japan) in the temperature range from 20°C to 700°C under nitrogen flow rate of 20 mL/min using a heating rate of 10°C/min [24].

4. Results and Discussion

4.1. Membranes characterization

The formed graft copolymers are new materials of modified properties than the original cellulose. Monitoring of the chemical structure changes by FT-IR analysis and thermal properties changes by TGA analysis are the primary evidence of occurring the grafting and the hydroxamic acid functionalization processes.

Figure 2, illustrated the FT-IR spectra of PMMA grafted membrane and hyrdoxamic acid-PMMA grafted membrane. From the Figure 2A, the IR-spectrum shows that absorption bands between 3250 and 3500 cm^{-1} arising from hydroxyl groups of the cellophane backbone. Figure 2B show a new band at 1728-1731 cm^{-1}, resulting from C=O stretching of ester group of PMMA which confirming the grafting of PMMA on the membranes [25, 26]. As a result of the functionalization process, the hydroxamic acid groups showed new absorption bands at 1680 and1650cm^{-1}corresponding to the C=O stretching and N–H bending modes with disappearance of C=O stretching of ester group of PMMA at 1728-1731 cm^{-1}; Figure 2C [19,17].

Thermo-Gravimetric Analysis of the cellophane membrane, PMMA grafted cellophane and the adsorbed Cu^{+2} Hydroxamic acid PMMA grafted cellophane membranes were carried out by Thermo-Gravimetric Analyzer in a nitrogen atmosphere at a heating rate 20°C/min. From Figure 3A, we can see that the first weight loss in case of the cellophane membranes occurs at 120°C due to the desorbed moisture lost. The second weight loss step observed between 285°C and 375°C, at a relatively high rate, where the membrane lost about 53% of its original weight due to pyrolysis.
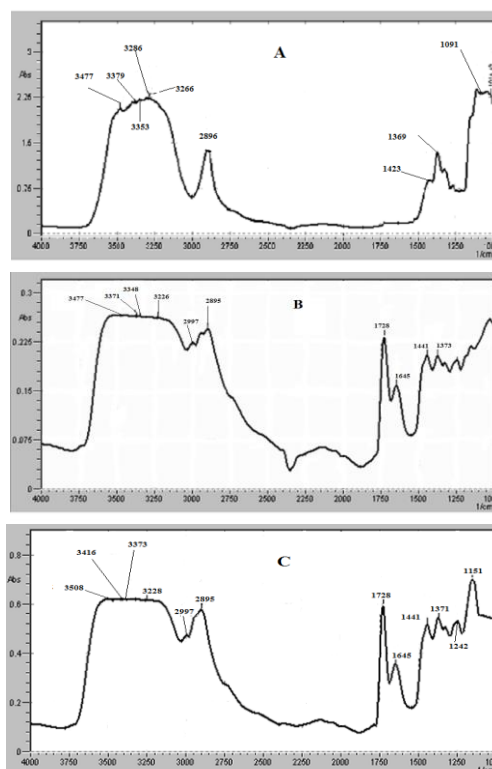

Figure 2: FT-IR spectra of the cellophane membrane (A), the PMMA grafted membrane (B), and the hydroxamic acid-PMMA grafted membrane (C).

The third and last degradation step observed between 380°C to 700°C where complete degradation occurred due to the charring process. On the other hand, PMMA grafted cellophane lost weight due to desorbed water is 6.4% due to the hydrophobic nature of PMMA graft branches (Figure 3B). The weight loss, due to pyrolysis, at 375°C is 42-45 %. That may be referred to the thermal stability of PMMA graft branches. For Cu^{+2} adsorbed grafted cellophane membranes (Figure 3C), the desorbed moisture loss has been increased to 18%. On the other hand, at 375°C, the second degradation step, a reduction in the weight loss to 38.2% has been noticed. That could be referred to the contribution of the introduction of the hydroxamic acid and the complexation action of the Cu^{+2} ions. This effect is confirmed at the higher temperature 600°C, Where 95 % and 65.9 % as weight loss of the grafted and adsorbed Cu^{+2} Hydroxamic acid PMMA grafted membranes.
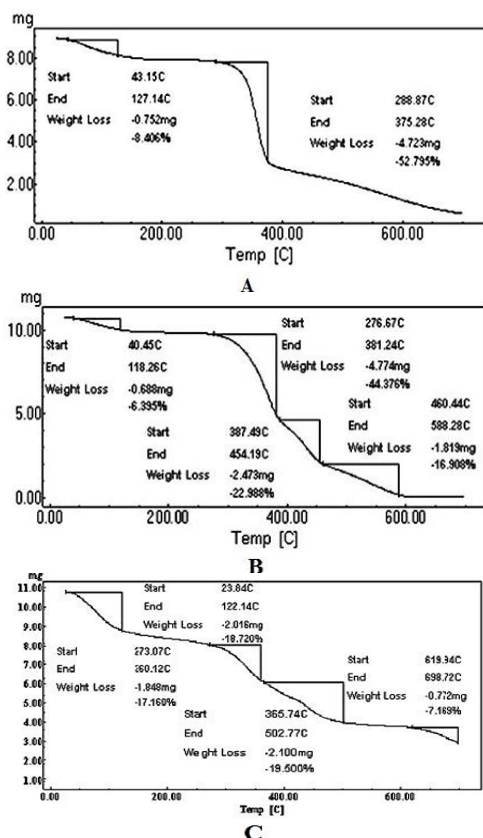
Figure 3: TGA thermographs of the cellophane membrane; (A), PMMA grafted cellophane membrane; (B), the Cu^{+2-} immobilized PMMA-grafted cellophane membrane (C).

4.2. Adsorption and recovery of Cu^{+2} ions

Different conditions affecting the adsorption process of Cu^{+2} ions were investigated, and the detailed results are discussed.

The effect of variation Cu^{+2} ions concentration on the amount of adsorbed Cu^{+2} ions was shown in Table 1. From the table, copper ions uptake increases with increasing of the Cu^{+2} ions concentration up to 40 mg/L. Further increase of the Cu^{+2} ions concentration was found has no effect. This behavior may be due to consumption of all the exchange centers with Cu^{+2} ions using 40 mg/L. The obtained result is in accordance with the results obtained by other authors [15,19]. On the other hand, we can realize that the adsorbed Cu^{+2} ions have been recovered completely from membranes using 0.1N HCl. This character gives an indication of the capability to reuse the membranes.

Also, Table 1 shows the effect of increasing the adsorption's time on the Cu^{+2} ions uptake. We can notice that with prolongation of the adsorption time,

copper uptake increases and the equilibrium reached after 90 min. The same findings were reported by other authors [15,19].

Table 1: Effect of the adsorption conditions on the amount of adsorbed Cu^{+2} ions and its recovery percent

Cu^{+2} Conc. (mg/L)	10	20	30	40	50	60
Cu+2 uptake (mg/m²)	4.64	8.16	12.0	14.12	13.80	14.1
Recovery (%)	98.3	97.2	98.0	96.3	97.0	98.0
Time (min)	**15**	**30**	**45**	**60**	**90**	
Cu^{+2} uptake (mg/m²)	8.08	1.00	16.5	17.8	18.2	
Recovery (%)	96.5	98.0	97.1	95.0	95.0	
Temp.(°C)	**30**	**40**	**50**	**60**	**70**	
Cu^{+2} uptake (mg/m²)	17.30	18.24	16.90	18.84	18.28	
Recovery (%)	93.30	95.00	95.20	97.30	94.00	
GP (%)	**6**	**14**	**20**	**34**	**58**	
Cu^{+2} uptake (mg/m²)	3.04	6.80	11.70	13.36	18.88	
Recovery (%)	98.2	96.2	97.0	94.2	95.0	

Table 2: Effect of the adsorption-recovery cycles on the amount of adsorbed Cu^{+2} ions and its recovery percent (Reusability)

Cycle number	1	2	3	5	6	7	8	9	10
Cu^{+2} uptake (mg/m²)	18.4	18	17.6	17.6	17.2	17.2	17.2	16.8	16.8
Recovery (%)	95	94	95	95	95	94	93.8	95	94

In contrary with the results obtained by Haron et al [15], no significant effect has been observed for the adsorption temperature increment on the amount of adsorbed Cu^{+2} ions. The small thickness of the membrane and the occurrence of the adsorption process mainly on its surface may give an explanation. A complete recovery of the adsorbed Cu^{+2} ions using 0.1N HCl solution has been observed.

Logic increment of the adsorbed Cu^{+2} ions has been observed with increasing of the PMMA grafting percentage due to its impact on the hydroxamic acid centers bearded on the membranes [14].

Due to the importance of the reusability, from the point of view of cost effectiveness, regeneration and adsorption cycles have been conducted. Very slow reduction of the adsorption and regeneration

processes has been detected after ten cycles; Table 2. Our results are in agreement with the results reported by other authors [17,19].

Table3: Adsorption of Cu+2 ions by different cellulose graft copolymers ions exchangers

Cellulose graft copolymer	Adsorption capacity	Reference
Cell-g-PAA	17 (mg/g)	[11]
Cell-g-PMMA-HA	74 (mg/g)	[14]
Cell-g-EMCA-HA	395 (mg/g)	[15]
Cell-g-PMMA-HA	320 (mg/g)	[16]
Cell-g- PMMA-HA	336 (mg/g)	[17]
Cell-g- PMMA-HA	19 (mg/m^2)	This work

A comparative study of the copper ions adsorption capacity by different functionalized grafted cellulose ions exchangers is presented in Table 3. From the Table it is clear that varied adsorption capacity was obtained depending on the type and concentration of the ions exchange centers, the ions exchanger physical form, and the grafting percentage.

4.3. Adsorption dynamics

They are used to model the process kinetics and determining particular parameters such as the kinetic rate constant and the adsorbed amount at equilibrium as a function of the operational conditions. Those coefficients are noteworthy for designing an effective adsorption process. In this study, we used the pseudo-first and second order [27], the Elovich [28], and the intraparticle diffusion models [29] for detecting the adsorption rate and mechanism. The adsorption capacity was calculated using this equation:

$$q_e = (C_o - C_e)V/A \qquad (1)$$

Where: q_e is the adsorption capacity of Cu(II) ions (mg/m^2) at equilibrium. C_o and C_e are the initial and equilibrium Cu(II) ions concentrations. V is the volume solution (L), and A is the adsorbent membrane working area (m^2).

4.3.1. Pseudo-first-order kinetics model

The linear equation that describes the pseudo-first-order kinetic model was:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

Where: qt and qe are the amounts of Cu(II) ions adsorbed on the adsorbent at time t and equilibrium (mg/m^2), respectively, and K_1 is the first-order reaction rate constant (min^{-1}).

4.3.2. Pseudo-second-order kinetics model

The linearized form of this model is described as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where: k_2 is the constant rate parameter of the pseudo-second sorption (m^2/mg.min).

The linear plot of t/qt vs t is illustrated in Figure 4b and the correlation coefficients (R^2) and the values of K_2 and $q_{e,cal}$ determined from the slope and intercept are listed in Table 4. From the obtained results it is evident that the obtained $q_{e,exp}$ do not agree with the $q_{e,cal}$ obtained from the linear plots of the pseudo-first-order-model (Figure. 4a). On the contrary, the $q_{e, exp}$ and the $q_{e,cal}$ values calculated from the second-order-model are closer to each other which suggest that the adsorption of Cu(II) ions is chemisorption [28, 30]. Thus, the interaction between the adsorbent-adsorbate may be occurring through their valence forces.

4.3.3. Elovich model

The following equation expresses the applicability of Elovich kinetic model:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \qquad (4)$$

If the adsorption of Cu(II) ions on Hydroxamic acid PMMA grafted membranes fits the Elovich model, a plot of qt vs ln(t) should yield a straight line with a slope of β and an intercept of βln(αβ) as shown in Figure 4c. From the plot, the R2 value is 0.941 which means that the adsorption process is chemisorption [31]. Also, the initial rate of Cu(II) ions adsorption is 0.595 while the constant desorption of Cu(II) is 3.6.

4.3.4. The intra-particle diffusion model

This model is used to distinguish the adsorption mechanism by plotting q_t vs t$^{0.5}$ (Figure 4d) that denotes multi linearity which specifies that two or more steps occur:

$$q_t = K_p \, t^{0.5} \qquad (5)$$

The external surface intraparticle diffusion rate k_p estimated from the slope of the plot is determined as 1.768 mg/m^2. min$^{0.5}$. The intraparticle diffusion rate is attributed to the immediate consumption of the most available active sites on the adsorbents external surface [27, 32]. Furthermore, the non-zero intercept clarifies that the intraparticle diffusion is engaged in

the adsorption process, but it is not the individual rate-controlling step for the adsorption process.
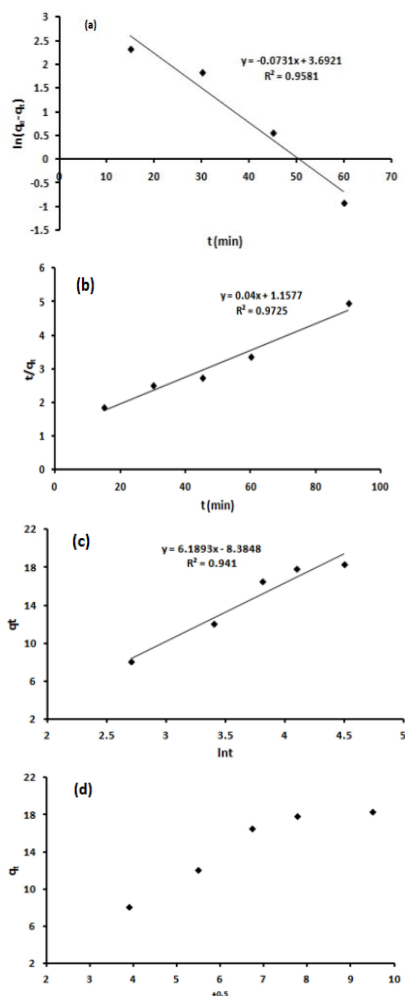

Figure 4: The kinetics models; (a) the pseudo-first-order (b), the pseudo-second-order, (c) the Elovich model, and (d) the intraparticle diffusion model.

Table 4: Kinetics parameters and correlation coefficients

Kinetic model	parameter			
Pseudo-first-order	$q_{e,cal}$ (mg/m^2) 10.036	$q_{e,exp}$ (mg/m^2) 18.24	K_1 (min^{-1}) 0.073	R^2 0.95
Pseudo-second-order	$q_{e,cal}$ (mg/m^2) 25	$q_{e,exp}$ (mg/m^2) 18.24	K_2 (m^2/mg. min) 0.00138	R^2 0.97
Elovich model	α (mg/m^2.min) 0.595	β (mg/m^2) 6.189	R^2 0.941	
Intraparticle diffusion	K_p,(mg/m^2. min$^{0.5}$) 1.916	C 1.7681	R^2 0.88	

4.4. Adsorption isotherm models

Equilibrium isotherm models are used to designate experimental adsorption data. The equation parameters and correlation coefficient (R^2) of these equilibrium equations frequently afford some awareness into both the adsorption mechanism and the surface properties and the adsorbent affinity. The experimental data of the adsorption of Cu(II) onto Hydroxamic acid PMMA grafted membranes were analysed at different Cu(II) ion concentrations (10-60 mg/L) at the equilibrium time (90 min) regarding the Langmuir [27] and the Freundlich [28] isotherms.

For the Langmuir model, the following linear equation was used:

$$C_e/q_e = 1/(q_{max} K_L) + C_e/q_{max} \qquad (6)$$

Where: q_e is the adsorbed amount of Cu(II) ions at equilibrium (mg/m^2), C_e is the Cu(II) ions concentration at equilibrium (mg/L). q_{max} and K_L are the Langmuir constants related to the maximum monolayer adsorption capacity and the adsorption energy.

The Freundlich equation constants were calculated using the following linear form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (7)$$

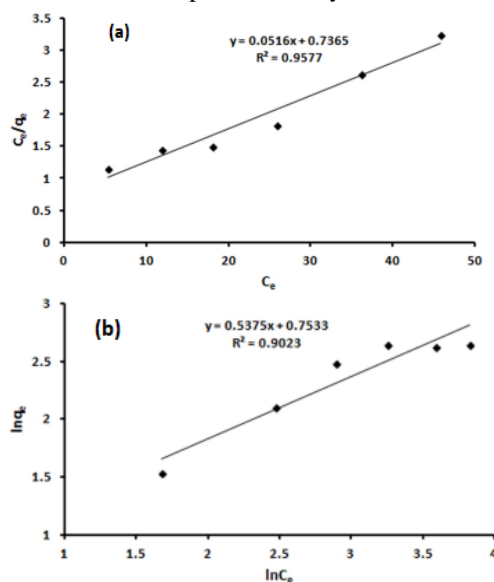Where; K_F is the multilayer adsorption capacity, and n is the adsorption intensity.

Figure 5: The equilibrium isotherm models, (a) the Langmuir and (b) the Freundlich.

From Figure 5 and Table 5 it can be concluded that the Langmuir isotherm represents the experimental equilibrium data better than the

Freundlich model with R2 of 0.957 and qmax equal to 19.38 mg/m^2. This observation indicates that the adsorption of Cu(II) ions on Hydroxamic acid PMMA grafted membranes is monolayer [33].

The separation factor (R$_L$) [29] which is the essential characteristics of the Langmuir isotherm can be determined using the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \tag{8}$$

Where: C$_o$ is the initial Cu (II) ions concentration (mg/L), and K$_L$ is the Langmuir constant.

From Figure 5a and the value of K$_L$, R$_L$ was calculated and was in the range of 0.192 -0.588 which is less than 1 and greater than 0 showing favourable adsorption [34] of the Cu(II) ions on the Hydroxamic acid PMMA grafted membranes.

Table 5: Isotherm parameters of the Langmuir and the Freundlich models

Isotherm	parameters		
	q$_{max}$ (mg/m^2)	K$_L$(L/g)	R^2
Langmuir	19.379	0.07	0.9577
	K$_F$ (mg/ m^2)	n	R^2
Freundlich	2.653	0.595	0.9

5. Conclusions

Cellophane membranes were first grafted with Poly (methyl methacrylate) (PMMA). Second, the PMMA grafted membranes were treated with hydroxylamine hydrochloride, to induce hydroxamic acid ion exchange groups, and finally used for Cu (II) ions separation from synthetic metal solutions. It was found that the Cu^{+2} uptakes increase by increasing the grafting percentage. The maximum uptake amount of Cu^{+2} ions (18.88 mg/m^2) obtained with membranes of grafting percentage 58%. However, the recovery of the adsorbed Cu^{+2} ions has not been affected by variation of the grafting percentage. Equilibrium has been obtained after 60 minutes of adsorption while the temperature was found of neglectable effect. The membranes show a very good applicability and reusability where very slow reduction of the adsorption and regeneration processes has been detected after ten cycles. Fourier transforms infrared analysis and thermal gravimetric analysis provided evidence of the grafting and the functionalization processes.

Moreover, the kinetics, isotherms and thermodynamics of the adsorption process have been monitored. The adsorption process was found following the second pseudo-order model where the q$_{e, exp}$ and the q$_{e,cal}$ values calculated from the second-order-model are closer to each other which suggest that the adsorption of Cu(II) ions is chemisorptions. Elovich model confirmed this conclusion. Thus, the interaction between the adsorbent-adsorbate may be occurring through their valence forces. The intraparticle diffusion model is engaged in the adsorption process, but it is not the individual rate-controlling step for the adsorption process.

The Langmuir isotherm represents the experimental equilibrium data better than the Freundlich model with R^2 of 0.957 and q$_{max}$ equal to 19.38 mg/m^2. This observation indicates that the adsorption of Cu(II) ions on Hydroxamic acid PMMA grafted membranes is monolayer.

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