Recyclable Functionalized Polymer for Cu(II) Decontamination from Aqueous Media

LAVINIA TOFAN[1], RODICA WENKERT[2], ION BUNIA[3], CARMEN PADURARU[1]*

[1]Department of Environmental Engineering and Management, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection "Gh. Asachi" Technical University of Iasi, 73 Prof. Dr.D. Mangeron Str., 700050, Iasi, Romania
[2]Soroka University Medical Center, Beer-Sheva, Ragher, Israel
[3]"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Str., 700487, Iasi, Romania

Abstract: In the endeavor to explore more and more materials, this work is focused on the study of the potential applicability of a chelating sorbent based on an acrylic copolymer functionalized with amidoethylenamine groups in Cu(II) removal from wastewaters in batch and dynamic conditions. The proposed sorbent was synthesized by the chemical transformation reaction of ethylacrylate (EA): acrylonitrile (AN):2% divinylbenzene (DVB) copolymer with ethylenediamine (EDA). Batch sorption results pointed out that the Cu(II) retention by the acrylic copolymer functionalized with amidoethylen-amine groups was dependent on the initial solution pH, initial metal concentration and contact time. The sorption of Cu (II) on the tested chelating copolymer obeyed both Langmuir and Freundlich isotherms. The Langmuir maximum sorption capacity was 65.21mg Cu (II)/g of polymer. The kinetic experimental data fitted well with the pseudo - second order model. The dynamic behavior of a fixed bed column filled with the acrylic copolymer functionalized with amidoethylenamine groups has been studied in terms of breakthrough curve. The experimental breakthrough data have been well described by Thomas model. The tested chelating copolymer is suitable for multiple processes of Cu(II) sorption-desorption. The column studies with real wastewater sample presented a removal efficiency of 100% for Cu (II) and a significant improvement of the wastewater quality. The acrylic copolymer functionalized with amidoethyleneamine groups can be successfuly applied for the Cu (II) removal - recovery - recycling.

Keywords: chelating polymer, copper, sorption, desorption, wastewater treatment

1. Introduction

Copper, found in the fourth period (group 11) of the periodic table is, at the same, an essential element and one of the most valuable metal with many and varied industrial applications [1,2]. Its strong toxicity, manifested even at low concentrations, strictly demands that the discharge of the in-dustrial wastewaters contaminated with copper in environment be preceded by applying of a proper treatment method for copper removal, such as: chemical precipitation, coagulation/ flocculation, ion exchange, cementation, membrane separation, reverse osmosis, electroflotation, sorption [3 - 5].

The prominence and popularity of the sorption by sorbents among all the removal methods out-lined above are mainly due to its high efficiency even at very low pollutant concentration, relative sim-plicity, flexibility, reversibility, kinetic and economic advantages, quality of the generated treated ef-fluents able to be re- used [6]. Amongst all the explored sorption materials, the chelating sorbents made up of a polymer network (support) carrying functional groups, capable of sequestering metal ions by coordinative bonds, are distinguished mainly by their broad spectrum of structures and physico-chemical features, large uptake capacity, favorable sorption rate, important selectivity for different concentrations, reusability, adjustability of the surface chemistry and tolerance for a wide range of wastewater parameters [7]. New chelating sorbents based on 5-aminopyridine-2-tetrazole immobilized on cross-linked polystyrene, poly(acrylamide) modified with pendent benzothiazole groups, pyri-dine–pyrazole ligands grafted onto polymethylhydrosiloxane, poly(6-(ethoxybenzothiazole acryla-mide), poly(MVE-alt-MA) polymer with Schiff base chelating groups, iminodiacetic acid functional-ized

D301 resin, glycidyl methacrylate grafted onto polystyrene resin have been recently reported in the literature as good performance materials for copper removal from aqueous media [8 - 13].

The goal of this research is to contribute to the broadening of the chelating polymers range with copper (II) sorption performances of significance for the development of copper recycling technology. In this context, the copper sorptive capability of an acrylic copolymer functionalized with amidoethylenamine groups has been evaluated through a comprehensive research. Batch experiments have been run for the influence of initial solution pH and concentration, contact time on the copper(II)uptake from mono-component aqueous solutions. Data of the batch studies have been processed by means of the equations of Langmuir and Freundlich isotherms. Kinetics of the sorption have been modelled with the aid of the well-known models. The dynamic behavior of the acrylic copolymer functionalized with amidoethylenamine groups-copper(II) sorption system have been studied in terms of breakthrough curve, which is the concept describing the performance of fixed bed column. The applicability of the Thomas and Yoon–Nelson models to the dynamic data have been evaluated. In order to assess the potential practical applicability of the proposed chelating copolymer, a desorption study of copper (II) from metal loaded and the removal of copper(II) from a sample of real wastewater has been performed

2. Materials and methods
2.1. Materials

To obtain the polymeric support of the acrylic sorbent the following materials were used: divinylbenzene (DVB) (80% DVB; 20% ethylvinylbenzene); acrylonitrile (AN), ethylacrylate (EA); toluene, benzoyl peroxide purum moisted with 20% water as initiator; ethylenediamine (EDA), C = 98 wt. %; dichloroethane, all from Fluka; thiourea puriss p.a. from Riedel deHaen, 99 wt. %.

In the sorption experiments, analytical grade $CuSO_4 \cdot 5H_2O$ (Sigma-Aldrich), H_2SO_4 and HCl supplied from Merck&Co have been used.

2.2. Preparation of the functionalized acrylic copolymer

The crosslinked acrylic copolymer was obtained by free radical suspension copolymerization in water of the mixture of mono-vinyl monomers. The reaction has been carried out in a glass reactor equipped with an anchor-type stirrer with possibility of stirring speed adjusting, heating stem and reflux condenser.

The reaction mixture is composed of two phases: (i) the aqueous phase containing 1200 mL distilled water and a polymeric stabilizer (0.5 wt. %) prepared by the hydrolysis of poly (styrene-co-maleic anhydride) copolymer with aqueous NH_3 solution;(b) the organic phase consisting of the mixture of (ethylacrylate (78 wt. %) and acrylonitrile (20wt. %) monomers, divinylbenzene(2wt. %) as crosslinking agent, benzoyl peroxide(1% of monomers amount) as initiator and toluene used as diluent at a dilution(D) of 0.4. Toluene content used throughout this study is calculated as follows [14]:

$$D = [mL \ diluent/(mL \ diluent + mL \ monomers)] \ x \ 100.$$

The AN and DVB amounts have been calculated versus the entire amount of the monomers

The aqueous phase was added into the glass reactor and was stirred for 30 min at 40-45°C.After this, the organic phase was added under continuous stirring. An organic to aqueous phase ratio of 1: 3(v/v) was kept constant for all copolymerizations. The reaction of polymerization was left to proceed at 65°C for 4 h and then at 85°C for 8 h. The yielded copolymer in the beads form was then sep-arated from the reaction medium by filtration, washed with warm distilled water to remove the suspen-sion stabilizer and dried at 50°C. The removal of residual monomers, oligomers and diluent has been done by Soxhlet extraction with dichloroethane. The content of DVB in the copolymer was assumed as be the same with that of mixtures of monomers.

The tested acrylic sorbent with amidoethylenamine groups has been prepared by the chemical transformation of the yielded copolymer with EDA. The aminolysis-hydrolysis reaction of EA: AN: 2%DVB copolymer with EDA at a copolymer: amine ratio of 1:3 was performed at 110°C for 16 h. For

this purpose, the copolymer beads were brought into an aminolysis reactor provided with stirrer and descending refrigerant. After the reaction completion, the aminolyzed product has been filtered and washed with distilled water to remove the reagents excess. Then the material was treated with 4%HCl, filtered and further washed with distilled water until to neutral *p*H. Afterwards, the prepared functionalized copolymer was treated with 4%NaOH, filtered and washed with distilled water until to neutral *p*H. The operation was repeated 2-3 times for a complete purification.

Finally, the yielded sorbent has been analysed for density(g/mL), weight exchange capacity(mequiv/mL) and volume exchange capacity (mequiv/mL) [14].

2.3. Preparation of solutions

Stock solutions of 1021 mg L^{-1} and were prepared by dissolution of analytical grade reagent CuSO$_4$ $\cdot$5H$_2$O in deionized water and was complexonometrically standardized. Working solutions of Cu (II) ions was prepared by the appropriate dilutions of the stock solutions.

A 10^{-2} mol/ L solution of H$_2$SO$_4$ was prepared by corresponding dilution and used in the medium acidity effect study.

2.4. Batch sorption experiments

Samples of about 0.05 g chelating sorbent were equilibrated with 25 mL of each aqueous solution containing defined amounts of Cu (II) ions at desired temperature and *p*H. At the end of predetermined time intervals, the phases were separated by filtration. The Cu (II) ion concentrations in the final solutions were determined by atomic absorption spectrometry.

The parameters characteristic to the Cu (II) ions sorption by the acrylic copolymer functionalized with amidoethylenamine groups were calculated with the following equations:

Retention percentage, R (%) $R = [(C_0 - C)/C_0] \cdot 100$

Retained amount of metal ion, q (mg/ g) $q = [(C_0 - C)/G]$.

where C0 is the initial concentration of metal ion (mg /L), C is the cation concentration after sorption (mg/ L), V is the volume of solution (L); and G is the weight of sorbent (g).

2.5. Dynamic sorption studies

By packing successively samples of 0.6754g and 0.6825g of the acrylic copolymer functionalized with amidoethylenamine into a column of glass (1.5 cm inner diameter and 15 cm in length), heights of bed of 6.8 cm and 7cm have been achieved. For supporting the polymer during experiments a wadding glass layer was fitted at the column bottom. Solutions with 50mg/L and 100mg/L initial concentrations in Cu (II) have been fed to the column top. The flow rate was 2.5mL/min. After collecting the samples of effluent at different times from the column bottom, their Cu (II) concentrations have been determined by atomic absorption spectrometry. The column operation has been stopped when inlet concentration of Cu(II) was approximately equaled with that at the outlet.

2.6. Reusability studies

Desorption and regeneration studies have been carried out in batch conditions. Samples of 0.1g of Cu (II) loaded sorbent were contacted with 0.1M HCl for 6 h, under intermittent shaking. After mixture filtration, the amount of desorbed Cu (II) has been determined by atomic absorption spec-trometry. The regenerated spent functionalized copolymer under study has been reused, the batch sorp-tion and desorption being repeated 8 times.

2.7. Treatment of sample of real wastewater

The sample of wastewater has come from a municipal deposit of wastes collecting. After sampling, the wastewater sample have been prepared and analyzed for its significant parameters. For the dynamic

sorption removal of Cu(II), 1L volume of wastewater has been passed through a column filled with the proposed functionalized copolymer in a bed of 6.8 cm height at a flow rate of 2mL / min.

2.8. Apparatus

For the characterization of the functionalized copolymer, FT-IR spectrometer Bruker Vertex 70 and Bruker AXS-Microanalyse GmbH microscope have been used. The pH of solution was measured with the Comsort C 863 pH - meter. The analysis for Cu (II) content has been performed on the 210 VGB Buck Scientific atomic absorption spectrometer.

3. Results and discussions
3.1. Synthesis and characterization of the tested acrylic sorbent

Being more physically and chemically stable and with an enhanced hidrophilicity than the sty-rene supports, acrylic copolymers are of special interest for functionalization [15]. In light of this, the preparation of the chelating sorbent under study is based on the following sequence of reactions: the free radical suspension copolymerization in water of ethylacrylate (EA) and acrylonitrile (AN) with 2% DVB→the aminolysis–hydrolysis reaction of EA: AN: 2% DVB copolymer with ethylenediamine (EDA) at a copolymer: amine ratio of 1:3 (Scheme 1).
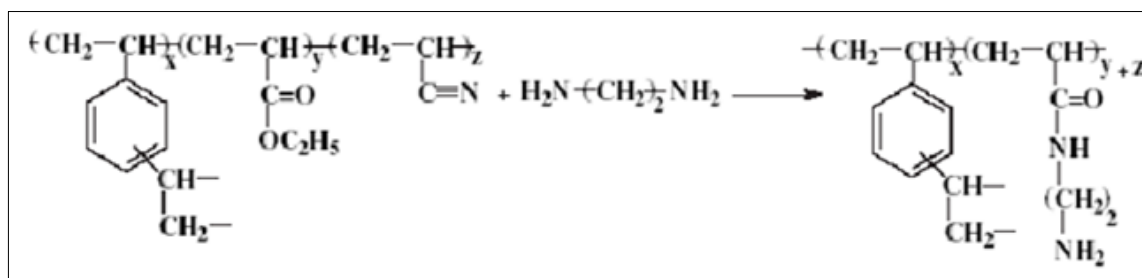
Scheme 1. Synthesis of the tested chelating polymer

It follows from Scheme 1 that the proposed sorbent is remarkable through the N and O - contain-ing groups which are recognized as being deeply involved in the efficient coordination interactions with copper ions [6, 16, 17]. The synthesized chelating copolymer is characterized by a volume weight of 0.0374 g/mL and a weak exchange capacity of 0.29 meq/ mL and 7.86meq/g, respectively.

In order to confirm this statement, infrared absorption spectra of the proposed functionalized acrylic copolymer before and after Cu (II) sorption have been recorded, being shown in Figure 1.

The highlighted modifications in the IR spectra in Figure 1 can be described as follows. Thus, in the region of 3500 - 3400 cm^{-1} appear bands that can be attributed to the N- H bond, specific to the sec-ondary amines of R_2NH type. At 3081 - 2854cm^{-1} there is an absorption band referring to the valence vibration and deformation of the C- H bonds. The decrease of peak in the 2131 - 2065cm^{-1} region may be due to the valence vibration of the C≡N or N=C=O bonds. The reduction of adsorption occurring at 1558.42 - 1557.45 cm^{-1} could be due to the valence vibration of the C=O bond, but also to the C=C bond in aromatic rings. At the same time, in this range appears the deformation vibration of the – NH$_2$ bond, giving bands of low intensities. The region of 1392 – 1317cm^{-1} is characterized by bands of me-dium intensity due to the deformation vibration of the - CH$_3$ and - CH$_2$ groups. The valence vibrations from the 1177- 1038cm^{-1} range are attributed to the C-O and C≡N bonds. The 854- 848 cm^{-1} range is dominated by bands characteristic to the substitution due to the hydrogen atoms existing in the aro-matic ring. The disappearance of the vibration band at 708.81cm^{-1} is connected with the presence of the aromatic groups in matrix, that are not affected by the complexation of metal [18].
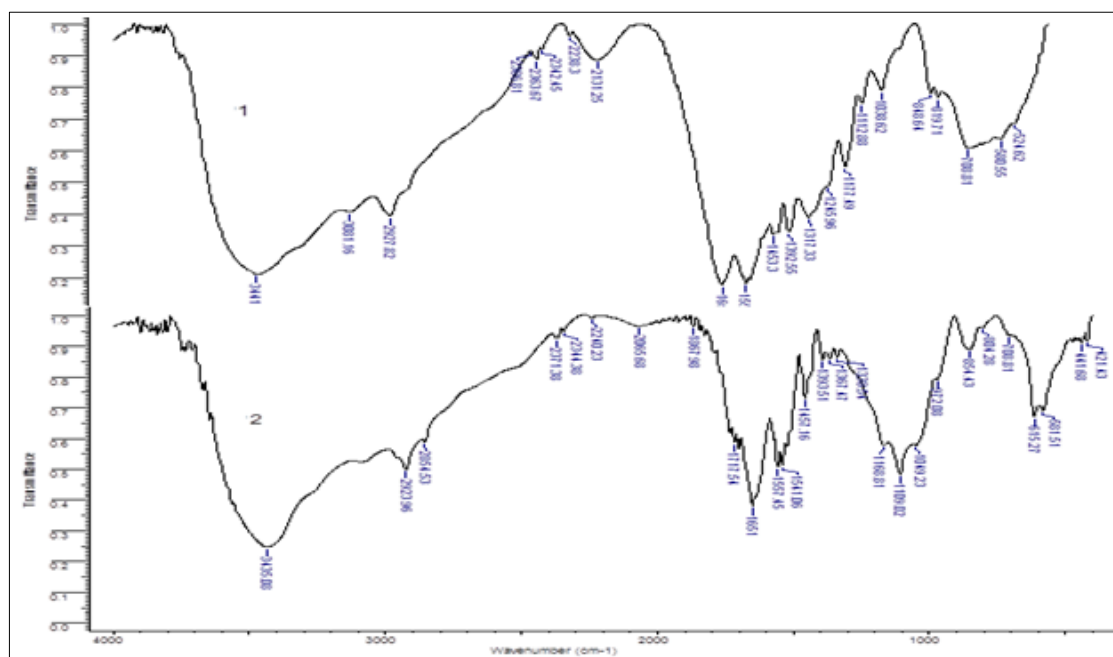
Figure 1. IR spectra: 1- functionalized acrylic copolymer; 2- functionalized acrylic copolymer+Cu(II)

Some bands overlapping, appearing or shrinking at 1717 cm^{-1} and 1651 cm^{-1} show disappearance or movement to the smaller wave numbers of the carbonyl group presenting in the copolymer structure.

The band modification around 1100cm^{-1} value suggest the possible protonation of the amine group [18], and the changes appearing at 1390cm^{-1} value lead to the identification of the absorption characteristic to the protonated carboxylic group [19].

The disappearance, shrinking and/ or modification of the bands in the IR spectrum of the chelating sorbent loaded with the metal ion suggests the involvement of the $-$ NH$_2$, C=O and C- O groups and aromatic ring, respectively in the process of Cu (II) retention. A change of the peak position to the smaller wave numbers shows the weakness of the chemical bond, while the modification to higher wave numbers emphasizes a stronger bond [20]

The appearance of the absorption bands at 615cm^{-1} and 518 cm^{-1} shows that the metal ion forms coordinate complexes with the oxygen and nitrogen existing in the copolymer matrix [21]

The analysis of the two IR spectra shows that, besides the electrostatic attraction between the metal ion and the sorbent, a mechanism based on chemical interactions could also be involved.

Scanning electron microscopy and energy-dispersion X-ray spectrometry (EDX) has been used for the morphological characterization of the functionalized copolymer and the proposed sorbent loaded with Cu (II) (Figure 2).

The analysis of the SEM images in Figure 2a reveals the presence of the Cu (II) ions on the surface of the particles. This finding is confirmed by the metal peak appeared in the EDX spectra given in Figure 2b.
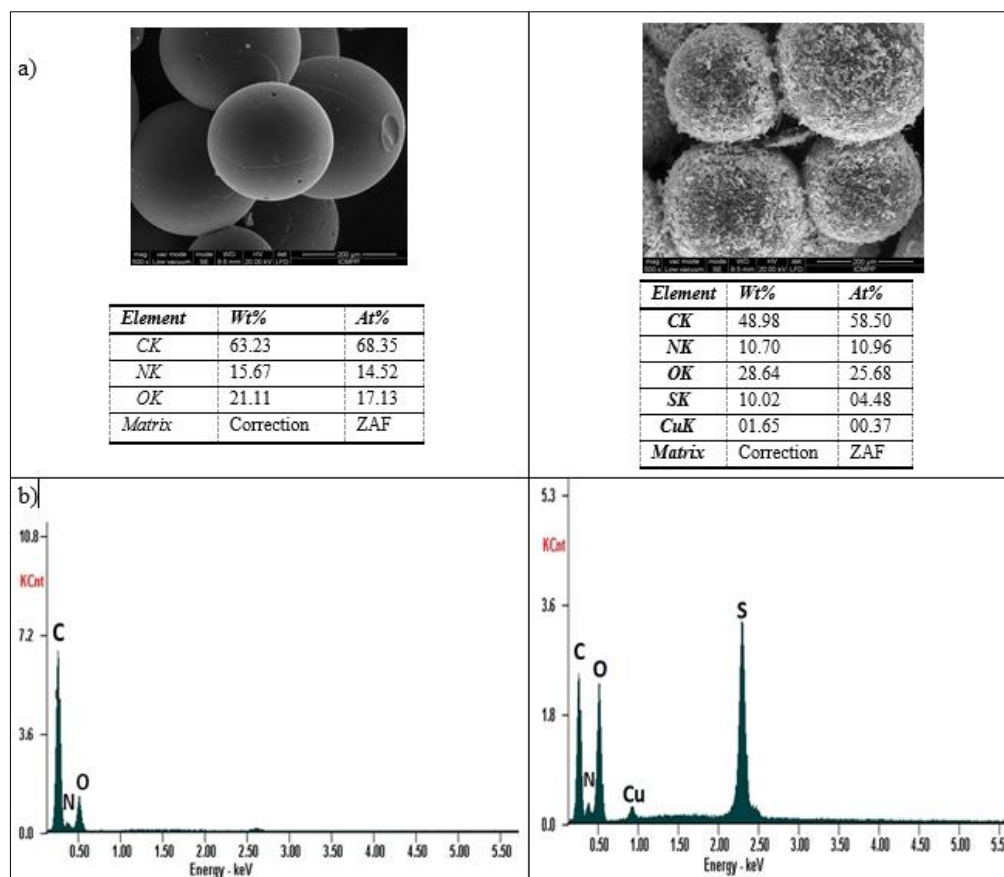
Figure 2. SEM images (a) and EDX spectra (b) for the tested chelating sorbent
before and after Cu(II) sorption

3.2. Batch sorption studies of Cu (II)

In the batch sorption studies undertaken, the affinity of the acrylic copolymer functionalized with amidoethylenamine groups for Cu (II) ions has been assessed as function of *p*H, concentration of the initial solution and contact time, respectively.

3.2.1. Effect of initial solution *p*H

The acrylic copolymer functionalized with amidoethylenamine groups exhibits a Cu(II) sorption behaviour which is highly dependent on the *p*H of initial solution (Figure 3). The avoidance of the Cu(II)precipitation is of stringent necessity. Therefore, the sorption experiments were performed using solutions with initial Cu(II) concentrations of 126.72 mg /L and initial *p*H varying from 1 to 5. As follows from Figure 3, the Cu (II) sorption ability of the acrylic copolymer functionalized with amidoethylenamine groups shows an increasing trend when initial *p*H is changed from 1 to 5, the maximum being reached at a *p*H value of 5. The explanation of this increasing trend relies on two factors with decisive action on the sorption performances of the acrylic copolymer under study: the protonation of the surface functional groups and the ionization degree of the metal ions. At low values of initial *p*H, the surface change is positive due to the functional groups protonation and the excess of protons, so that the predominant kind of interaction with metal ions is the electrostatic repulsion and the chelating ability is very small. The increase of initial *p*H results in a marked decrease of the protonation degree, being favored strong coordination interaction, meaning copper complex formation via nitrogen atoms of the amidoethylenamine functional groups.
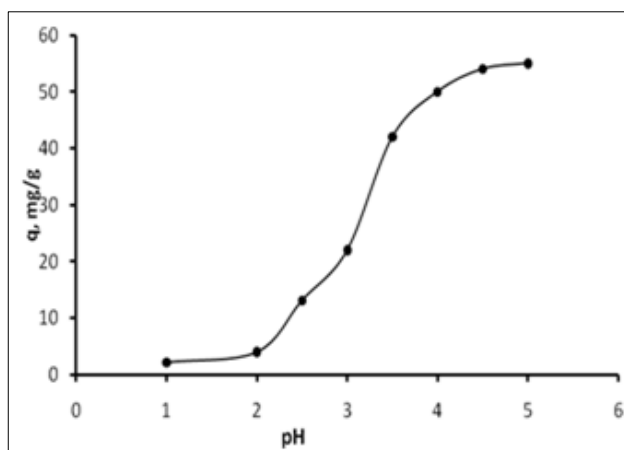
Figure 3. The influence of *p*H of initial solution on the sorption of Cu(II) by the acrylic resin functionalized with amidoethylenamine groups (C_0= 126.72mg Cu(II)/L; sorbent dose= 2g/L, time= 24 h, t= 20°C)

3.2.2. Effect of initial concentration of Cu(II) solution

The potential applicability of the acrylic copolymer functionalized with amidoethylenamine groups in the efficient removal of the tested heavy metal ion from industrial effluents with low content in Cu(II) is supported by the results describing the influence of initial concentration of Cu(II) in the batch sorption under study (Figure 4). As can be from Figure 4, the rise of initial concentration of Cu(II)(C0) from 42.24 mg/L to 338 mg/L leads to the decrease of the Cu(II) sorption percentage (R%) from 94.02% to 75%, respectively. This decreasing trend emphasizes the key role of the superficial amidoethylenamine groups in the Cu (II) sorption process [9]. Thus, at low initial Cu (II) concentration, the significant availability of the superficial amidoethylenamine groups determines large values of the Cu(II) sorption percentage. On the other hand, the saturation of the superficial functional groups occurring at high initial concentration of Cu(II) results in lower percentage of Cu(II) sorption.
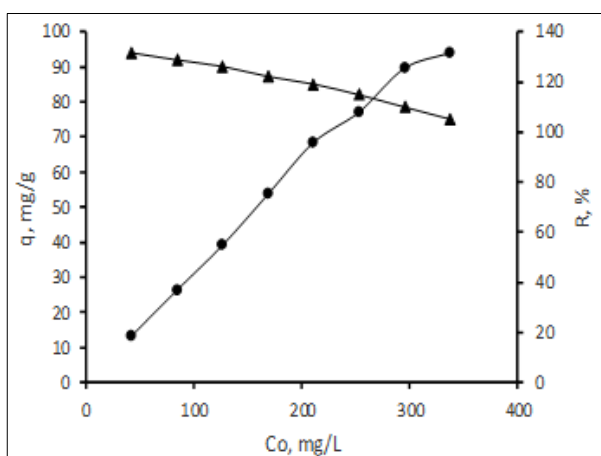

Figure 4. Influence of Cu(II)initial concentration(C_0) on the Cu(II) sorption in the batch sorption system Cu(II) - acrylic copolymer with amidoethylenamine groups; (•) q=f(C_0); (▲)R=f(C_0); (sorbent dose= 2g/L, time= 24 h, t= 20°C)

At the same time, due to the increasing gradient of concentration playing the leader role in the overcoming of the resistance to the mass transfer, the amount of Cu((II) retained on the acrylic co-polymer with amidoethylenamine groups has increased 7.2 times for an increase of initial concentration of Cu(II) from 42.24 mg/L to 338 mg/L.

3.2.3. Influence of contact time

The contact time effect in the acrylic sorbent with amidoethylenamine groups – Cu(II) batch sorption system is recorded in Figure 5.
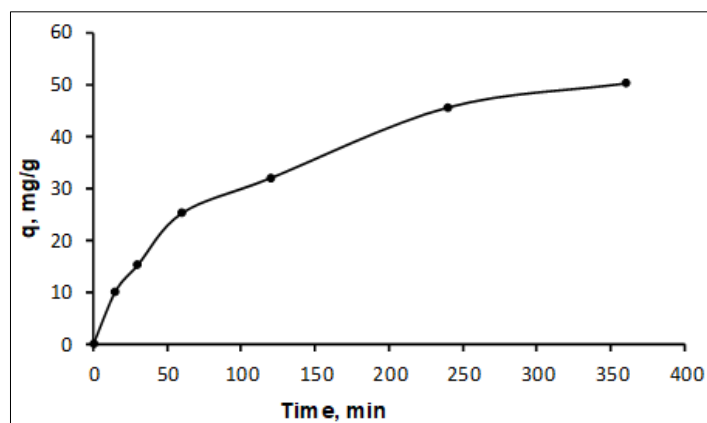
Figure 5. The effect of contact time on the Cu(II) retention
by the acrylic resin functionalized with amidoethylenamine
groups (C_0= 126.72 mg Cu(II)/L; sorbent dose= 2g/L)

Figure 5 points out the increasing tendency of the Cu(II)amounts sorbed on the targeted chelating polymer at the increase of contact time from 0 to 400 min. The increase is sharp in the first range of about 100 min and slight as the Cu(II) sorption process tends to reach equilibrium. In good agreement with the well known great stability of the copper amine complexes, the high strength of the bond by which Cu(II) has been retained on the tested functionalized copolymer is indicated by the decreasing concentration of Cu(II) remaining in the solution.

3.2.4. Equilibrium and kinetics modelling
Sorption isotherms

Starting from the wide applicability and the high value of the provided informations, the Cu (II) sorption data have been characterized with the aid of models of Langmuir and Freundlich isotherms (Table 1)

Table 1. A brief presentation of the isotherm models used in present work for the
description of the sorption equilibrium

Langmuir isotherm [22]	Freundlich isotherm [23]
Langmuir equation $$q = q_0 \frac{K_L \cdot C}{1 + K_L \cdot C}$$ *Langmuir parameters*: q_0 is the maximum capacity of sorption, corresponding to the sorbent surface and K_L is the equilibrium constant (Langmuir) Determination of the Langmuir constants: from the intercept and slope of the corresponding linear Langmuir plot, expressed by the following equation: $$\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}$$ Assumptions : - the restriction of sorption to a monolayer; - the homogeneity of the sorbent surface; -the existence of a limited number that are equivalent from energetic and molecules accessibility point of view; - the reversibility of the sorption; - absence of the interactions between the retained species	Freundlich equation $$q = K_F \cdot C^{1/n}$$ *Freundlich parameters* K_F and n are related to all factors affecting the retention process: sorption capacity (K_F) and energy of sorption (n), respectively. Determination of the Freundlich constants: - from the plot of the logarithmic Freundlich equation: $$\lg q = \lg K_F + \frac{1}{n}\lg C$$ Assumptions : - the sorption occurs on heterogeneous surface of an sorbent with interaction between the sorbate molecules

The relevant parameters for Cu(II) sorption on the acrylic copolymer functionalized with amidoethylenamine groups were calculated on the basis of the corresponding linearized Langmuir and Freundlich isotherms, given in Figure 6. The yielded values are listed in Table 2.
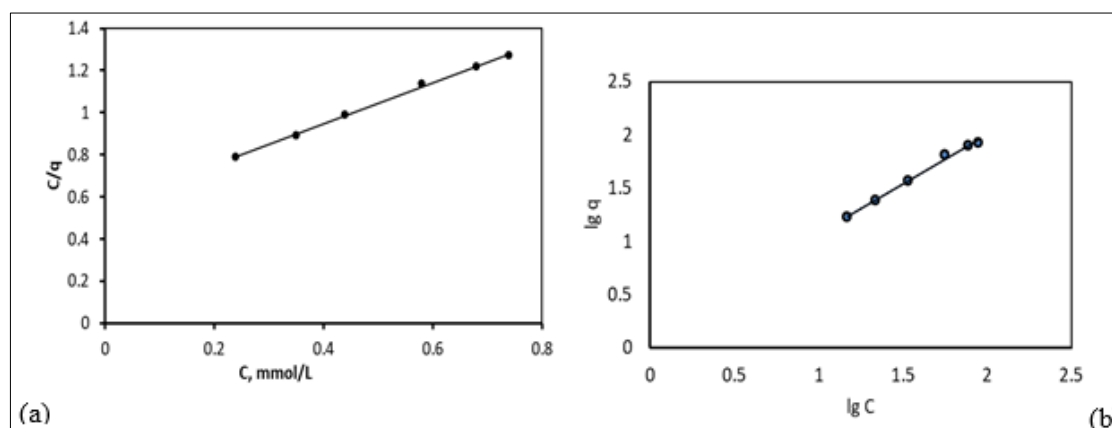

Figure 6. Linearized Langmuir (a) and Freundlich (b)isotherm plots for the sorption of Cu(II) on tested functionalized acrylic copolymer (dose= 2g/L, time= 24 h, t= 20°C)

Table 2. Isotherm parameters

Langmuir isotherm			Langmuir isotherm		
K_L (L.mol^{-1})	q_o (mg.g^{-1})	R^2	K_F	$1/n$	R^2
1751.31	65.21	0.9981	5.12	0.63	0.9965

The high value of the K_L Langmuir constant in Table 2 suggests that in the sorption process are involved strong interactions. According to Table 2, the maximum capacity of sorption, q_0, has a significant value, highlighting the potential applicability of the proposed sorbent for remediation purpose. The K_F parameter in Table 2 is associated with the sorption capacity as Langmuir q_0. As can be seen from Table 2, the value of $1/n < 1$, being consistent with the chemical nature of the sorption process. Table 2 also shows that the calculated values of the corresponding correlation coefficients of linear regression (R^2) were very close. This signifies that the Cu(II) sorption process on the acrylic copolymer functionalized with amidoethylenamine groups may be properly depicted by both Langmuir and Freundlich isotherms. This finding suggests that the surface of the proposed sorbent is neither typically homogeneous nor typically heterogeneous and indicates the multilayer manner of the sorption process. A similar behavior has been reported in the literature for the retention of Cu(II) ions on a chelating sorbent prepared by bonding (2- acrylamido- 2 – methylpropanesulfonic acid) onto silica gel [24].

Kinetics modelling

Taking into account their relevance and significance, the experimental results of this study have been correlated with Lagergren (pseudo–first order) and Ho (pseudo–second order) kinetic models [25, 26]. The fundamental assumption of both models is the proportionality between the rate of sorption and the number of free sites on the surface of the sorbent in the proper power (first or second). The equations of the pseudo-first order and pseudo-second order kinetic model are as follows:

$$\text{Lagergren pseudo- first-order:} \qquad q_t = q_e(1 - e^{-k_1 t}) \qquad (1)$$

$$\text{Pseudo-second-order} \qquad 1/q_t = 1/h + (1/q_e).t \qquad (2)$$

where qt and qe are the amounts of Cu(II) sorbed (mg/g) at time t and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 (mg/g·min) are the rate constants of pseudo-first-order and pseudo-second-order sorptions, respectively, and h = k_2·q (mg/ g ·min) can be regarded as the initial sorption rate constant of the pseudo-second-order sorption (g/ mg* min).

The corresponding kinetic parameters derived from the plots of the liniarized forms of the applied kinetic equations (Figure 7) are summarized in Table 3. Their correlation coefficients (R_2) are also recorded in Table 3.
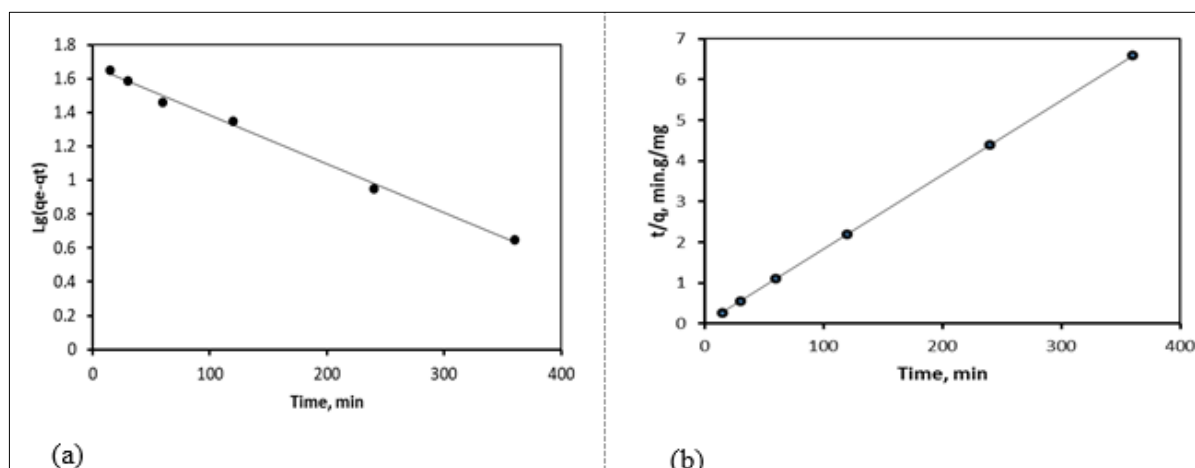

Figure 7. Liniarized plots of the pseudo– first order (a) and pseudo – second order (b) equations for the sorption of Cu(II) on the acrylic copolymer functionalized with amidoethylenamine groups

Table 3. Kinetic description of Cu(II) retention by the proposed chelating sorbent

Pseudo- first order			Pseudo-second order			
k_1, min^{-1}	q_e, mg/g	R^2	k_2, g/ mg·min	h, mg/ g·min	q_e, mg/g	R^2
6.67x10^{-3}	46.93	0.9852	2.76x10^{-3}	0.8256	54.64	0.9999

In accordance with Table 3, the value of R_2 for the pseudo – second order kinetic model is higher than that of the pseudo – first order model. This finding lead to the following conclusions: (i) the process of Cu(II) retention on the acrylic copolymer with amidoethylenamine groups follows best a pseudo– second order kinetics; (ii)the dominant mechanism may be the chemisorption. Other chelating sorbents for Cu(II) retention had a similar behaviour [20,27].

3.3. Fixed bed column studies

The informations provided by the batch studies can not be extrapolated to the design of columns operating on industrial scale. The scarcity of dynamic studies reported in literature on the one hand, and the importance of these studies on the other hand highlight the stringent need for works on the behavior of the fixed bed column sorption. The dynamic studies gravitate around the breakthrough curve (the evolution of the solution concentration as a function of time or volume of the processed solution), which is the most important parameter to be determined.

In this context, the description of the performances of the Cu(II) - acrylic copolymer functionalized with amidoethylenamine groups fixed bed column sorption system has been performed by processing and modelling of the experimental breakthrough data.

3.3.1. Breakthrough curves

The breakthrough curves for the dynamic sorption of Cu(II) ions from aqueous solutions on the acrylic copolymer functionalized with amidoethylenamine groups are presented in Figure 8 as the relation between normalized concentration(C_t – effluent Cu(II) concentration)/C_0- influent Cu(II) concentration). According to Figure 8, the resulting curves are characterized by a "S" shape, that is strongly dependent on the influent concentration of Cu(II) .
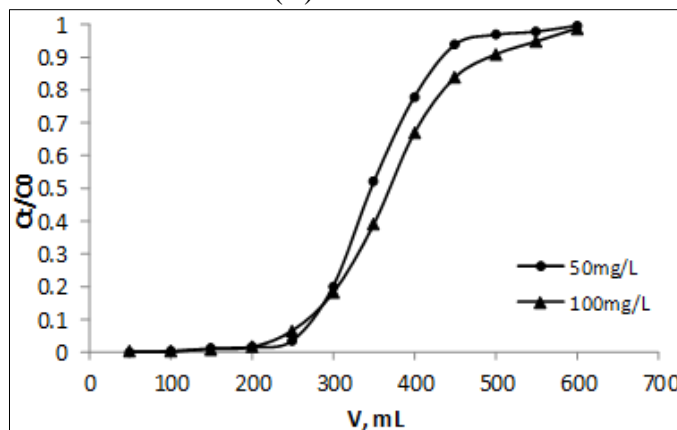

Figure 8. Breakthrough curves of the sorption of Cu(II) on tested acrylic copolymer at varied concentrations of influent (• 50mg/L; ▲-100mg/L)

The two significant points of the experimental breakthrough curves are usually analyzed on the basis of the following parameters [28]:

-the breakthrough time (t_b, min) that represents the time required to reach the breakthrough point (the point in which Cu(II) reaches the column end and leaves with the effluent of column),considered on the basis of the effluent discharge limit for Cu(II);

- the saturation time (t_{sat}, min) that is defined as time required to the saturation point reaching, meaning the time to which the effluent concentration remains close to influent concentration.

On the basis of breakthrough time(t_b) and saturation time(t_s), the active surface of the sorbent bed in which the sorption process take place, namely, the mass transfer zone (MTZ, cm) has been computed by means of the following equation:

$$MTZ = H\left(1 - \frac{t_b}{t_{sat}}\right)$$

(3)

where H is length of the sorbent bed (cm).

The obtained values for the breakthrough parameters are listed in Table 4. It is possible to observe from Table 4 that the Cu(II)sorption at breakthrough and saturation has been faster at high influent concentration, which yields a more powerful driving force. The decreased values of MTZ pointed out a lower capability of Cu(II) treatment at increased concentrations. In addition, an increase in the concentration of influent is correlated with a higher amount of copper ions for the same amount of acrylic copolymer, resulting in a lower volume of solution before the sorbent becomes saturated [29].

Table 4. Experimental parameters of the breakthrough curves for fixed bed column sorption of Cu(II) on the tested sorbent

Influent concentration C_0 (mg/L)	t_b (min) (C_t/C_0 = 0.1)	V_b (mL)	t_s(min) (C_t/C_0 =0.9)	V_s (mL)	MTZ (cm)
50	106	243.9	194	485	3.17
100	96.2	215	165	454.5	2.83

where C_t and C_0 are the effluent and influent metal concentration (mg/L.

3.3.2. Modelling of fixed bed column

The experimental breakthrough data have been verified by both Thomas and Yoon-Nelson models.

The most commonly used model in the dynamic studies is the Thomas model which assumes that the rate driving force obeys second–order reversible reaction kinetics [30]. The linearized form of Thomas equation is [31]:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_T \cdot q_{0(T)} \cdot m}{F} - \frac{K_{T.} \cdot C_0}{F} \cdot V \tag{4}$$

where C_0 is the initial metal ion concentration (mg/L); C_t is the equilibrium concentration (mg/L) at time t (min); k_T is the Thomas constant (L/min·mg); F is the volumetric flow rate (L/min); $q_0(T)$ is the maximum column capacity (mg/g), determined by the Thomas model; m is mass of sorbent (g); V is the volume (L).

The main assumption of the Yoon − Nelson model is that the probability of the decrease of the sorption rate for each sorbate molecule is proportional to the sorbate breakthrough probability on the sorbent [32]. TheYoon-Nelson model is based on an equation having the following linearized form [33]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN} \cdot t - \tau \cdot k_{YN} \tag{5}$$

where C_0 is the initial metal ion concentration (mg/L); C_t is the equilibrium concentration (mg/L) at time t (min); k_{YN} is Yoon–Nelson rate constant (min-1); τ is time required for 50% sorbate breakthrough; t is sampling time (min)

According to the Yoon–Nelson model, the amount of metal ion sorbed in a fixed bed is half of the total metal ion entering the adsorption bed within 2τ period [34]. In this context, for a given bed, the column sorption capacity in the Yoon–Nelson model, $q_0(YN)$ can be computed with the following equation:

$$q_{0Yn} = \frac{q_{(total)}}{m} = \frac{\frac{1}{2}C_0[(r/1000)\times 2\tau]}{m} = \frac{C_0 \cdot r \cdot \tau}{1000 \cdot m} \tag{6}$$

where C_0 is the initial concentration (mg/L); r is flow rate (mL/min); m is weight of sorbent (g) and τ is time required for 50% sorbate breakthrough.

The fixed bed sorption of Cu(II) on the acrylic copolymer functionalized with amidoeth-ylenamine groups is described in Table 5 by means of Thomas and Yoon − Nelson model parameters, derived from the slope and the intercept of the corresponding liniar equations plots (Figure 9)
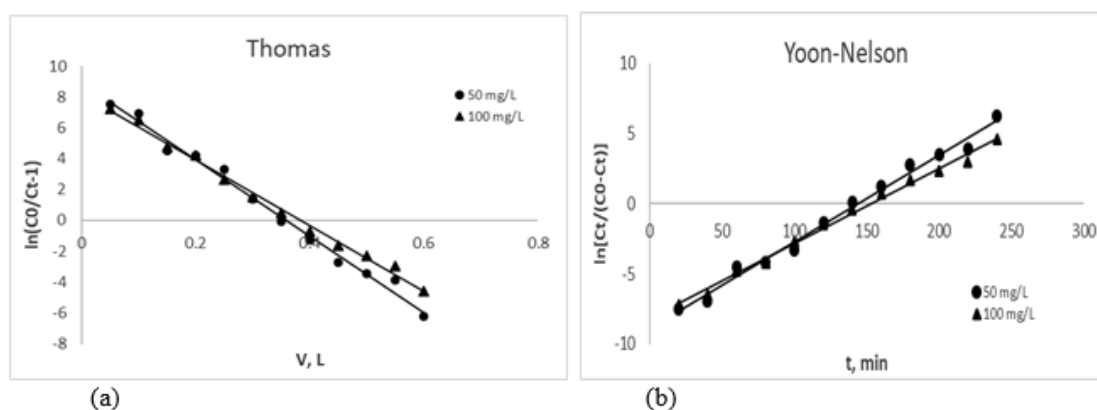

Figure 9. Linear Thomas(a) and Yoon-Nelson(b) plots for column sorption of Cu(III) on the tested chelating polymer at 2 initial concentrations

Conforming to Table 5, the obtained values of the linear regression coefficients (R_2) for the Thomas plots are higher than those for the Yoon – Nelson plots. This means that the fixed bed column sorption of Cu(II) on the proposed functionalized copolymer is best described by the Thomas model, based on the Langmuir sorption/ desorption model and a second – order reversible reaction kinetics.

Table 5. Thomas and Yoon – Nelson model parameters

C_0, (mg/L)	Thomas model			Yoon – Nelson model			
	K_T, (L/min·mg)	$q_{0(T)}$, (mg/g)	R^2	k_{YN}, (mg/g)	τ, (min)	$q_{0(YN)}$, (mg/g)	R^2
50.00	$1.23 \cdot 10^{-3}$	11.40	0.993	0.053	154.42	13.24	0.939
100.00	$5.33 \cdot 10^{-4}$	24.84	0.989	0.062	143	30.28	0.973

where: k_T is Thomas rate constant and requiq $q_{0(T)}$ is Thomas maxium sorption capacity

k_{YN} is Yoon–Nelson rate constant; τ is the time for 50% breakthrough and $q_{0(YN)}$ is Yoon-Nelson column sorption capacity

3.4. Evaluation of the proposed chelating sorbent

Figure 10 records the Langmuir and Thomas maximum capacity of Cu(II) sorption for the tested acrylic copolymer functionalized with amidoethyleneamine groups and other chelating sorbents. Although the sorption capacity is strongly dependent on the nature of the sorbent, Figure 10 clearly shows thar the proposed functionalized copolymer is very compatible with other sorptive materials. The chelating copolymer under study is eligible as a performance sorbent for Cu(II) removal– recovery from aquatic environments.
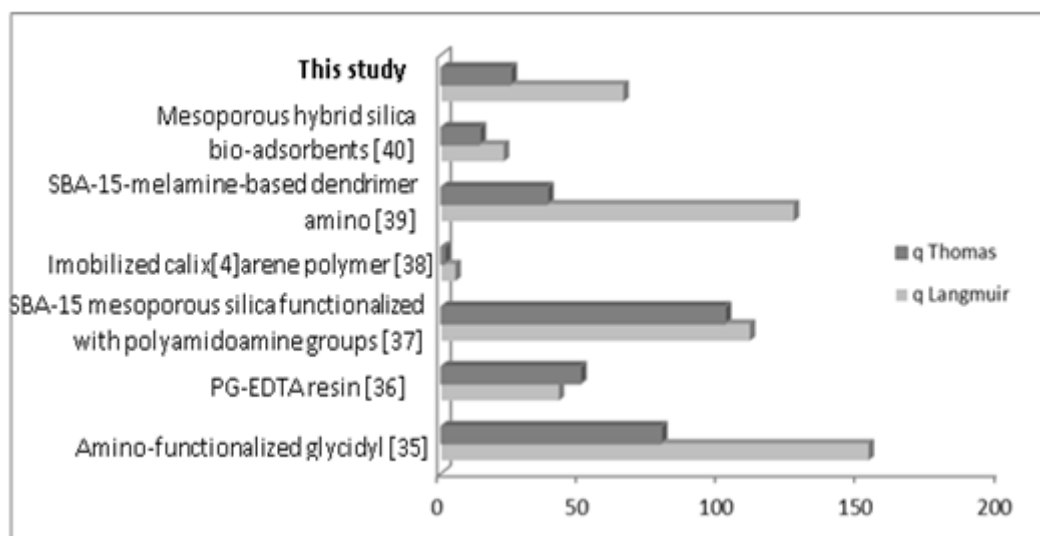

Figure 10. Comparison of the proposed acrylic copolymer functionalized with amidoethyleneamine groups with other reported chelating sorbents for Cu(II) removal

3.5. Practical applicability
3.5.1. Reusability studies

In order to check the reusability of the tested chelating acrylic copolymer, the Cu (II) desorption and the recycling of the sorbent have been studied in batch conditions (Figure 10). According to the literature findings, the desorbing agent, which the best fulfill the economic and ecological requirements is HCl [40]. Because of this, copper was desorbed from the metal loaded acrylic copolymer functionalized with amidoethyleneamine groups by using 0.1M HCl. As can be seen from Figure 11, successive sorp-tion-

desorption cycles have demonstrated the possibility of chelating polymer regeneration and its reuse at least 6 times with a copper recovery efficiency of over 90%.
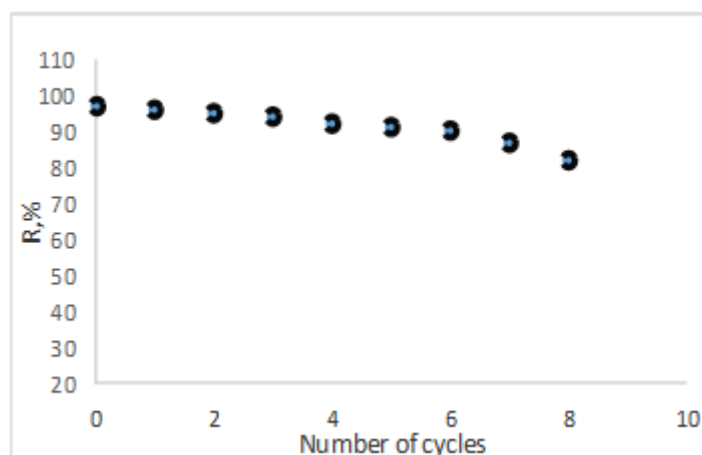

Figure 11. Repeated use studies

3.5.2. Treatment of sample of real wastewater

In order to evaluate the efficiency of the acrylic copolymer functionalized with amidoethyleneamine groups in the treatment of real wastewaters, the removal of Cu(II) from a wastewater sample originating from a municipal deposit of wastes collecting has been investigated in fixed bed column conditions (Table 6). The results in Table 6 distinctly shows that the proposed chelating copolymer use results in a significant improvement of the tested wastewater quality, with a special mention on the retention of the Cu(II) entire amount

Table 6. Quality of the tested wastewater before and after treatment with the chelating copolymer under study

Wastewater parameters	Before treatment	After treatment
pH	4.01	6.87
Turbidity (NTU)	0.85	0.05
Total hardness (^{0}G)	25	3.15
Chloride (mg/L)	82	25
CCOCr (mgO$_2$/L)	95	< 30
Cu(II) (mg/L)	10	0.00
Mn(II) (mg/L)	2.75	0.02
Zn(II) ((mg/L)	1.25	0.01

According to Figure 11 and Table 6, the acrylic copolymer functionalized with amidoethyleneamine groups can be cyclic used, with benefits of ecological (removal of Cu(II) form wastewaters) and economical (Cu(II) recovery in concentrated metal solutions) relevance (Figure 12).
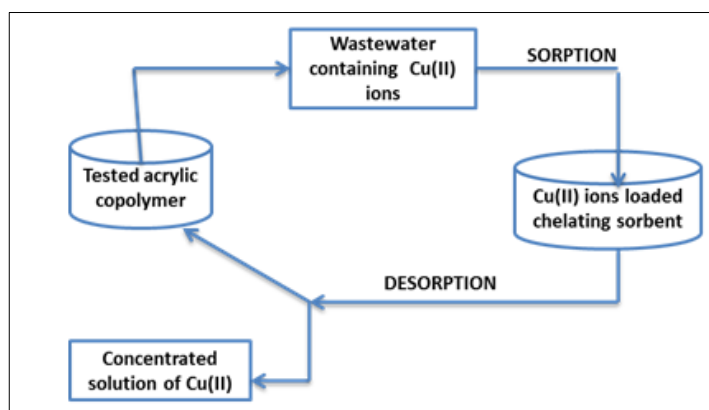

Figure 12. Schematic representation of the potential cyclic use of the tested sorbent

4. Conclusions

The results of this work give the evidence of the possible benefits of using an acrylic copolymer functionalized with amidoethyleneamine groups for the Cu(II) removal– recovery–recycling. The initial *p*H of the solution, initial metal ion concentration and contact time have marked effect on the Cu(II) batch sorption process. The equilibrium data fit well with both Langmuir and Freundlich isotherms. The process of Cu (II) retention on the acrylic copolymer with amidoethylenamine groups follows best a pseudo– second order kinetics. The Thomas model is the optimal solution for the description of the proposed chelating copolymer fixed bed column. Successive sorption-desorption cycles in batch conditions have demonstrated the possibility of chelating polymer regeneration and its reuse at least 6 times. Dynamic studies with real wastewater showed an efficiency of Cu(II) removal of 100% for and a promising amelioration of the quality of wastewater .

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