Testing of Alginate/Chitosan/Glass Bubbles Adsorbent for Copper Removal from Wastewater

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Abstract: *The present paper reported the obtaining of an environmental friendly adsorbent based on sodium alginate, chitosan and glass bubbles. $CaCl_2$ was used as crosslinking agent for sodium alginate favoring the interactions by physical bonds between the negative groups (-COO) of biopolymer and the Ca ions. The experimental study to determine the Cu(II) uptake using an atomic absorption spectrometer was conducted in the testing stand at the 1:50 and 1:100 ratios between the adsorbent mass and the amount of pollutant in solution. The number of cycles of regeneration of the adsorbent material was also evaluated. The characterization of alginate/chitosan/glass bubbles adsorbent by scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS) and Fourier transform infrared spectroscopy (FTIR) showed that the Cu(II) was found out on the surface of adsorbent.*

Keywords: microspheres, adsoption, copper(II), testing stand, regeneration

1. Introduction

Due to the good resistance to corrosion and easily transfer the electricity and heat, copper (Cu) is a most valuable metal widely used in different industries such as electrical, machinery, building construction and allows. A huge amount of Cu(II) results from waste mine water [1] and corrosion of brass in plumbing fixtures [2]. It can contaminate the soil and water, becoming a danger element for environmental and health of people. In the same time, if copper exceeds 2mg L^{-1} in drink water it becomes very toxic, according to World Health Organization [3]. The recovery of Cu(II) from wastewater is a major concern for researchers and industrial field. The conventional processes for removing Cu(II) from wastewater include chemical precipitation, flotation, electrochemical deposition and photocatalysis [1, 3, 4]. The main disadvantages of these processes are refer to high operational cost, long duration time and limited applications.

Recently, adsorption has become an alternative to conventional processes to remove the heavy metals due to the low cost, a broad range of pollutants that can be remove and high efficiency [5]. Among adsorbents, natural polymer materials (sodium alginate, cellulose, chitosan, clay) can be widely used in the removal of heavy metals from wastewater [6].

Sodium alginate is a natural biodegradable polymer who owns nontoxic, gel-enhancing properties, easy of handling [7]. Sodium alginate can be ionically cross-linked by the addition of divalent cations in aqueous solution [8]. The capsule of alginate gelatinized by Ca ions has been used as green adsorbent for retaining of heavy metal pollutants [9-12]. Yang et al. [13] explained the adsorption mechanism for Cu(II) removal by the use of calcium alginate due to the negative groups (COO-) of adsorption sites, which adsorb the cation in the solution. Rapa et al. [14] investigated calcium alginate/starch/clay systems with different ratios between components for removal of Cu(II). High removal efficiencies of Cu(II) were found after 24 h of contact of the adsorbent with the contaminant solution, in the case of system contained starch calcium alginate in ratio of 2:1.

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Chitosan is a unique cationic polysaccharide, which shows adsorption activity [15, 16], film-forming, gelling properties, antimicrobial [17], encapsulation and biocompatibility properties [18,19]. Adsorbents for heavy metals based on chitosan/alginate beads were successfully prepared [20,21]. Chitosan derivatives have used as both flocculants and adsorbents to remove colloidal particles and dyes [22]. Culita et al. [23] tested a chitosan-based magnetic composite in mass ratio 1.25/1 for removal of Pb(II) and Cu(II) from aqueous mono and bi-component solutions.

Glass bubbles spheres are an inorganic material, used as filler in composites in order to decrease the density of components and to improve the processability through their high surface ratio [24]. The literature reveled the use of borosilicate glass spheres as support to immobilize the titanium dioxide [25]. Micro and nanobubbles were also used to remove of Fe^{3+} ions as precipitates and nanoparticles of $Fe(OH)_3$ by flotation process [26].

In the present paper, the new adsorbent based on sodium alginate, chitosan and glass bubbles, as alternative to clay, was prepared by extrusion process, and the microspheres shape and its Cu(II) uptake were analyzed. Surface morphology by SEM coupled with EDS, the change in the functional absorption groups by FT-IR assessment were investigated in order to evidence the Cu(II) uptake.

2. Materials and methods
2.1. Materials
Alginic acid sodium salt $(C_6H_7O_6Na)_n$ (provided by BioChemica), low molecular weight chitosan (Sigma-Aldrich), glass bubbles (3M™ Glass Bubbles, USA) and calcium chloride $(CaCl_2 \cdot 2H_2O)$ were used as raw materials. Glass bubbles are hollow spheres with thin walls, consisting of soda-lime-borosilicate glass, with a surface area of 0.22 g/cm^3, and a median particle diameter of 35 μm [27]. Different Cu(II) solutions ranging from 6 mg L^{-1} to 1 mg L^{-1} have been prepared from 1000 mg L^{-1} $Cu(NO_3)_2$ in 0.5 M HNO_3 stock solution (Merck).

2.2. Preparing of Alginate/Chitosan/Glass Bubbles Adsorbent
In order to test the adsorbent material in the testing stand, the microspheres were prepared by extruding a solution consisting of 2% by weight sodium alginate, 1% by weight chitosan powder and 1% by weight glass bubbles in a calcium chloride bath, followed by their washing and drying. The solution of 2% sodium alginate was obtained on a heating bath with magnetic stirring, at a temperature of 130°C, for 2h at 600 rpm. Chitosan and glass bubbles were added to the obtained sodium alginate solution and the stirring continued for another one hour in order to obtain a good homogeneity of the solution. Before extrusion, the solution obtained was subjected to ultrasonication in order to eliminate air bubbles. A device provided with a pumping system (TONG LI TECH device), at a flow rate of 195 mL h^{-1} and a syringe with 50 mL volume provided with a 18 gauge needle was used to obtain microspheres. The cross-linking of the formed microspheres took place in the $CaCl_2$ solution bath. The microspheres were then dried at 30°C for 48h in order to remove the water. The size of alginate/chitosan/glass bubbles microspheres after drying was 1.2±0.05 mm. The preparation of adsorbent microspheres is illustrated in Figure 1.

Figure 1. Obtaining of alginate/chitosan/glass bubbles microspheres

2.3. Testing

The adsorption experiments were conducted in the testing stand consisted of testing two quantities of adsorbent material, 10 g and 5 g, respectively, in a volume of 500 mL Cu(II) solutions of 4 mg L^{-1} concentration, stirring at temperature of 25°C and 300 rpm, for contact times of 50 min and 125 min, respectively. The ratios between the adsorbent mass and the amount of pollutant in solution were 1:50 and 1:100, respectively. Figure 2 shows images with the testing of adsorbent material. The air blower was used to agitate the material.

Figure 2. Testing stand for removal of Cu(II)
with the alginate/chitosan/glass bubbles microspheres

In this experiment the adsorption capacity of Cu(II) at a concentration of 4 mg L^{-1} was investigated with an atomic absorption spectrometer (GBC 932 AB PLUS, from GBC Scientific Equipment PTY Ltd., Australia) with acetylene flame. After use, the microspheres were immersed in a 10% HCl solution, kept for about one hour, after which they were washed with abundant distilled water until the washing solution no longer contained chlorine (verification with AgNO$_3$ solution). Then the drying process of the microspheres and their use in the testing stand were investigated. These operations were repeated 5 times in order to determine the number of regeneration cycles.

The adsorption capacity of metallic ions, q_e (mg g^{-1}), was calculated according to the Eq. (1).

$$q_e(mg \cdot g^{-1}) = \frac{(C_0 - C_e) \, x \, V}{m} \qquad (1)$$

The percentage removal of metallic ions can be expressed using the Eq. (2).

$$\% \, Cu(II) = \frac{(C_0 - C_e)}{C_0} x 100 \qquad (2)$$

where C_0 and C_e are the initial and equilibrium time of metallic concentration (mg L^{-1}), V is the volume of metallic solution (L) and m is the mass of adsorbent (g).

The retaining of Cu(II) pollutant by the adsorbent material was investigated by scanning electron microscope (SEM, QUANTA 450 FEG) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, INTERSPEC 200-X Spectrophotometer, Interspectrum, Tartumaa, Estonia) analyses.

3. Results and discussions
3.1 Adsorption experiment

Figure 3(a, b) shows the efficiency of retaining Cu(II) and the maximum amount of metal retained at equilibrium.

From Figure 3(a) it is observed that in the first 10 min there is an adsorption of the pollutant of over 70%, after which the adsorption increases slowly up to ~80%. The adsorption equilibrium is reached at 20 min. From the first minutes of testing, the sites on the surface of the microspheres are occupied almost entirely by pollutants, which demonstrates the economic efficiency of the adsorbent material in the process of depollution of industrial waters. In the case of using a ratio of 1:100 between the amount of material being in contact with the pollutant solution, a slow increase of Cu(II) retention is observed, the highest value being of 87% recorded at 125 min (Figure 3(b)). The amount of metal retained is higher than in the previous case. Other authors [11] reported high uptake of Cu(II) of 140.55 mg g^{-1} using low cost adsorbents in a concentration of 200 mg L^{-1} Cu(II) solution. The authors explained the adsorption mechanism due to the negative groups (COO-) of adsorption sites, which adsorb the cations in the solution [11].
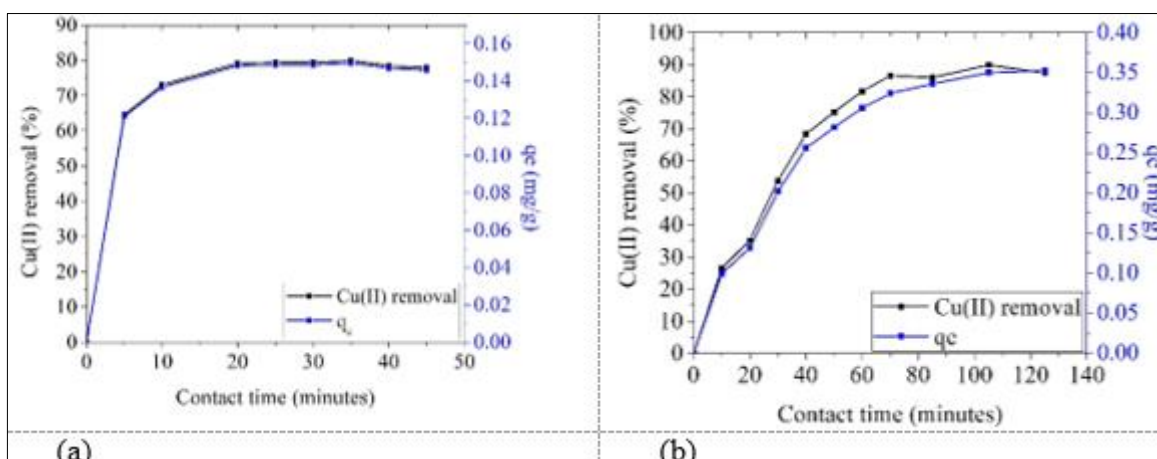

Figure 3. Efficiency of adsorption and qe in the case of use of microspheres in solution of 500 mL solution of Cu(II) 4 mg L^{-1}, contact times maxim 50 min and 125 min, respectively (a) 1:50 ratio between adsorbent and pollutant solution; (b) 1:100 ratio between the adsorbent and pollutant solution

From the practical point of view it is intended both the reduction of costs with the raw materials for the preparation of the adsorbent materials and the increase of the adsorption capacity of material. The material based on sodium alginate, chitosan and glass spheres corresponds very well to this retention strategy.

3.2 Regeneration of adsorbent material
In order to determine the reuse capacity of the adsorbent microspheres, their behavior was analyzed at five regeneration cycles, at 30 min contact with the, 4 mg L^{-1} concentration of Cu(II) solution, at a ratio of 1:100 between the adsorbent material and the pollutant solution. The results are shown in Figure 4.
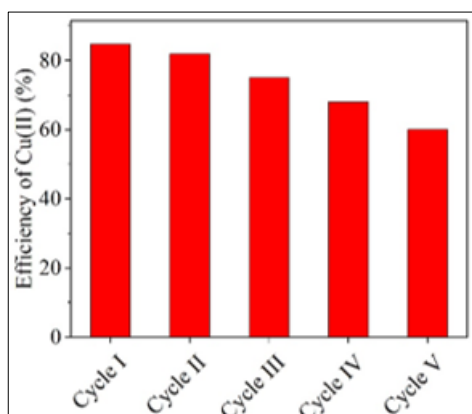

Figure 4. Graphic representation of regeneration cycles for alginate/chitosan/glass spheres microspheres at contact time of 30 min

From the analysis of Figure 4 it is found that the adsorbent material tested shows a decrease of the adsorption capacity of about 10% compared to the previous cycle. Even at five regeneration cycles, the alginate, chitosan and glass microspheres have a Cu(II) retention of about 60%.

3.3 ATR-FTIR

The retention of Cu(II) on the adsorbent material was investigated by ATR-FTIR analysis, and highlighted in comparison with the spectrum of the initial microspheres.
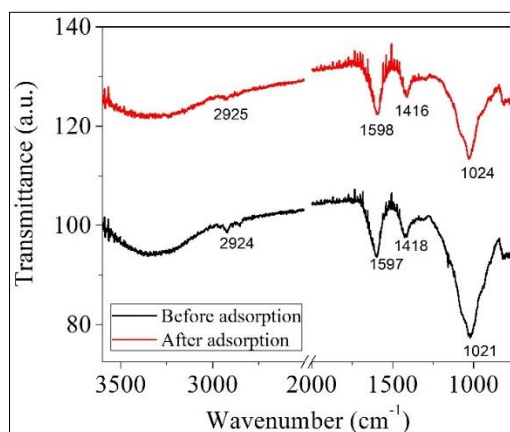

Figure 5. ATR-FTIR spectra for alginate, chitosan
and glass spheres, before and after Cu(II) retention

Figure 5 shows the spectrum of adsorbent materials characterized by a broad peaks around $3250 \, cm^{-1}$ corresponding to the intermolecular hydrogen bonded O-H stretching and stretching vibration N-H, 1597 cm^{-1} due to the $v(C–N) + \delta(N–H)$ from chitosan, 1418 cm^{-1} due to the $v(COO^-)$ from sodium alginate, 1021 cm^{-1} due to $v_{as}(C–O–C)$ from sodium alginate and 2924 cm^{-1} due to the $v(C–H)$ from chitosan. Almost the same absorption bands were reported in the case of alginate/chitosan beads [17, 18]. The formation of electrostatic interactions between positively charged amino groups ($-NH_3^+$) of chitosan and negatively charged carboxylic units ($-COO^-$) of sodium alginate is evidenced by the absence of the adsorption band assigned at $1160 \, cm^{-1}$ due to the amine group [17].

From the comparative analysis of the two FTIR spectra shown in Figure 5, it is found that the presence of Cu(II) was evidenced by the decrease of the intensity and the displacement of the specific adsorption bands due to the valence vibration of the CH_2 bond (2925 cm^{-1}), NH_2 chitosan bond (1598 cm^{-1}), $v(COO)$ group (1416 cm^{-1}), as well as the $v_{as}(C-O-C)$ bond (1024 cm^{-1}). These demonstrate electrostatic interactions between the pollutant and the adsorbent material. The displacement of the specific absorption bands of alginate/chitosan/glass microspheres by the Cu(II) adsorption can be explained by the weakening of the stretching and torsional vibration of the functional groups, as a result of increased ionic volume [11].
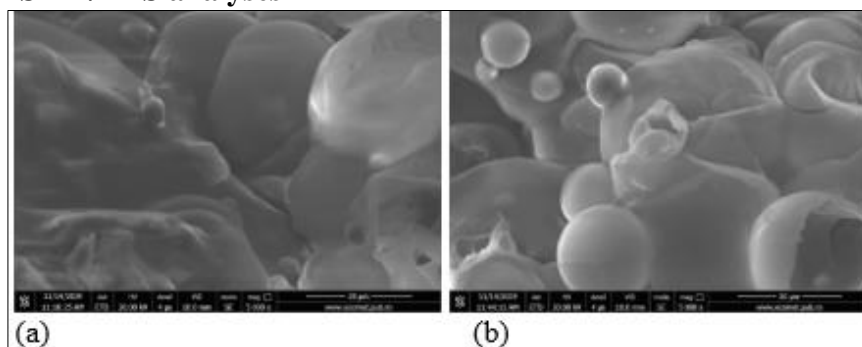
3.4 SEM/EDS analyses

Figure 6. SEM images for alginate/chitosan/glass bubbles microspheres (a) before adsorption; (b) after Cu(II) adsorption

The SEM image shown in Figure 6(a) revealed the spherical appearance created by the glass spheres. This aspect leads to the increase of the contact surface between the adsorbent and the pollutant material. The presence of Cu(II) is evidenced by the penetration inside the glass bubbles (breaking the surface of the glass spheres, Figure 6(b)).

Figure 7 shows the electron diffraction energy spectrum (EDS) diagram for the alginate/chitosan/ glass bubbles microspheres in order to highlight the Cu retention after adsorption process.
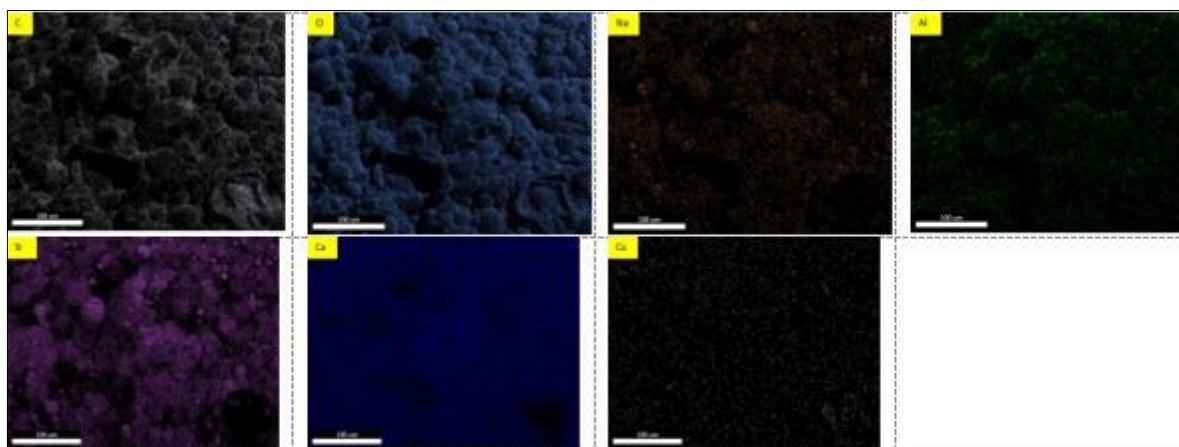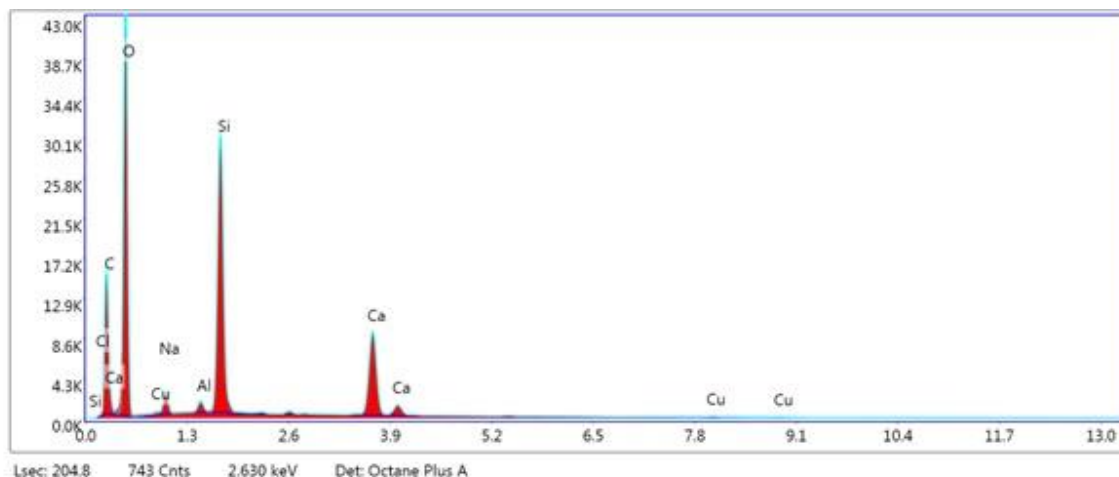

Figure 7. EDS analysis for alginate/chitosan/glass spheres after Cu(II) retention

The elemental composition evaluated from the EDS analysis is presented in Table 1.

Table 1. Elemental composition of microspheres based on alginate, chitosan and clays, after Cu(II) adsorption

	C	O	Na	Al	Si	Ca	Cu
wt. (%)	27.37	52.22	1.89	0.50	10.68	7.15	0.18
at. (%)	36.61	52.68	1.33	0.30	6.14	2.88	0.06

Strong peaks of Si, Na, and Al elements are due to the composition of glass bubbles (SiO_2, Na_2O, Al_2O_3) from adsorbent material, while the peak of Cu showed the strong adsorption for Cu(II). The presence of N from the chitosan structure was not evidenced, maybe due to the low amount in the adsorbent material. Also from Figure 7 it is observed that the Cu(II) was widespread onto the all material surface.

4. Conclusions

Microspheres based on alginate, chitosan and glass bubbles were prepared and tested in two experimental variants, as the ratios between the adsorbent material and the pollutant solution were 1:50 and 1:100, respectively.

It was found that in the case of experimentation of the microspheres dispersed into the pollutant solution in the 1:50 ratio, the adsorption equilibrium of ~80% is reached up to 20 min. In the second case (1:100 ratio between the amount of material and the pollutant solution), a slow increase of Cu(II) adsorption was obtained, up to 125 min with a maximum efficiency of 87%. The amount of metal retained is higher than in the previous case.

By analyzing the regeneration capacity of the adsorbent material, it was found that after 5 cycles of regeneration, the retention of Cu(II) was about 60%.

The presence of Cu(II) on the microspheres surface was highlighted by ATR-FTIR, SEM and EDS analyses.

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