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ALGINATE/CELLULOSE COMPOSITE BEADS FOR ENVIRONMENTAL APPLICATIONS

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Synthesized composite beads based on natural polymers, cellulose/alginate were chemically crosslinked using calcium chloride ($CaCl_2$) and zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and further used in cooper removal from aqueous solutions. Cellulose was introduced in proportion of 10 and 25% in the viscous sodium alginate 3% solution. The composite beads obtained were morphologically (SEM) and compositionally (FTIR, EDS) tested before and after Cu^{2+} ion adsorption. Adsorption studies were performed using a UV-Vis spectrophotometer, at λ=620nm, to determine Cu^{2+} removal degree during 0-168 h.

Keywords: alginate, copper, adsorption studies, cellulose, heavy metal ions

1. Introduction

Intensification of industrialisation and population growth are generating many environmental issues, such as air, water, and soil pollution [1-3]. Due to their non-biodegradable nature, heavy metals are considered the most harmful existing environmental pollutants. Copper is a widely used element in the electric and electroplating industries [4]. It is considered one of the extremely hazardous heavy metals, and may cause various forms of cancer, if ingested in large amounts [5]. Due to the high solubility of heavy metals in aquatic environments, they can be adsorbed by living organisms, and as they move up the food chain, they may accumulate in the human body in much higher concentrations than the allowed limits [6]. Once ingested, they may cause serious health problems, such as developmental retardation, various cancers [7], kidney damage [8], autoimmunity, and in extreme cases, even death [9].

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Thus, removing heavy metal from water has become an acute problem, and as a result, it is necessary to find out and apply effective methods to decontaminate wastewaters from various industrial branches before they are discharged in the environment.

Many types of natural adsorbents or bio-adsorbents from renewable resources [10, 11] have been recently investigated as effective substitutes for the current costly wastewater treatment methods, to remove heavy metals, among which cellulose or carboxymethyl cellulose [12], chitosan [13, 14], alginate, lignin [15], walnut shells [16], etc. are frequently used. Granular activated charcoal [17] and ferruginous powders [18], have used in recent years, for the depollution of water with heavy metals ions. Due to the presence of various reactive groups on the polymer chains, biopolymers are considered the most attractive adsorbents, as they possess high selectivity and reactivity towards heavy metal ions [19].

Alginate is a natural polysaccharide extracted from brown seaweed [20]. It is preferred as bioadsorbent compared to other materials because of its various advantages: biodegradability, hydrophilic properties, abundance and presence of binding sites due to its carboxylate functions. Carboxyl groups of the polymer induce the ability to form biodegradable gels in the presence of polyvalent cations, and in particular with calcium ions (as $CaCl_2$, $CaSO_4$, $CaCO_3$, $Ca(C_2H_3O_2)_2$, $C_{12}H_{14}CaO_{12}$ salts) [21], through ionic interactions. Other commonly used ions for chemical crosslinking of the alginate are: Ba^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+} or Fe^{3+}. However, the use of alginate as adsorbent to remove heavy metals is limited due to the relatively low tensile strength and durability. Mechanical properties of alginate were improved by combining with other materials such as activated carbon [22], cellulose, etc. Alginate-based products have been used also as a substrate for a variety of active agents such as microorganisms, algae, chitosan, sludge, cellulose and humic acid [23]. These types of systems have been tested in terms of their capacity to adsorb different metallic species [24].

Cellulose is a bio-based raw material, due to its abundance, availability and low price [25]. It is a linear polysaccharide with long chains that consists of β-D-glucopyranose units joined by β-1.4 glycosidic linkages. In one repeating unit of cellulose molecule, there are methylol (1) and hydroxyl (2) groups as functional groups. It is a semi-crystalline polymer, containing both crystalline and amorphous phases, and because of the absence of branching, the cellulose chains can be found in an ordered structure. Although it is a linear polymer and contains hydroxyl groups, primary hydroxyl from the methylol group – CH_2-OH in C-6 and secondary –OH in C-3 and C-4, both hydrophilic, it does not dissolve in water and common solvents due to strong hydrogen bonds existing between cellulose chains [1].

Numerous studies for removal of Cu (II) ions were performed using alginate/carbon nanotube/maghemite composite magnetic beads [26], carbon nanotube/calcium alginate composites [27], calcium alginate immobilized kaolin composites [28], etc.

The purpose of this work is the synthesis, characterization and testing of the adsorption capacity of composite beads based on alginate/cellulose for removal of Cu^{2+} ions from synthetic aqueous solutions.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade. Sodium alginate (viscosity – 5.0 – 40.0 cps, pH = 5-8, content of As $\leq$ 3 ppm, Cd $\leq$ 1 ppm, Hg $\leq$ 1 ppm, Pb $\leq$ 10 ppm), anhydrous calcium chloride, zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), ammonium hydroxide solution (NH_4OH - assay: 28.0-30.0% NH_3 basis, vapor pressure: 115 mmHg (20°C)) and cellulose – (bulk density 3.1 - 4.3 g/cc) were purchased from Sigma Aldrich.

2.2. Synthesis of cellulose/alginate composite

Cellulose/alginate-based composites were obtained in several stages. In the first stage, using an adequate amount of sodium alginate and distilled water, a viscous 5% solution of alginate was obtained by vigorous stirring. From the viscous solution obtained previously, we used a volume of 600 mL which was transferred into a 1 L volumetric flask and brought to volume with distilled water to obtain a dilute solution of alginate 3%.

To obtain composites, cellulose was introduced in proportion of 10 and 25%, respectively, in relation to the amount of pure alginate. The composite beads were obtained using 30 mL of 3% alginate solution to which, according to calculations, 0.09 g or 0.225 g cellulose were added. After magnetic stirring, the mixture obtained (alginate and cellulose) was introduced in the form of droplets with a syringe into a 5% solution of $CaCl_2$ or zinc acetate, and kept for 2 hours for crosslinking to take place. Once crosslinked, the composite beads were filtered and dried in Petri dishes at room temperature. Composite beads were used in adsorption studies for removal of Cu^{2+} ions from synthetic aqueous solutions.

2.3. Adsorption/removal studies for Cu^{2+} from aqueous solution

To conduct adsorption studies, in the first stage a stock solution was prepared by solubilizing 12.484 g of copper sulfate in a volumetric flask of 0.5 L and brought to volume with distilled water, and the final concentration of the solution according to the calculations was 0.1 M. The stock solution was then used to obtain more dilute solutions having the following concentrations: 0.05, 0.025, 0.02 and 0.01 M. Based on these concentrations, the calibration curve was drawn by using a UV-Vis spectrophotometer at 620 nm which was found to correspond of the maximum absorptivity of Cu^{2+} solutions.

Kinetic assays for Cu^{2+} ion adsorption were performed by immersing the composite adsorbent beads based on alginate/cellulose (~ 0,200-0,300 g) in 30 mL synthetic solution with molar concentration of 0.025 M. At different preset time intervals, an amount of 2.5 mL was removed and filtered using a 0.20 μm filter. To this solution an amount of 200 μL ammonium hydroxide solution was added for complexation of copper ions and finally, the residual concentration of copper ions was determined.

After equilibrium, the final concentration (*Cf*) of Cu^{2+} was determined and the removal of cooper was calculated using the initial and final at equilibrium concentrations of Cu^{2+} (mol L^{-1}).

2.4. Equipment

After synthesis, the polymer based on alginate 3%, and composites based on alginate 3% reinforced with varied percentages of cellulose, crosslinked with Ca^{2+} and Zn^{2+} ions solutions, were characterized morphologically (SEM) and structurally (EDS, FTIR). SEM images were recorded on a HITACHI S2600N electron microscope coupled with an EDS detector, on samples covered with a very thin silver layer. FTIR microscopy using a Thermo iN10 MX FTIR microscope operated in reflection mode was employed to identify functional groups present on the surface or formed among the system components. UV-Vis measurements were made using a Thermo Evolution 300 spectrometer operated in transmission or diffuse reflectance over the range of 190-1100 nm.

3. Results and discussion

3.1. Characterization of beads composite

Fig.1 A-C presents the characteristic SEM images of beads composites performed at 100x magnification, after a contact time of 168 h with the synthetic copper ion solution. Even at low magnification, the addition of the cellulose strongly modifies the surface of these beads and, at 10kX magnification (Fig.1D), even the cellulose micro-fibres penetrating the surface of these beads can be visualized. The shape of the beads is ellipsoidal and the average size of the beads is less than 1 mm. At 10kx magnification (Fig.1 E and F), the surface of the alginate 3% / 25% cellulose / zinc acetate and alginate 3% / 25% cellulose / $CaCl_2$ are presented after 168 h of immersion in $CuSO_4$ solution. It can be seen that the surface of the sample obtained by using $CaCl_2$ strongly differs comparing with that obtained with zinc acetate. The highest content of the acicular structures is a qualitative proof that Cu^{2+} is better removed when the samples are obtained by crosslinking with zinc acetate comparing with calcium chloride. The removal capacity of Cu^{2+} was further quantified by UV-Vis.

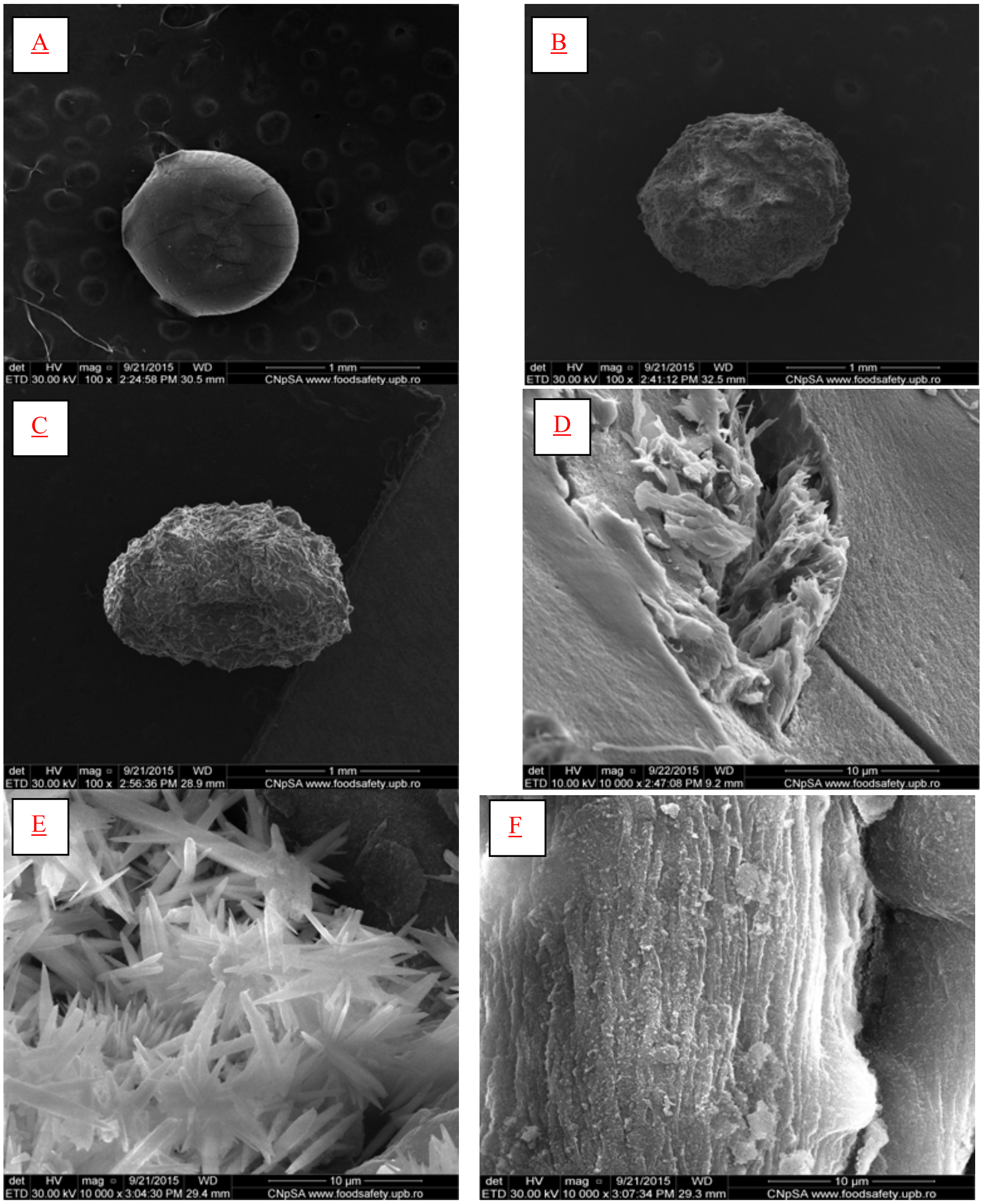

Fig.1. SEM images characteristic for beads composite: **A)** alginate 3% / zinc acetate - 100x, **B)** alginate3% / 10%cellulose / zinc acetate - 100x, **C)** alginate3% / 25% cellulose / $CaCl_2$ - 100x, **D)** details recorded at 10kx magnification highlighting defects induced by the presence of 25% of cellulose microfibrils; **E)** surface of alginate 3% / 25% cellulose / zinc acetate / $CuSO_4$ – 10kx and **F)** surface of alginate3% / 25% cellulose / $CaCl_2$ / $CuSO_4$ - 10kx

Fig.2 presents the energy dispersive (EDS) spectra of the two alginate 3% / 25% cellulose beads crosslinked with calcium chloride (image A) and zinc acetate (image B) after 168 h of Cu^{2+} removal from synthetic solution. The EDS spectra of the other materials are not presented even if they were recorded and will be discussed accordingly.

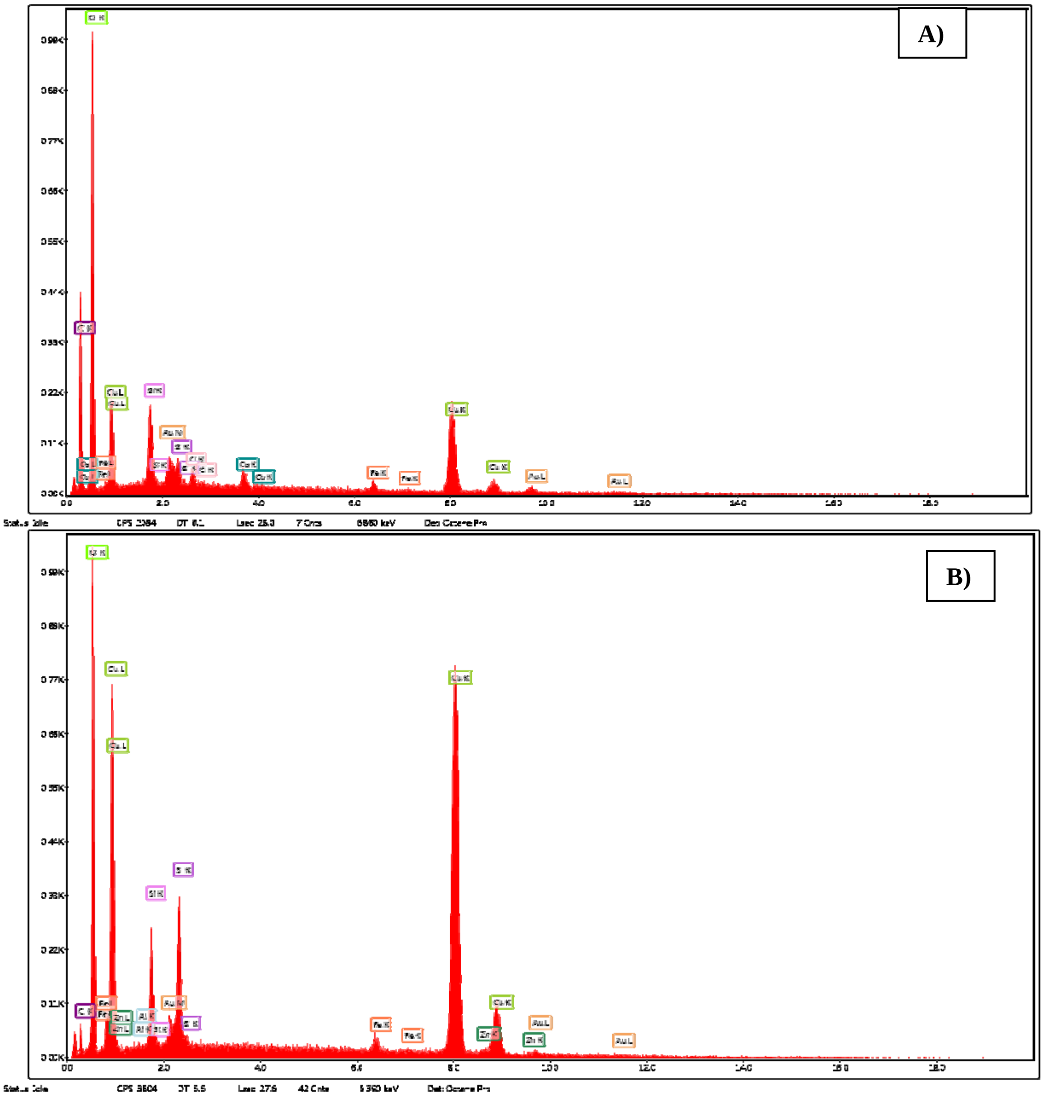

Fig.2. EDS spectra of the alginate 3% / 25% cellulose beads crosslinked with calcium chloride (A) and zinc acetate (B) after Cu^{2+} adsorption/removal

Based on EDS elemental analysis the following chemical elements were identified: O, C, Ca, Zn, Fe, Cu, Si, S and Cl. Ca and Cl appear only in the samples obtained by crosslinking with calcium chloride due to the incomplete exchange of Ca with Cu and contamination of the beads with chloride while S, Si and Fe appear because of the support and not because of the sample. Zinc can be easily identified in the EDS spectra of the alginate sample crosslinked with zinc acetate after Cu^{2+} removal study but its content decreases very much in the case of 10 or 25% of cellulose most probably because of the high exchange rate of Zn with Cu. It can be concluded that copper content (after 168 h of immersion in copper solution) is higher in the case of alginate 3% / 25% cellulose crosslinked with zinc acetate comparing with the same sample crosslinked with calcium chloride. The same result was obtained in the case of samples containing 10% of cellulose, while in the case of pure alginate the intensity of the copper peaks is similar.

FTIR spectroscopy can be used for characterizing crystalline or amorphous phases of most materials. The FTIR spectra of the six samples are presented in Fig.3.

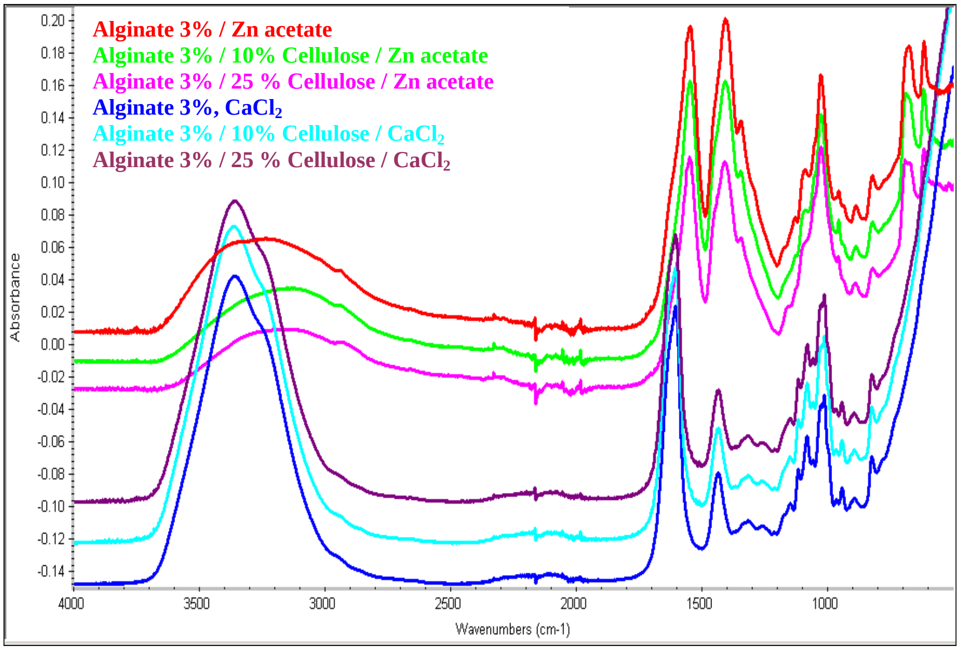

Fig.3. FTIR spectra of alginate based materials loaded with 0, 10 or 25%cellulose and crosslinked with Ca^{2+} or Zn^{2+}

It can be seen that the use of Ca^{2+} or Zn^{2+} crosslinking agents induces significant changes into the FTIR spectra of these materials, while the addition of the cellulose induces only a marginal modification of the FTIR spectra of these materials. In fact, the addition of the cellulose induces an increase of the peaks assigned to cellulose (which are overlapped over the peaks of alginate, at 670, 1030 and 1100 cm^{-1}). The use of Ca^{2+} as crosslinking agent leads to the formation of calcium alginate which presents minor changes in the FTIR spectrum comparing with the sodium alginate [29]. The use of Zn^{2+} induces strong changes on the FTIR spectrum of alginate, especially in the 1400 – 1700 cm^{-1} region. The main peaks assigned to the C-O, C-C and C-H bonds are marginally shifted regardless of the crosslinking agent. The asymmetric and symmetric stretching vibrations of carboxylate groups are very sensitive to the used crosslinking agents because of the direct bonding of these ions with the carboxylate moieties. In this case, the use of Zn instead of Ca induced the strongest shift of these two bands while the relative intensity of these two peaks was strongly changed.

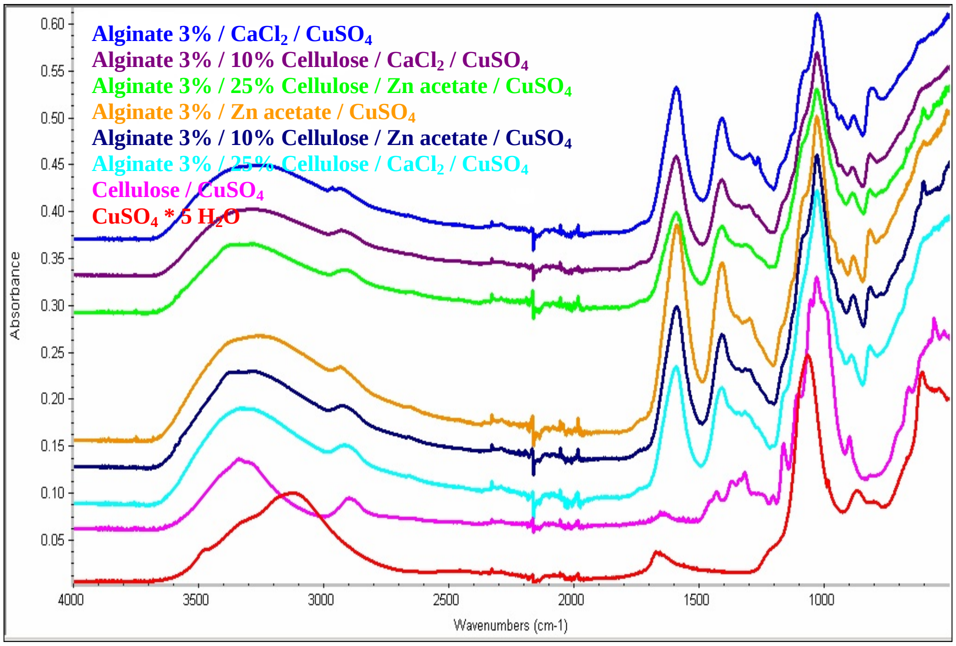

Fig.4. FTIR spectra of the alginate based materials after Cu^{2+} removal

The removal of the Cu^{2+} was also analyzed by FTIR, the characteristic spectra of the above presented materials after cooper removal (after 168 h of contact of alginate based materials with Cu^{2+} solution) being presented in Fig.4. The FTIR spectra of all these materials changed, especially in the 1400 – 1700 cm^{-1} region as a consequence of the substitution of Ca^{2+} and Zn^{2+} with Cu^{2+}. However, most important, the FTIR spectra can be used for analyzing the capacity of these materials to bind Cu^{2+} and consequently to remove these ions from solutions. For this purpose, the peak from ~600 cm^{-1} must be analyzed, this peak being characteristic to hydrated $CuSO_4$. The intensity of this peak is the highest for the systems obtained by crosslinking alginate based materials with Zn^{2+} most probably due to the strongest removal capacity as further proved by UV-Vis spectroscopy.

3.2. Adsorption studies of Cu^{2+} ions on composite beads

Fig.5 shows that the removal of metal ions increases with contact time, for all tested composites. During tests the following parameters: adsorbent amount, copper ion concentration in the synthetic solution (0.025 M) and contact time (0-168 h) were kept constant. The results obtained from adsorption indicate that the type of crosslinking agent strongly influences the copper ion removal capacity of the alginate based systems.

Thus, in the case of crosslinking alginate 3% beads with zinc acetate and containing the highest content of cellulose, a removal rate of ~**80%** is obtained after a contact time of 168 h with the synthetic copper ion solution having 0.025 M. In the case of composites based on alginate 3% / 10% cellulose, adsorption percentage was **68%** while in the case of alginate 3% / 25% cellulose composite beads crosslinked in zinc acetate solution, adsorption rate decreases significantly reaching only **19%**. In the case of using calcium chloride as crosslinking agent ($CaCl_2$), Cu^{2+} ion removal rate was similar and varied insignificantly for all types of composites tested. Thus, in the case of beads based on alginate 3% / $CaCl_2$, removal rate was **18%**. In the case of alginate 3% / 10% cellulose composite, copper ion removal percentage was **23%** and decreased to **14%** in the case of composites based on alginate 3% /25% cellulose / $CaCl_2$.

As noticed, cellulose has very low removal ability and therefore a low affinity for Cu^{2+} ions. After a contact time of 168 h of cellulose with the synthetic solution of Cu ions, adsorption percentage was ~**11%**.

Adsorption process kinetic results show that beads based on alginate 3% crosslinked with zinc acetate and loaded with various amounts of microcrystalline cellulose have a higher metal ion adsorption ability, on the one hand, by ion exchange, and on the other hand, due to functional groups on the surface of alginate. Moreover, zinc ions are more stable compared to calcium ions. As the cellulose amount increases, it is noticed that the metal ion removal ability increases (even if the content of alginate decreases). The better removal capacity of the samples crosslinked with Zn^{2+} is most probably due to the faster exchange rate between Cu and Zn while cellulose microfibres allow a faster shrinking of the composite beads.

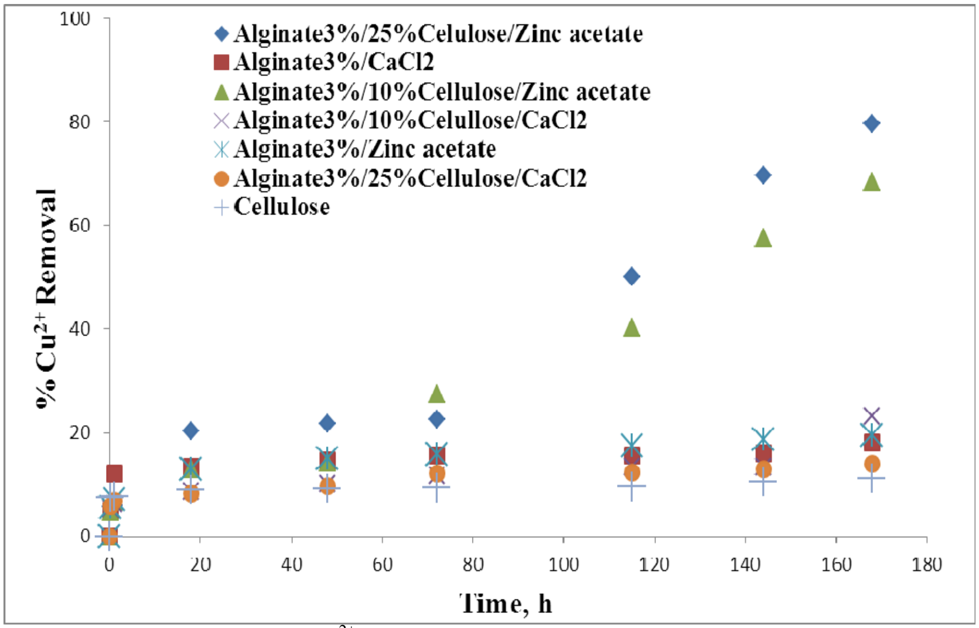

Fig.5. Cu^{2+} removal capacity of composite beads

4. Conclusions

In this paper the ability of composite beads based on alginate and various content of cellulose to remove copper ions from synthetic aqueous solutions was evaluated. Alginate was crosslinked using two types of agents, zinc acetate and calcium chloride. The influence of the crosslinking agent and content of cellulose on the copper ion removal ability was analyzed. Adsorption tests were conducted using a UV-Vis spectophotometer, at a wavelength of 620 nm. Influence of contact time of the synthetic copper ion solution of 0.025 M with composite beads was determined. Results showed a good Cu^{2+} removal capacity, up to **80%** in the case of contact with beads based on alginate 3% / 25% cellulose / zinc acetate and **68%** in the case of composite beads based on alginate 3% / 10% cellulose. When using calcium chloride as crosslinking agent, the removal capacity obtained after a contact time of 168 h of the composite beads with the synthetic copper solution, showed very low values. This proves that the type of crosslinking agent and content of cellulose decisively influence the adsorption ability, most probably because of the formation of defects which allow a better contact between the interior of the beads and the synthetic copper ion solution. It is also worth to mention that the surface of the beads was strongly modified by the presence of cellulose while the use of zinc acetate instead of calcium chloride, after 168 h of immersion of these beads into the Cu^{2+} solution, led to the formation of a very important quantity of acicular structure containing Cu^{2+}.

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