

STRUCTURAL, MORPHOLOGICAL AND THERMAL ANALYSIS OF SOME ALGINATE/STARCH/DELLITE HPS COMPOSITES FOR AQUEOUS Cu(II) REMOVAL

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The aim of the present paper is to investigate the properties of three binary systems based on 2% w/v sodium alginate (AlgNa) and 3% w/v starch, prepared by means of a magnetic stirrer. 3% w/v n-clay was added over the binary mixtures, while the amount of n-clay to all mixtures was 1.5% and 3%, respectively. Microspheres were obtained by crosslinking the prepared mixtures with 1.5 M CaCl₂·2 H₂O. The resulted composites were evaluated in terms of surface morphology (scanning electron microscopy – SEM), elemental composition (energy dispersive X-ray – EDX), swelling, thermal analysis (differential scanning calorimetry – DSC), electrochemical surface properties (zeta potential) and batch adsorption-desorption. The obtained results evidenced that the tested alginate/starch/n-clay 1/2/3 composite has the most promising properties for a biomaterial with potential applications in recovery of Cu(II) from polluted water.

Keywords: alginate, starch, n-clay, Cu(II) removal, swelling, point of zero charge, regeneration

INTRODUCTION

Copper (Cu) is a metal occurring in the environment in three major valence states: copper metal (Cu⁰), Cu(I) and Cu(II). Cu(II) is the most stable form.¹ Cu(II) is widely found in aquatic systems originating from both natural and anthropogenic sources. Natural sources of copper in aquatic systems include geological deposits, volcanic activity, weathering and erosion of rocks and soils. Anthropogenic sources of copper include mining activities, agriculture, metal and electrical manufacturing, as well as the use of pesticides.² It is used in the building industry for hot- and cold-water pipes, electrical wires, hose nozzles, and castings due to its malleability, ductility, and electrical conductivity properties. This metal is also used for the formation of haemoglobin and haemocyanin, the oxygen-transporting pigments in the blood of vertebrates and shellfish, respectively. A considerable source of copper is represented by drinking water due to Cu leaching from plumbing. Copper concentrations that exceed 20 μg g⁻¹ can be toxic for human and aquatic organisms and ecosystems.³ Therefore, treatment measures are

necessary in order to prevent and reduce the exceeded levels of copper. Till now, various technologies have been developed to sequester Cu(II) from waters, such as chemical precipitation,⁴ ion exchange,⁵ adsorption,^{6,7} solvent extraction,⁸ membrane separation,⁹ and electrochemical methods.¹⁰ Among all the water treatment methods used to remove Cu, adsorption is now recognized as the most attractive option, due to its simple operation, low investment, high potential recovery and reuse of metals and adsorbents.

Lately, numerous researches have been made in order to find inexpensive and effective adsorbents for Cu(II) removal. Examples of such adsorbents include: chitosan-Fe₃O₄ nanoparticles,¹¹ amino-functionalized magnetic nanoparticles,¹² carbon nanotube/calcium alginate composites,¹³ alginate-graphene oxide hybrid gel beads,¹⁴ *etc.* Recently, it was reported that these nanomaterials can be combined with other environmental pollutants, increasing their toxicity.¹⁵

Currently, new environmentally friendly adsorbents for Cu(II) removal from aqueous solutions have attracted increased attention. Some of these natural materials that have been widely used for water purification include: clays,¹⁶⁻¹⁸ tree sawdust,¹⁹ algae,²⁰ silice,²¹ chitosan,²² starch,^{23,24} *etc.* Sodium alginate and clay hybrid composites are known for being used as adsorbents to remove the total organic acid anions, as a heat-stable salt from the industrial solvent methyl diethanolamine.²⁵ Ely *et al.*²⁶ have successfully encapsulated clay into alginate with the purpose to remove Cu(II). Tan *et al.*²⁷ reported that immobilized bentonite clay into alginate led to a high sorption efficacy of Cu(II) adsorption (114.70 mg g⁻¹). This composite had a high reusability potential, with desorption throughout three consecutive adsorption-desorption cycles. It was found that the optimum conditions for adsorption are as follows: pH in the range of 4-5 and initial Cu(II) concentrations of 400 mg L⁻¹.

These natural adsorbents present an attractive option due to their high abundance, relatively low cost, low carbon footprint and reduced environmental impact.^{25,28}

The objectives of the present paper were to prepare adsorbent materials based on sodium alginate-starch-n-clay, in the form of microspheres, and to explore their properties in terms of surface morphology and particle size (SEM), elemental composition (EDX), swelling, thermal analysis (DSC) and electrochemical surface properties (zeta potential). It is expected that the developed material would serve as a new environmentally friendly adsorbent with the ability to remove Cu(II) from aqueous solutions.

EXPERIMENTAL

Materials

Sodium alginate salt (C₆H₇O₆Na)_n supplied by BioChemica, has a molecular weight 10,000-600,000 g/mol and is characterized by purity of 90.8%, heavy metals (Pb) of max. 0.002%, loss at drying of max. 15%, pH (1% water) 5.5-8.0, 18-27% sulfated ash and 350-550 mPas viscosity (1% at 20 °C). An aqueous solution of sodium alginate (2 w/v%) (AlgNa) was dissolved in distilled water by stirring at 90 °C for 4 h and at 200 rpm.

Starch (C₆H₁₀O₅)_n supplied by Chimreactiv S.A. Bucharest, extracted from potato, is characterized by 50 g/L solubility in water (90 °C), 6.0-7.5 pH value (2% water), 0.7% reducing matter (maltose), and max. 10% drying loss (105 °C). An aqueous solution of starch (3 w/v%) was prepared by means of a magnetic stirrer at 90 °C for 30 minutes.

Dellite HPS, hydrated aluminum silicate (n-clay), (Laviosa Chimica Mineraria S.P.A.) was used for preparing a solution containing 3% of Dellite HPS in distilled water, by sonication for 1 h.

1.5 M calcium chloride (CaCl₂·2H₂O) was used as crosslinker.

Preparation of alginate/starch and nanoclay composite microspheres

Binary systems based on sodium alginate/gelatinized starch of 1:1, 1:2 and 2:1 vol. ratios were obtained by dispersing 2% w/v sodium alginate (AlgNa) with 3% w/v starch solution by means of a magnetic stirrer at 60 °C for 30 min. The gelatinization process of starch means the disruption of molecular orderliness of starch molecules²⁹ and was carried out according to the method previously described by F. Liu *et al.*²⁸ To each binary mixture system, a solution of 1.5% and 3%, respectively n-clay previously prepared was added. The codes and compositions of the prepared composites are shown in Table 1.

The solutions thus obtained were dripped with a syringe in a crosslinking bath containing 1.5 M aqueous solution of CaCl₂. Immediately upon contact with the crosslinking solution, spheres were formed. After 24 h of immersion in the crosslinking bath, the formed spheres were filtered and washed with distilled water, then dried at ambient temperature. Uniform spheres of approximately 3 mm were obtained. It was noticed that the obtained spheres became opaque and firmer after the introduction of n-clay in the composition. In order to determine the absorption of pollutants from wastewaters, the obtained microspheres were dried to completely remove interstitial water molecules.

Investigation methods

Scanning electron microscopy (SEM)

The morphology and structure of the materials were examined using a QUANTA 450 FEG scanning electron microscope, equipped with a field emission gun and a 1.2 nm resolution X-ray energy dispersive spectrometer, with a resolution of 133 eV. The specimens were gold sputtered prior to microscopy.

Swelling index

The weighed microspheres (w₁) were immersed into water at 23 °C for 24 h, and then they were removed, patted dry with tissue paper, and weighed again (with 0.1 mg accuracy). The swelling index was determined using the following equation:

$$\% \text{ Swelling index} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W₂ is the weight of swollen microspheres (g) and W₁ is the weight of microspheres before swelling (g).

Three tests for each microsphere composition were performed, and the results were expressed as the mean value ± standard deviation.

Differential scanning calorimetry measurements (DSC)

DSC analyses were performed by means of a Mettler Toledo (Model DSC 823e, Switzerland) Calorimeter from 25 °C to 220 °C, at a heating rate of 10 °C/min. DSC curves were processed with the aid of STARe 9.10 software from Mettler-Toledo.

Point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) of the prepared composites was measured by means of electrophoretic mobility (Zetasizer Nano, Malvern Instruments, UK), based on the dynamic light scattering (DLS) technique. The solution surface charge at the pH values ranging from 3 to 7 was evaluated using 1 mM NaCl or 1 mM HCl to adjust the pH. The pH_{pzc} value was determined from a plot of initial pH *versus* pH of the samples.

Table 1
Coding and composition of samples

System	Sample code	Composition		
		AlgNa, vol%	Starch, vol%	n-Clay, wt%
System I	AlgNa/starch 1/1	50	50	-
	AlgNa/starch/n-clay 1/1/1.5	50	50	1.5
	AlgNa/starch/n-clay 1/1/3	50	50	3.0
System II	AlgNa/starch 1/2	33.33	66.66	-
	AlgNa/starch/n-clay 1/2/1.5	33.33	66.66	1.5
	AlgNa/starch/n-clay 1/2/3	33.33	66.66	3.0
System III	AlgNa/starch 2/1	66.66	33.33	-
	AlgNa/starch/n-clay 2/1/1.5	66.66	33.33	1.5
	AlgNa/starch/n-clay 2/1/3	66.66	33.33	3.0

Batch adsorption experiments

Adsorption of Cu(II) was performed in the batch mode by shaking 500 mg of adsorbent with 100 mL of Cu(II) solution, with the concentration of 2 mg L⁻¹ at room temperature, for specific time intervals (maximum of 24 h). The pH of the solutions was 6. It is known that a precipitate of copper hydroxide will be produced at pH > 5.8.¹³ After reaching equilibrium, the solutions were filtered (Whatman filter paper No. 1) and the Cu(II) concentration in the filtrate was detected at $\lambda = 324.7$ nm by an atomic absorption spectrometer (GBC 932 AB PLUS, from GBC Scientific Equipment PTY Ltd., Australia) with acetylene flame.

The % of Cu(II) removed from synthetic aqueous solutions was calculated using Equation (2):

$$\% \text{ Cu(II)} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

where C_0 and C_f are the initial and final Cu(II) concentration in the solution (mg/L) at the tested time.

Desorption studies

Desorption studies employed 0.1M HCl solution. After the initial adsorption of Cu(II) containing 2 mg L⁻¹ of metal ions for 24 h, the composites microspheres were immersed into 30 mL of 0.1 M solution of HCl. After removal of Cu, the composites were gently washed with distilled water till no Cl ions were detected (checked with AgNO₃ solution). Then, the adsorbents were again immersed into 100 mL of metal ion solution of 2 mg L⁻¹ concentration at room temperature for 24 h. The concentrations of the removed metal were analyzed by an atomic absorption

spectrometer. This procedure was repeated twice. The amount of Cu ions adsorbed per unit weight of sorbent (q_e) at equilibrium was calculated by Equation (3):

$$q_e (\text{mg} \cdot \text{g}^{-1}) = \frac{(C_0 - C_f) \times V}{m} \times 100 \quad (3)$$

where C_0 and C_f are the concentration of the Cu(II) solution before absorption and after reaching adsorption equilibrium, respectively (mg L⁻¹); V is the volume of adsorbate (L) and m is the mass of adsorbent (g).

RESULTS AND DISCUSSION

SEM and EDX

SEM images of AlgNa/starch/n-clay composites are shown in Figure 1 (a-i) and the energy dispersive X-ray (EDX) patterns of the composites are shown in Figure 2 (a-c).

The morphology examination revealed non-aggregated microspheres with irregular surfaces. The incorporation of n-clay led to a pronounced tendency of roughness, sphericity and porosity (Fig. 1). The largest surfaces (1.621-1.738 mm²) were obtained in the case of the composites containing a vol. ratio of 1/2 of alginate/starch. By the addition of n-clay into the alginate/starch composites, the dimensions of the microspheres slowly increased. This is attributed to strong hydrogen bonds between sodium alginate and starch, as well as to CaCl₂ crosslinking.

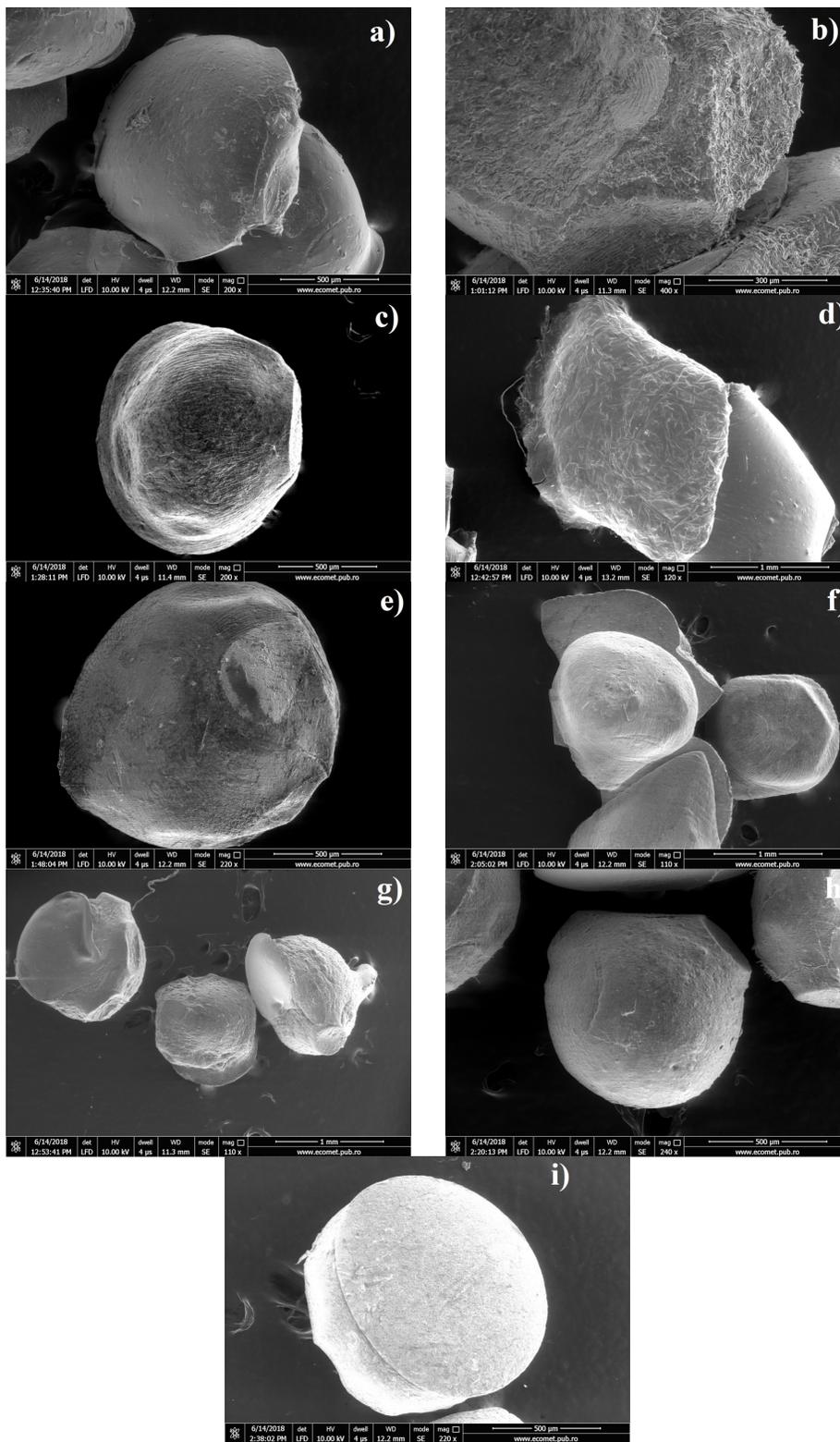


Figure 1: SEM micrographs of a) AlgNa/starch 1/1 (200x); b) AlgNa/starch/n-clay 1/1/1.5 (400x); c) AlgNa/starch/n-clay 1/1/3 (200x); d) AlgNa/starch 1/2 (120x); e) AlgNa/starch/n-clay 1/2/1.5 (220x); f) AlgNa/starch/n-clay 1/2/3 (110x); g) AlgNa/starch 2/1 (110x); h) AlgNa/starch/n-clay 2/1/1.5 (240x); i) AlgNa/starch/n-clay 2/1/3 (220x)

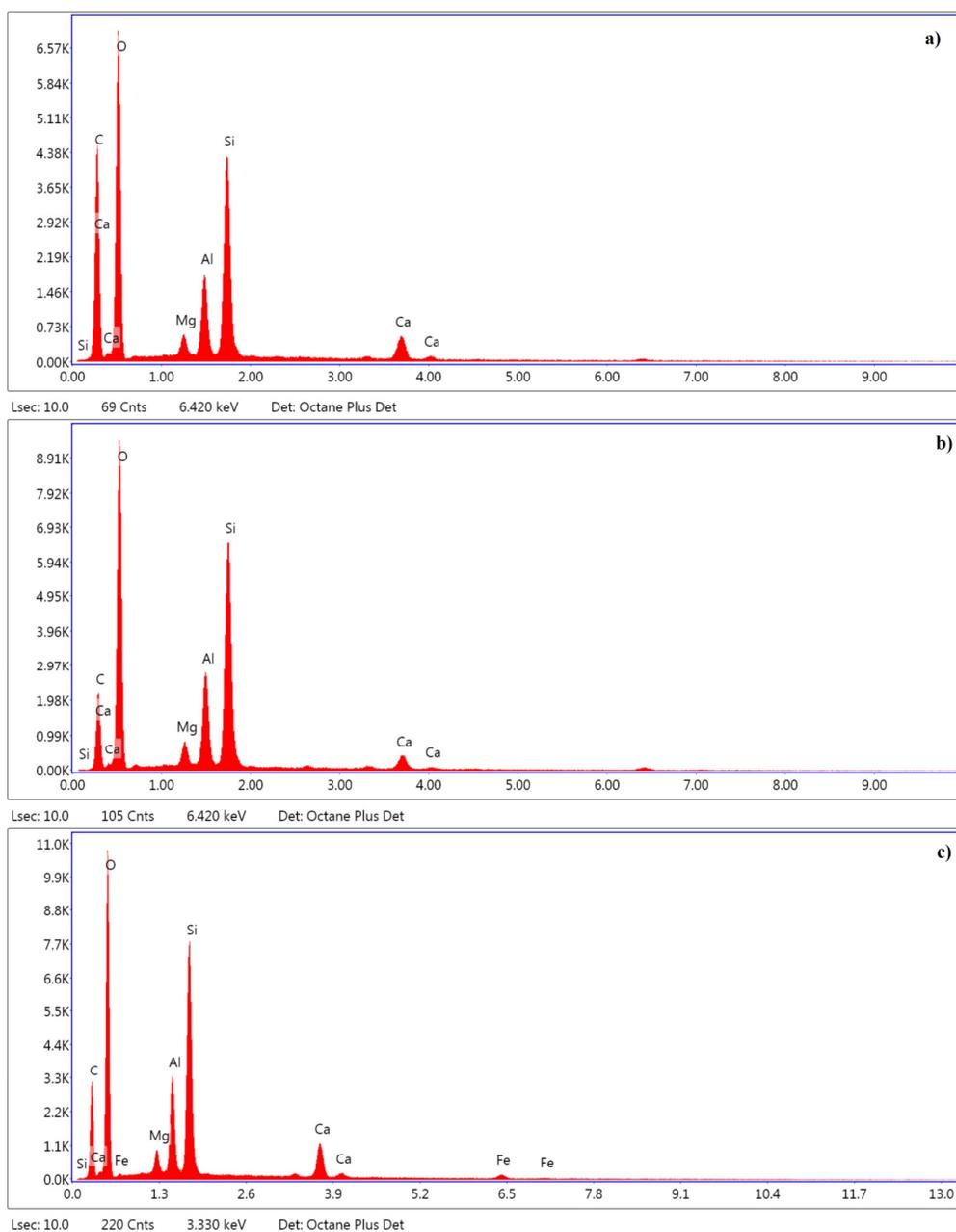


Figure 2: EDX spectra of a) AlgNa/starch/n-clay 1/1/3; b) AlgNa/starch/n-clay 1/2/3; c) AlgNa/starch/n-clay 2/1/3

The condensation reaction between the carboxyl groups of the calcium alginate and the hydroxyl groups found in the starch and n-clay facilitates the adsorption of metal ions by the alginate/starch/n-clay systems. It is expected the systems containing more starch to have a stabilizing effect, preventing their degradation.³⁰

The energy dispersive X-ray (EDX) patterns of AlgNa/starch/n-clay composites exhibit carbon content in the range of 26.25-39.72 wt%, oxygen in the range of 42.76-51.41 wt%, aluminum of 3.75-6.06 wt%, and silicate of 9.63-15.26 wt%. The intense peaks of Si, Mg and Al confirmed the presence of n-clays in the composite beads. Table 2 summarizes this EDX analysis. From Table 2, it

can be observed that Mg, Al and Si were found in higher amounts in the composites containing an alginate:starch ratio of 1:2.

Swelling behavior

The behavior of the microspheres after immersion into water for 24 h is shown in Table 3. A gradual increase in the swelling index profile, with starch loading in the composites, is observed (Table 3). Maximal swelling is observed for System II (AlgNa/starch 1/2) and minimal swelling – for System III (AlgNa/starch 2/1). This behavior at swelling can be explained by the hydrophilicity of starch.³¹ The linear component (amylose) from the starch structure in contact with water forms networks to hold water molecules.³² Also, the interaction of reactive -OH groups from n-clays and starch with the reactive sites of alginate resulted in superabsorbent

composites.³³ It is expected the increased interaction between water, starch and n-clay on the accessible surfaces of the beads to contribute to high adsorption of Cu(II).

Differential scanning calorimetry measurements (DSC)

The DSC curves shown in Figure 3 indicate a maximum endothermic peak around the temperature of 70 °C due to the evaporation of crystallization water. The degradation onset temperature occurred in the range of 184-206 °C, 163-199 °C and 185-201 °C for the composites containing alginate/starch ratios of 1/1, 1/2 and 2/1, respectively. Thermal analysis by DSC showed that the introduction of n-clay into binary systems had the effect of delaying degradation.

Table 2
Elemental composition of AlgNa/starch/n-clay composites

Elements	AlgNa/starch/n-clay 1/1/3		AlgNa/starch/n-clay 1/2/3		AlgNa/starch/n-clay 2/1/3	
	Concentration					
	wt% ^a	at% ^b	wt%	at%	wt%	at%
Carbon	39.72	50.26	26.25	35.79	29.24	38.55
Oxygen	42.76	40.61	48.46	49.59	51.41	50.89
Magnesium	0.94	0.59	1.59	1.07	1.40	0.91
Aluminum	3.75	2.11	6.06	3.68	4.47	2.62
Silicate	9.63	5.21	15.26	8.90	10.25	5.78
Calcium	3.19	1.21	2.37	0.97	2.97	1.17
Iron	-	-	-	-	0.27	0.08

^a wt% – weight percentage from EDX analysis; ^b at% – atomic percentage obtained from EDX analysis

Table 3
Swelling index for AlgNa/starch/n-clay microsphere composites

Sample	Swelling index, %
AlgNa/starch 1/1	141.14±15.12
AlgNa/starch/n-clay 1/1/1.5	110.82±10.42
AlgNa/starch/n-clay 1/1/3	131.70±13.31
AlgNa/starch 1/2	250.76±15.92
AlgNa/starch/n-clay 1/2/1.5	161.28±13.26
AlgNa/starch/n-clay 1/2/3	226.00±17.21
AlgNa/starch 2/1	147.05±12.03
AlgNa/starch/n-clay 2/1/1.5	114.64±10.78
AlgNa/starch/n-clay 2/1/3	86.98±6.62

Determination of pH_{pzc}

The behavior of the composites in the pH range from 1 to 7 is plotted in Figure 4. The stability tests carried out indicated a general dissolution tendency in aqueous media up to pH ≤

4. For the composites containing alginate/starch in ratios of 1/1 and 2/1, the dissolution trend is observed in the entire pH range. As the pH decreased, the surface of the alginate/starch/n-clay exhibited an increasingly positive

characteristic, which is not favorable for Cu(II) adsorption. At lower pH, Cu(II) is present in solutions as a free cation (Cu^{2+} and CuOH^+), which can compete with protons for the surface binding sites.³⁴ In the case of the composite

containing an alginate/starch ratio of 1/2 (System II), a more stable behavior up to pH 7 is observed. Other studies also reported that Cu(II) adsorption increased as the solution pH increased.^{5,6}

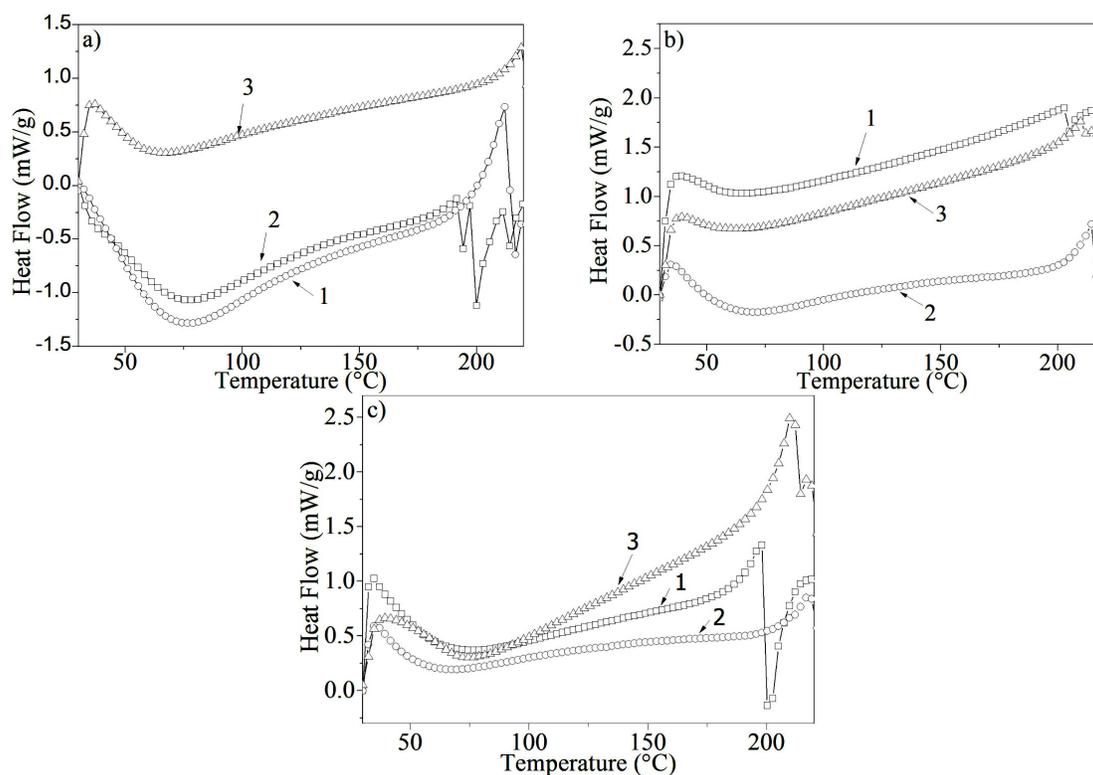


Figure 3: DSC curves of AlgNa/starch/n-clay; a) System I (1 – AlgNa/starch 1/1; 2 – AlgNa/starch/n-clay 1/1/1.5; 3 – AlgNa/starch/n-clay 1/1/3); b) System II (1 – AlgNa/starch 1/2; 2 – AlgNa/starch/n-clay 1/2/1.5; 3 – AlgNa/starch/n-clay 1/2/3); c) System III (1 – AlgNa/starch 2/1; 2 – AlgNa/starch/n-clay 2/1/1.5; 3 – AlgNa/starch/n-clay 2/1/3)

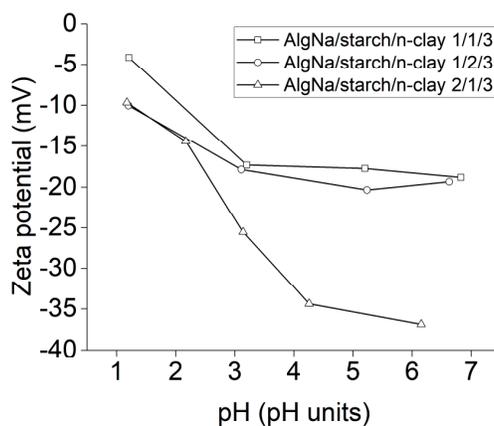


Figure 4: pH_{pzc} of AlgNa/starch/n-clay composites

Adsorption of Cu(II)

The efficiency of adsorption (%) for alginate/starch/n-clay microspheres after 24 h contact time with 2 mg L^{-1} concentration of Cu(II) is plotted in Figure 5. From Figure 5, it can be observed that the adsorption capacity depends on the composition of the adsorbents. Thus, System I containing a 1/1 ratio of alginate/starch exhibited higher affinity to Cu(II) pollutant than System II (alginate/starch ratio of 1/2) and System III (alginate/starch ratio of 2/1), showing 38%, 10% and 4%, respectively, removal of the pollutant after 2 h. High removal efficiencies were recorded by the binary systems after 24 h of contact with the contaminant solution. In the case of System I, which incorporated n-clay, it is observed that the adsorption slowly decreased compared with the adsorption efficiency of AlgNa/starch 1/1 (Fig.

5a). In the case of alginate/starch 2/1 adsorbent (System III), the increase of the carboxyl groups led to an unsaturation of the active adsorption sites due to Cu(II) deficiency (Fig. 5c). Thus, it is possible to use n-clay as a filler, as it reduces the internal surface area of accessible microspheres.

The incorporation of n-clay into System II led to an improved adsorption of Cu (II). AlgNa/starch/n-clay 1/2/3 adsorbent showed the highest removal capacity (95% after 24 h), followed by AlgNa/starch/n-clay 1/1/3 adsorbent (82%) and AlgNa/starch/n-clay 2/1/3 adsorbent (76%). With increasing the starch and n-clay concentrations, it can be assumed that the adsorption active sites on alginate/starch/n-clay 1/2/3 adsorbent increased, so that the pollutant uptake is favored (Fig. 5b).

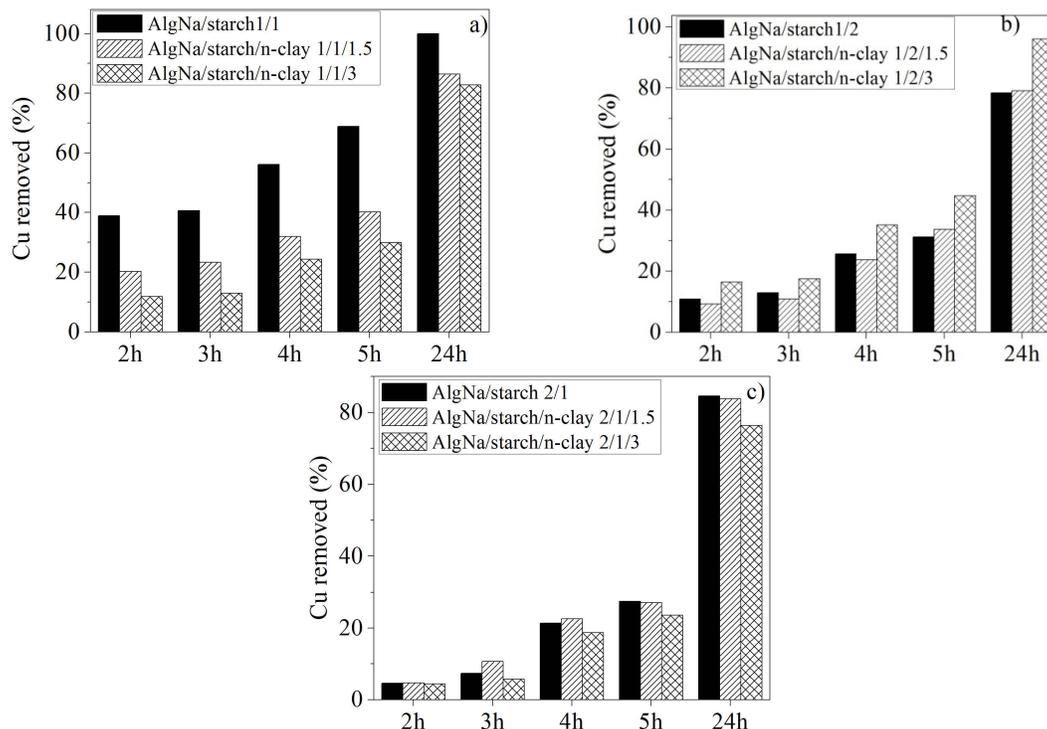


Figure 5: Efficiency of Cu(II) adsorption (%) by AlgNa/starch/n-clay systems; a) System I (AlgNa/starch/n-clay with 1/1 ratio of alginate/starch); b) System II (AlgNa/starch/n-clay with 1/2 ratio of alginate/starch); c) System III (AlgNa/starch/n-clay with 2/1 ratio of alginate/starch). Experimental conditions: 0.5 g AlgNa/starch/n-clay microspheres dispersed in 100 mL of copper (II) at concentrations of 2 mg L^{-1} for maximum 24 h

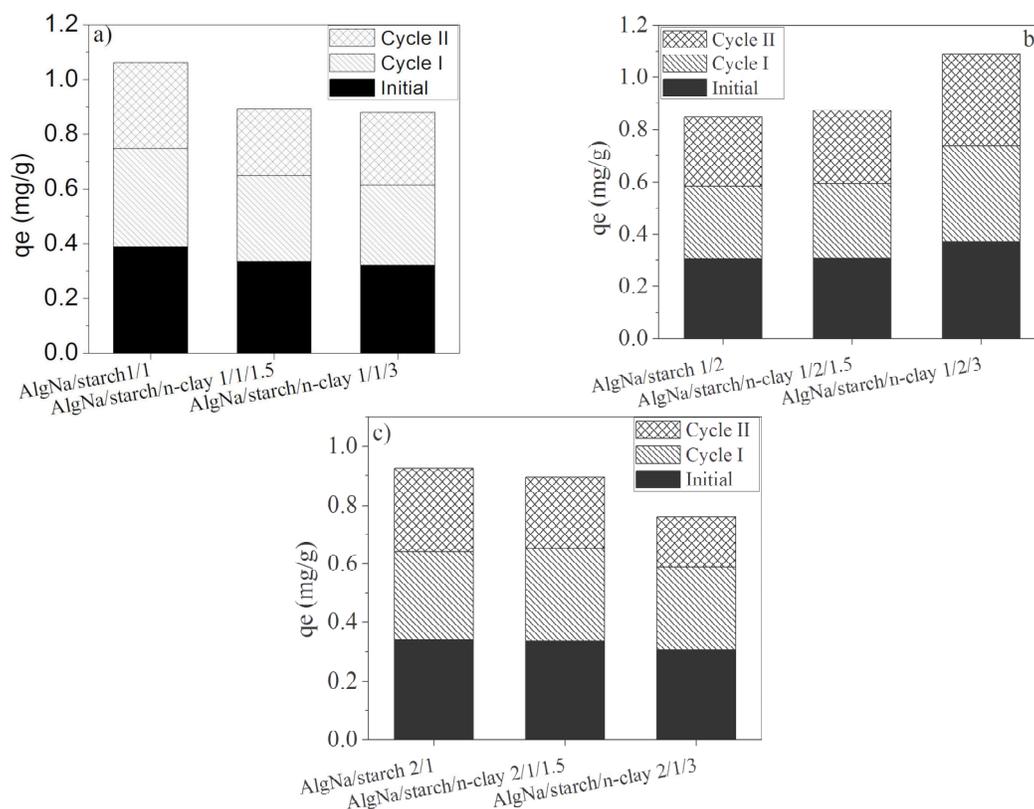


Figure 6: Reutilization of AlgNa/starch/n-clay microspheres for Cu(II) removal during two cycles; a) System I; b) System II; c) System III. Experimental conditions: 0.5 g AlgNa/starch/n-clay microspheres containing Cu(II) adsorbed for 24 h, kept in contact with 0.1 M HCl, washed with distilled water and then immersed into 100 mL of pollutant in concentration of 2 mg L^{-1} for 24 h

This result is correlated with the swelling behavior of AlgNa/starch/n-clay 1/2/3 adsorbent – Table 3 and pH_{pzc} – Figure 4. Around pH 6, the alginate, starch and n-clay exhibited a significant amount of negative charges due to the deprotonated carboxyl and hydroxyl groups. These negative charges allowed the polysaccharides to induce repulsive electrostatic forces, causing both swelling and interaction with positively charged ionic groups. These results are in agreement with those reported by other authors.^{14,16,22}

Desorption study

According to the experiments carried out in this study, maximum adsorption of Cu(II) was considered after 24 h. The regeneration of the adsorbent systems was examined by reusing twice the alginate/starch/n-clay microspheres of different compositions. Thus, after the microspheres were treated with 0.1 M solution of HCl in order to remove the retained Cu(II), the adsorption/desorption tests were performed in

order to record the amount of adsorbate adsorbed per unit weight of sorbent (q_e). The obtained results, in comparison with those before desorption, are shown in Figure 6 (a, b, c).

From Figure 6, it is observed that the AlgNa/starch/n-clay microspheres show a decrease of the amount of pollutant retained by about 10% after each regeneration cycle. The highest q_e was found for System II (containing 1/2 ratio of alginate/starch and 3% n-clay) – 0.3624 mg g^{-1} and 0.3546 mg g^{-1} after the first and second regeneration, respectively. System I (AlgNa/starch 1/1) and System II (AlgNa/starch 2/1) showed a decreased amount of metal on the adsorbent; the increased n-clay amount was explained by the dissolution behavior (pH_{pzc} – Fig. 4). AlgNa/starch/n-clay 1/1/3 showed q_e values of 0.2924 mg g^{-1} and 0.2662 mg g^{-1} , while AlgNa/starch/n-clay 2/1/3 recorded q_e values of 0.2846 mg g^{-1} and 0.1712 mg g^{-1} after the first and second regeneration, respectively.

This regeneration study demonstrates the economic efficiency of the alginate/starch/n-clay

1/2/3 adsorbent. Successful adsorption-desorption cycles were found for modified chitosan used for the removal of Cu(II) ions from aqueous medium.^{22,35} The sorption performance of heavy metal ions was also reported for other cheap and widely available adsorbents, such as chitosan/poly(vinyl amine),³⁶ hemp fibers,³⁷ lignin,³⁸ thiol-functionalized cellulose,³⁹ *etc.* Therefore, removing Cu contaminants from waste waters with adsorbent materials made from abundant and inexpensive polysaccharides, with tailored composition, could be a feasible approach to tackle the pollution problem.

CONCLUSION

Binary systems from alginate/starch with different vol. ratios (1/1, 1/2 and 2/1, respectively), loaded with 1.5 and 3% n-clay, were prepared and tested as possible sorbents for Cu(II) removal from waste water.

From SEM images, it was observed that the microspheres did not exceed 2 mm and the incorporation of n-clay led to a pronounced tendency of roughness, sphericity and porosity. The EDX analysis of the composites indicated intense peaks of Si, Mg and Al, due to the presence of n-clays in the composites. Elemental distribution was in the following range: carbon 26.25-39.72 wt%, oxygen 42.76-51.41 wt%, aluminum 3.75-6.06 wt%, silicate 9.63-15.26 wt%. It was established that the AlgNa/starch/n-clay 1/2/3 composite showed the highest adsorption of Cu(II) due to increased interactions between water molecules, starch and n-clay on the accessible surfaces of the beads. From the pH_{pzc} , it was observed that the composites containing the 1/1 and 2/1 ratios of alginate and starch had the tendency to dissolve at pH values lower than 4. AlgNa/starch/n-clay 1/2/3 was considered a more stable system. From the DSC curves, it was found that n-clay had the role of delaying the degradation temperature of the AlgNa/starch systems. The incorporation of n-clay into adsorbent compositions had different effects on their adsorbent properties: for the alginate/starch binary systems 1/1 and 2/1 it acted as a filler, reducing the internal surface area of accessible microspheres to remove the cation, while in the case of alginate/starch 1/2, it contributed to the highest removal capacity (95% after 24 h). The highest amount of Cu(II) adsorbed per unit weight of sorbent (q_e) was found for System II (containing a 1/2 alginate/starch ratio and 3% n-

clay) – 0.3624 mg g⁻¹ and 0.3546 mg g⁻¹ after the first and second regeneration, respectively.

The obtained results evidenced that the tested alginate/starch/n-clay composite, with the ratio of 1/2/3 between the components, can be a promising biomaterial with potential applications in recovery of Cu(II) pollutant from aqueous systems.

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