Alginate-based biopolymers for wastewater purification

[1]Mihaela Hetvary, [2]Ecaterina Matei, [1]Dumitru Vâju, [1]Daniela Ignat, [1]Csaba Bartha, [1]Măriuța Popanton, [2]Maria Râpă, [2]Claudia Ionela Tarcea, [2]Cristian Predescu

[1] SC ICPE Bistrița SA, Bistrița, Romania; [2] University POLITEHNICA of Bucharest, Bucharest, Romania. Corresponding author: E. Matei, ecaterinamatei@yahoo.com

Abstract. A major challenge for environmental protection represents removing the heavy metals from the industrial wastewaters using materials such as biosorbents. In the present research, a test bench was developed for testing the alginate-based filtering materials. The said device consists in a column in which the filtering materials that are to be tested are inserted, in four digitally controlled volumetric membrane pumps, in a microblower for hot air, used to dry the filtering material, and in a supply and automation electrical panel. The tests carried out aimed at recovering the copper from the water by using spheres made of sodium-starch-glass alginate. The whole process comprises two sets of experiments using a concentration of 1 mg/L Cu in the presence of 0.5 g of spheres made of sodium-starch-glass alginate during 2 hours (120 minutes). The results indicated that the adsorption equilibrium is reached after 60 minutes of contact, under stirring, recording a maximum value of Cu adsorption around 88% on the tested microspheres.
Key Words: Biosorption, heavy metals, wastewater, biopolymers.

Introduction. One of the most difficult problems faced by the planet nowadays is the faster and faster deterioration and degradation of the water quality. The industrial activities generate a large amount of wastewaters, residues and sludge, which can be classified as hazardous waste that call for difficult treatments (Das et al 2008). As even small amounts of heavy metals are very toxic, the interest in removing the heavy metals from wastewaters has greatly increased, also thanks to the strict legislation. Rigorous regulations have been established for wastewaters, in order to reduce the exposure of the environment to hazardous chemical substances to the minimum.

The heavy metals present in the wastewaters and in the industrial effluents represent a major challenge for environmental protection (Nagajyoti et al 2010). The most numerous polluting elements are highly soluble in water, toxic and carcinogenic (Esmaeili & Beni 2018). The following elements are deemed to be heavy metals: copper, silver, zinc, cadmium, mercury, lead, chrome, iron, nickel, tin, arsenic, selenium, molybdenum, cobalt, manganese and aluminum. These ones pose serious threats to man, as well as to the fauna and the flora of the water organisms (Babel & Kurniawan 2004). They can be absorbed and accumulated in the human body and can cause such serious effects to health as cancer, organ lesions, modifications at the level of the nervous system and, in extreme cases, death.

Biosorption is considered to be a method of purification and separation easy to use, efficient in removing the heavy metals from the industrial wastewaters, the advantages being its specific affinity, the low costs and the simple design (Gupta & Bhattacharyya 2006). Pollutant removal by means of absorbents derived from agricultural and industrial sub-products is used on a large scale, in order to eliminate the heavy metals from an aqueous solution, thanks to their abundant availability, low cost and favorable physical-chemical features.

Biosorption can be defined as the ability of certain biomaterials to accumulate heavy metals from aqueous solutions by a metabolically-controlled mechanism, by physical-chemical processes - adsorption and precipitation reactions (Opeolu et al 2010). The advantages of the biosorption methods as compared to the conventional ones are: the low cost, the far greater efficiency, the possibility of retrieving the biosorbant and the heavy metals and so forth (Kariuki et al 2017). Biopolymers are substances with a different number of functional groups, such as hydroxyls and amines, which enhance the efficiency of the metal ion adsorption. They are used on a large scale in industry, because they are able to reduce the concentrations of metal ions (García et al 2016).

The materials based on polysaccharides are used as adsorbing biopolymers (derived from chitin, chitosan and starch) for removing the heavy metals from wastewaters. The sorption mechanisms for the polysaccharides-based materials are complicated and pH-dependant (Crini 2005). Furthermore, the hydrogels, which are reticulated polymers, are used on a large scale for wastewater purification. The maximum capacity of binding increases by a higher pH because of the polymerisation-reticulation reaction.

Alginic acid is a polysaccharide plentifully found in nature and extracted from brown algae and soil bacteria. From the chemical standpoint, it is a linear copolymer, composed of two monomers, (1-4) b-D-manuronic acid (M) and a-L-glucuronic acid (G) - in various ratios and distributions along the chains (Figure 1). In case of the neutral pH, the alginate contains a significant amount of negative loads, due to the acid groups of the protonated carboxyl. These negative loads allow the alginate to induce electrostatic repulsion forces for increasing the volume and for interacting with positively loaded ion groups. The sodium alginate displays a soil-gel transition when the counter sodium ions are substituted by divalent cations, such as calcium, zinc or barium. The spheres obtained from alginic acid salts have proved to be adequate as a matrix support for cellular immobilisation, according to the countless publications.

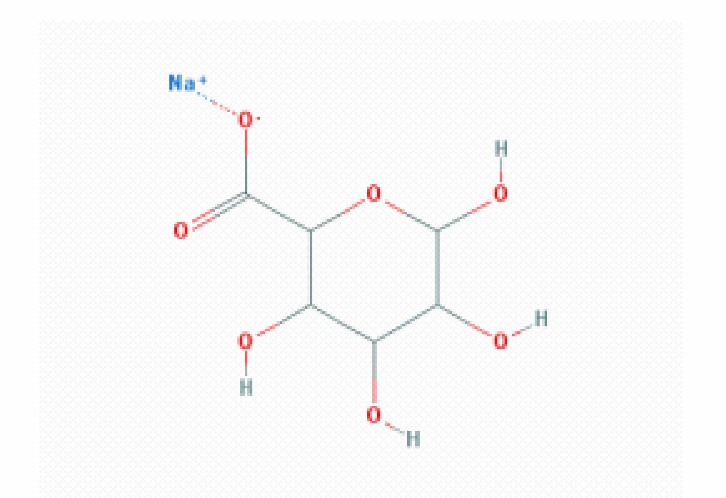

Figure 1. The chemical structure of the sodium alginate.

Hybrid composites based on sodium alginate and clay are known to have been used as adsorbents for removing the anions of the organic acids as stable salt at heat (also produced by the reaction between oxygen and CO_2/H_2S) and the ions of certain heavy metals (chrome and iron) (produced by the metal corrosion) from the methyl diethanolamine industrial solvent (MDEA, weighing 50 %) (Edathil et al 2018).

Material and Method. In order to carry out the tests we chose a column-type adsorption plant (Figure 2), with countersunk gravity parallel flow, operating in a fluidised bed, where the filtered water is recirculated for accelerating the contact and separation processes. The parallel flow characteristic of the system is provided by the direction in which the regenerant passes over the layer of ions identical to that of the water. The solution collection still takes place at the bottom, via a valve located on the evacuation route. In the column, above the filtering layer, there is enough room for the expansion during the affinage operation. The water gets in the upper part, by means of a system of distribution it crosses the separation layer and is collected in the lower part, in a tank, thus allowing it to be recirculated within the process (Figure 3).

Figure 2. Overview of the experiment bench.

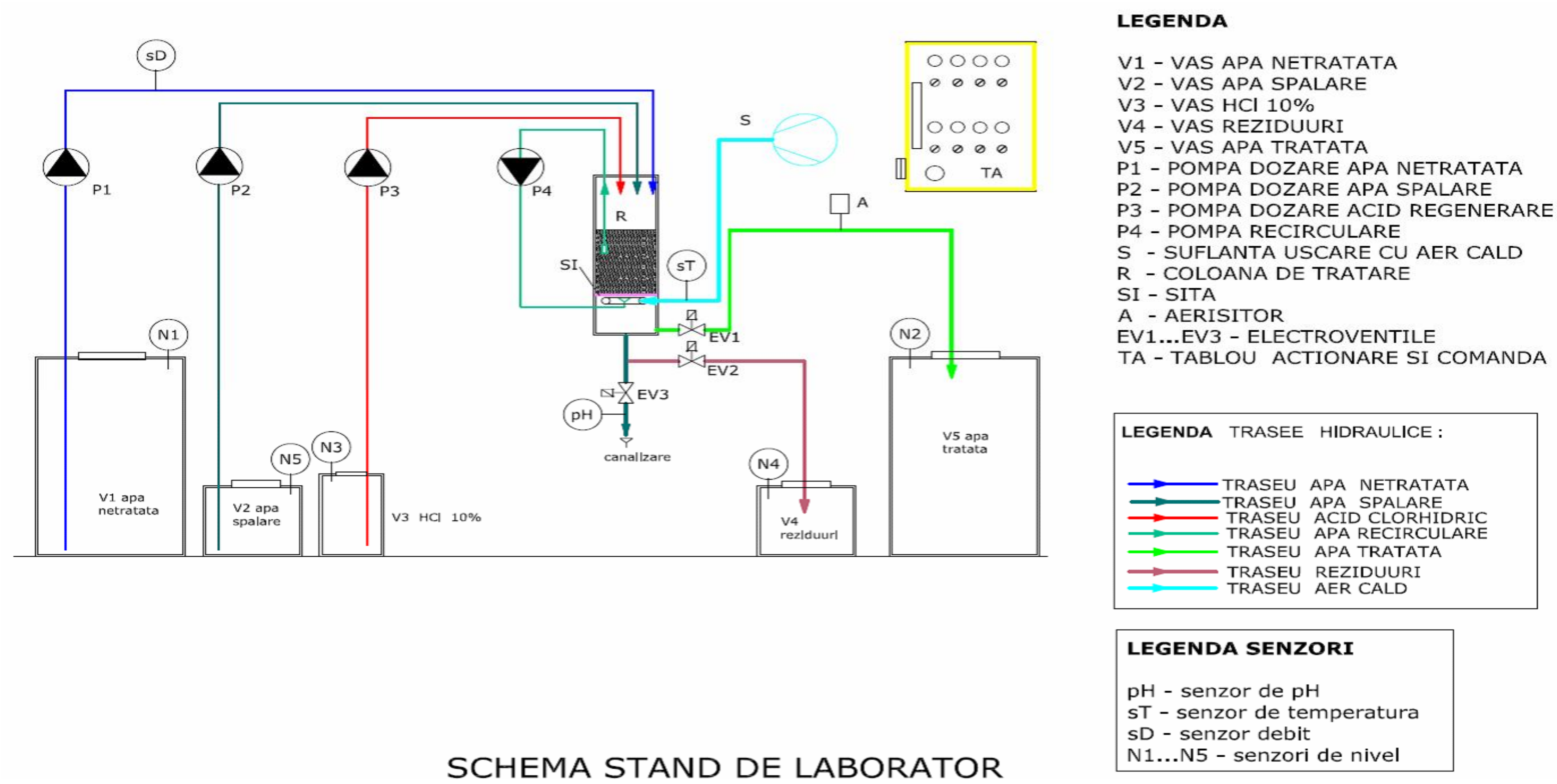

Figure 3. Technological drawing of the experiment bench.

KEY: V1 - UNTREATED WATER VESSEL; V2 - WASHING WATER VESSEL; V3 - HCl 10 % VESSEL; V4 - RESIDUES VESSEL; V5 - TREATED WATER VESSEL; P1 - UNTREATED WATER DOSING PUMP; P2 - WASHING WATER DOSING PUMP; P3 - REGENERATION ACID DOSING PUMP; P4 - RECIRCULATION PUMP; S - HOT AIR DRYING BLOWER; R - TREATMENT COLUMN; SI - SIEVE; A - VENTING DEVICE; EV1 ... EV3 - ELECTROVALVES; TA - OPERATION AND CONTROL PANEL

Sewerage: V5 - treated water; V1 - untreated water; V2 - treated water; V4 - residues.

KEY: HYDRAULIC ROUTES: UNTREATED WATER ROUTE; WASHING WATER ROUTE; CHLORINE HYDRIDE ROUTE; RECIRCULATION WATER ROUTE; TREATED WATER ROUTE; RESIDUES ROUTE; HOT AIR ROUTE.

SENSORS KEY: pH - pH sensor; sT - temperature sensor; sD - flow rate sensor.

LABORATORY BENCH DRAWING: N1...N5 - level sensors.

The technological process comprises two stages:

- the adsorption stage;
- the adsorbing material regeneration stage.

The water that is to be processed on the column for purging purposes comes from the V1 contaminated water tank. This water is supplied on the route that links the tank to the treating column complete with the P1 pump. The EV1 electrovalve is some place on the route for the evacuation of the water from the treating column to the treated water tank. This valve will be opened in the contaminated water treating stage. The electrovalves EV3 from the washing water tank and EV2 lying on the pipe that connects the tank where the residue solution concentrated in metal ions will be stored will be closed. During the treatment activity, the P4 pump will also be active and will recirculate a water flow in reverse current, from the chamber of the treatment column into the chamber underneath, in order to fluidize the active mass and to provide a better contact of the water with the active material.

The treated water flows through a level plate, which adjusts the height of the water from the treating column, after which it gets accumulated in vessel V5. Test specimens are periodically taken, in order to determine the adsorption capacity of the bioadsorbing spheres. When the adsorbing material no longer treats the water at the sought-for efficiency, it will be regenerated by means of a weakly acid solution. The P1 and P4 pumps stop, the EV1 electrovalve closes and the EV3 electrovalve opens, after which the P3 pump, which fuels the treating column, gets started. The acid solution regenerates the treatment material and runs down in the V4 retrieval vessel. After this stage, the EV2 electrovalve closes, the EV3 electrovalve opens and the P2 pump, which fuels the treatment column with washing water, gets started, the said water being to subsequently run down towards the sewerage. The regenerated and washed up active material will then be dried off by means of the hot air coming from air blower S. All throughout this time, all the electrovalves will be closed and the hot air will pass through the filtering material bed and will get discharged in the upper part, through the lid of the treatment column. A new treating cycle may begin, by the supply of the treatment column with water.

Results and Discussion. The tests aimed at retrieving the copper from the water by using spheres made of sodium-starch-glass alginate.

The first set of experiments consisted in pumping 100 mL of synthetic solution of 1mg/L Cu towards pump P_1 from vessel V_2 into the reaction column R, where 0.5 g of the afore-mentioned spheres had been put. After each transfer of the solution (the 100 mL) was completed, the timer was started and samples for measuring the Cu concentration were taken. Each experiment was monitored for 2 hours (120 minutes). The experimental data are set out in Table 1.

Table 1

The efficiency of retaining the Cu(II) pollutant on the sodium alginate microspheres - without agitation

Contact time (min.)	*Sodium-starch-glass microspheres alginate*	
	Reduction efficiency [%]	*qe(t), [mg/g]*
15	2.8	0.006
30	4.9	0.010
45	6.3	0.013
60	14.6	0.031
90	17.9	0.038
120	25.3	0.054

Experimental conditions: 0.5 g of adsorbent; 100 mL of pollutant solution, concentration of 1 mg/L; observation time 120 min.

The second set of experiments took place in the same manner as the first one, meaning that a Cu solution with the 1 mg/L concentration was put in vessel V2 and 0.5 g of alginate-starch-glass microspheres were put in the reaction column. In this case, 200 mL of Cu solution were pumped in each set of experiments, after which the recirculation pump P4 was set going. The recirculation pump can provide a maximum water flow rate of 54 L/h. The automation system set up a recirculation flow rate of 12 L/h, so that the 200 mL amount is recirculated in one minute. The experiments were monitored for 120 minutes. After each experiment, the reaction column was washed up with distilled water and the type of microspheres was changed (0.5 g). The experimental data are set out in Table 2.

Table 2

The efficiency of retaining the Cu(II) pollutant on the sodium and starch alginate microspheres - with agitation

Contact time (min.)	*Sodium-starch-glass microspheres alginate*	
	Retaining efficiency Cu [%]	*qe(t), [mg/g]*
15	32	0.128
30	48	0.192
45	58	0.232
60	88	0.352
90	88	0.352
120	90	0.36

Experimental conditions : 0.5 g of adsorbent; 200 mL of pollutant solution, concentration of 1 mg/L.

Conclusions. The testing operations on the adsorbing microspheres for the Cu retention shows the fact that the adsorption balance is reached after 60 minutes of contact, under agitation, and that the maximum adsorption is around 88 % after 60 minutes. Consequently, we may say that the microspheres of the Na/starch/glass type represent the best variant of adsorbent for Cu(II) retention, for 60 minutes.

Acknowledgements. The work has been funded by the European Union through POC Program, Project ID: P_40_253, Contract 130/23.09.2016, SMIS 105558, Subsidiary Contract 5048/23.03.2018, and Subsidiary Contract 25501/18.12.2018 and POC Program, Grant no. 49/05.09.2016, Project ID P_37_649.

References

Babel S., Kurniawan T. A., 2004 Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere 54(7):951-967.

Crini G., 2005 Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Progress in Polymer Science 30(1):38-70.

Das N., Vimala R., Karthika P., 2008 Biosorption of heavy metals – an overview. Indian Journal of Biotechnology 7(2):159-169.

Edathil A. A., Pal P., Banat F., 2018 Alginate clay hybrid composite adsorbents for the reclamation of industrial lean methyldiethanolamine solutions. Applied Clay Science 156:213-223.

Esmaeili A., Beni A. A., 2018 Optimization and design of a continuous biosorption process using brown algae and chitosan/PVA nano-fiber membrane for removal of nickel by a new biosorbent. International Journal of Environmental Science and Technology 15(4):765-778.

García R., Campos J., Cruz J. A., Calderón M. E., Raynal M. E., Buitrón G., 2016 Biosorption of Cd, Cr, Mn, and Pb from aqueous solutions by *Bacillus* sp. strains isolated from industrial waste activate sludge. TIP 19(1):5-14.

Gupta S. S., Bhattacharyya K. G., 2006 Adsorption of Ni (II) on clays. Journal of Colloid and Interface Science 295(1):21-32.

Kariuki Z., Kiptoo J., Onyancha D., 2017 Biosorption studies of lead and copper using rogers mushroom biomass *Lepiota hystrix*. South African Journal of Chemical Engineering 23:62-70.
Nagajyoti P. C., Lee K. D., Sreekanth T., 2010 Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters 8(3):199-216.
Opeolu B. O., Bamgbose O., Arowolo T., Adetunji M., 2010 Utilization of biomaterials as adsorbents for heavy metals removal from aqueous matrices. Scientific Research and Essays 5(14):1780-1787.

Received: 23 September 2019. Accepted: 26 November 2019. Published online: 30 December 2019.
Authors:
Mihaela Hetvary, SC ICPE BISTRITA SA, Str. Parcului nr.7, 420035, Bistrita, Romania
Ecaterina Matei, University POLITEHNICA of Bucharest, Splaiul Independentei 313, 060042, Bucharest, Romania, e-mail: ecaterinamatei@yahoo.com
Dumitru Vâju, SC ICPE BISTRITA SA, Str. Parcului nr.7, 420035, Bistrita, Romania
Daniela Ignat, SC ICPE BISTRITA SA, Str. Parcului nr.7, 420035, Bistrita, Romania
Csaba Bartha, SC ICPE BISTRITA SA, Str. Parcului nr.7, 420035, Bistrita, Romania
Măriuța Popanton, SC ICPE BISTRITA SA, Str. Parcului nr.7, 420035, Bistrita, Romania
Maria Râpă, University POLITEHNICA of Bucharest, Splaiul Independentei 313, 060042, Bucharest, Romania
Claudia Ionela Tarcea, University POLITEHNICA of Bucharest, Splaiul Independentei 313, 060042, Bucharest, Romania
Cristian Predescu University POLITEHNICA of Bucharest, Splaiul Independentei 313, 060042, Bucharest, Romania

How to cite this article:
Hetvary M., Matei E., Vâju D., Ignat D., Bartha C., Popanton M., Râpă M., Tarcea C. I., Predescu C., 2019 Alginate-based biopolymers for wastewater purification. Ecoterra 16(4):1-7.