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Research Article

PSI-CHITOSAN COPOLYMER CROSSLINKED WITH EDTA FOR HEAVY METALS ADSORPTION

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ABSTRACT

Environmental protection became an important element of modern European societies. Old chemical industry technologies are being replaced by modern ones. Waste become a rich source of precious metals, plastics, natural biopolymers and biomass. To decrease the extraction of valuable minerals, metals and oil, a new technologies allowing to convert waste into useful products are extensively studied. Chitin is one of the most abundant carbohydrate that may be converted during basic hydrolysis into chitosan, which is a long chain polymer consisting of N-acetylglucosamine units found in exoskeletons of arthropods and in cell walls of fungi. Free amine and hydroxyl groups are reactive under microwave radiation that makes chitosan a good raw material susceptible to chemical modification. Chitosan may be used as a natural sorbent. Heavy metals ions occurring in drinking water are a big threat to the health of humans and animals. In this paper a chitosan based hydrogels synthesis under microwave radiation as a heavy metal sorbent, is presented. Chitosan was modified by EDTA, aspartic acid and 1,2-propanodiol. The obtained hydrogels, after drying and rehydration, were examined as a heavy metal ions sorbents. Sorption of Hg^{2+}, Cr^{3+} and Al^{3+} ions was examined during six days.

INTRODUCTION

In recent years an interesting attention in European Union to air and water pollution caused by human activity and industrial development, was observed. Heavy metals entrapped for millions of years in rocks and minerals became released to produce building materials, anticorossive layers, batteries and accumulators, decorative and utility products, electronic devices and catalyst for chemical synthesis. Unfortunately, most of the metallic elements even, some of the noble metals like copper, can corrode in atmospheric conditions. Extracted by acid rain from garbage dump or metal surfaces free ions are accumulated in surface waters and soil. Electroplating processes, mining, tanneries, textile industry, cars and electronic waste are one of the most dangerous sources of heavy metals pollution.

Another important problem is reduction of the value of raw materials. For example, excess activated sludge ashes are an excellent source of phosphorous for mineral phosphorous fertilizers production. Even 45 % of the dry mass of the ash may be P_2O_5, however due to high heavy metal contamination these ashes may become unsuitable as a high concentrated phosphorous source Akpor et al (2014). Living organisms adapted to strictly defined concentrations of metal ions occurring in water and soil. Even strongly toxic heavy metals ions like cobalt, copper, zinc or nickel are necessary to proper operation of enzymes and metalloproteins. Cobalt ions are present in vitamin B_{12} – cobalamin. Carbonic anhydrase can operate only in the presence of zinc ions. Blue copper proteins catalyses the transfer of electrons in reactions. Molluscs have blue blood thanks to hemocyanin – a copper metalloprotein. Nickel ions are present in an enzyme – urease Lippard et al (1994). On the other hand, a long exposure to lead ions may cause damage of the nervous system. Mercury ions cause spontaneous abortion, gastrointestinal disorders and its organic

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forms – neurobiological disorders. Chromium (VI) ions are known of its high oxidising properties. These ions are especially dangerous because of damage of enzymes, proteins and DNA. To decrease the concentration of heavy metal ions in water, adsorption techniques based on bioadsorbers may be adopted. Organic waste after modification can be used to produce a lot of types of heavy metals adsorbents. The increasing importance of waste from the food industry, can be observed. For example, shells from nuts, vegetable peels or shells of crustaceans may be used as biosorbents. Thanks to these waste materials a lot of proecological technologies were implemented. A good adsorption properties of activated carbon are known from years, but due to high cost of production, new technologies and materials are investigated. Materials based on hemicellulose pentetic acid and chitosan were able to adsorb 2.90, 0.95 and 1.37 [mg/g] of Pb^{2+}, Cu^{2+} and Ni^{2+} ions, respectively Ayoub et al (2013). Also biomaterials like: coffee, green tea, yuzu, aloe and Japanese coarse tea, were used. The adsorption capacity was comparable to activated carbon and zeolite Minamisawa et al (2004). Hami melon peels had a sorption capacity 7,9 [mg/g] of Pb^{2+} and 9,5 [mg/g] of Ni^{2+} ions.

Chitosan based adsorbents may become more important because of high reactivity of the hydroxyl and amine groups included in the carbohydrate ring, that allows various modifications. Thanks to chemical treatment chitin mixed with hot concentrated sodium hydroxide solution is deacetylated. N-acetyl bonds break and free amine groups are exposed (Fig. 1). That chemical modification changes all chemical and physical properties of chitin. The product of the reaction is named chitosan (Fig. 2).

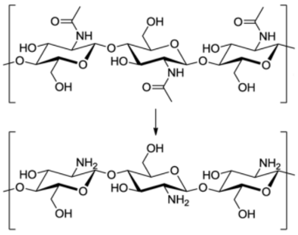

Figure 1. Deacetylation of chitin in strongly basic conditions. N-acetyl bond breaks and primary amines are formed

Figure 2. Commercial sample of chitosan flakes produced by Vanson company (Deacetylation Degree 74%)

The typical deacetylation degree of the chitosan is about 70%. As it was said, amine and hydroxyl groups are able to form new chemical bond and incorporate into the carbohydrate polymer a molecule of new substituent. The chitosan chains can be also crosslinked and hydrogel material can be produced. All these reactions may be carried out in homogenous solution. Free amine groups of chitosan in acid conditions are protonated and below pH = 6.3 chitosan starts to dissolve in water. Increasing pH above pH = 6.3 cause precipitation of the polymer. The modification reactions are fast and efficient under microwave radiation. The microwave energy allows to obtain hydrogel material. Under conventional heating, formation of these materials was not observed Mallampati (2015).

MATERIALS AND METHODS

All synthesis were carried out in PROLABO SYNTHWAVE 402 single-mode microwave reactor. Chitosan sample was from Institute of Chemical Fibres Łódź (Poland). D, L-aspartic acid was produced by XENON Rąbień (Poland). Mercury (II) chloride, chromium (III) sulphate, aluminium chloride, hydrochloric acid, chloroform, acetic acid, ammonia, hydrogen peroxide, sodium hydroxide, dithizone, autintricarboxylic acid ammonium salt, propylene glycol and standard buffer solutions were from POCh (Poland). Monitoring of sorption kinetics was carried out colorimetrically on Carl Zeiss SPEKOL 11 spectrophotometer. The pH of the buffer solutions and polymer mixtures were measured by Elmetron CX-551 universal electrochemical device equipped with Hydromet universal pH electrode, which was calibrated on standard pH solutions (pH 4.00, 7.00 and 9.00).

Synthesis and conditioning of crosslinked chitosan hydrogels

To synthesize chitozan hydrogels 0.500 [g] of chitosan was mixed with 25 [cm^3] of water, than different proportions of EDTA and aspartic acid were added. The solutions were mixed and heated until all chitosan flakes dissolved. After that, crude solution was transferred to reaction vessel and placed inside microwave reactor. The temperature of reaction was set at 140 [^oC]. Firstly water was boiled out to Dean–Stark adapter and then dry air was blown by pipe on the reaction mixture. After about 10 minutes of crosslinking reaction in all syntheses, one big gray mass precipitated from solution. The mass was transferred to beaker with distilled water (details presented in Table 1 and Fig. 3). The main problem was to determine the right time of reaction. After several test, the best results were obtained after observation of consistency of the reaction mixtures. Next the samples were transferred to beakers with water.

Soaking in water is necessary to remove unreacted components of the mixture. Distilled water was replaced and solutions were mixed from time to time. Half mass of the gels removed from dishes with water were dried in 60 [^oC] overnight. The mass after drying was gray–brown and hard (Fig. 4). Dried samples were again placed in water. After one month pH of the crosslinked hydrogel solutions was measured (results are presented in Table 2). The crosslinked chitosan hydrogel without EDTA acid fully biodegraded during that time. The samples with EDTA acid were stable and elastic. Next, swelling degree of hydrogels was determined. Dry polymer samples were weighted and placed in water. After several days increment of the mass was measured. The results are presented in Table 3 and Fig. 5.

Table 1. Reaction mixtures and parameters of synthesis process

Sample	Chitosan [g]	Aspartic acid [g]	EDTA acid [g]	Reaction Time [min]	Reaction Temperature [ºC]
0	0.500	0.840	0.000	10	140
1		0.133	0.730		
2		0.266	0.584		
3		0.399	0.438		
4		0.532	0.292		

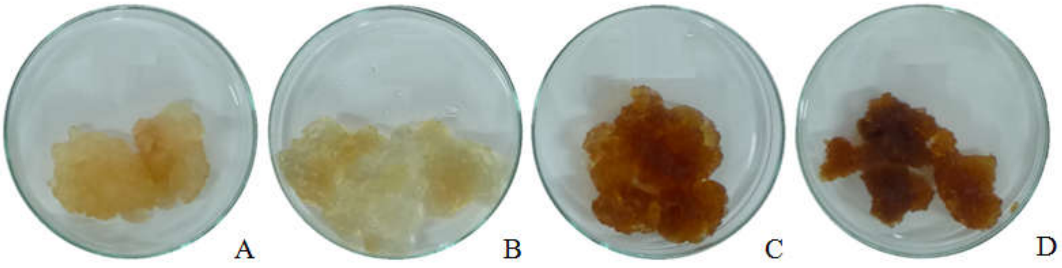

Figure 3. Chitosan/aspartic acid/EDTA/propylene glycol hydrogels (Samples A, B, C, D after reaction) synthesized according to program from Table 1

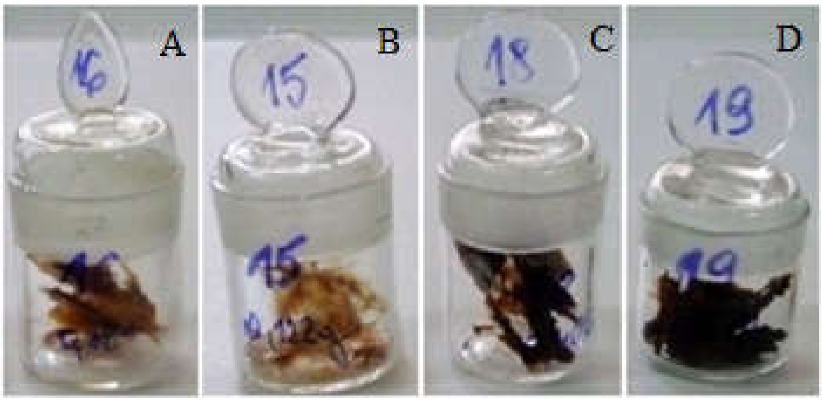

Figure 4. Dried hydrogel samples (Samples A, B, C, D)

Measuring of heavy metals sorption capacity

To measure the sorption capacity of heavy metals by synthesized chitosan hydrogels, three separate standard stock solutions of mercury(II) chloride, aluminium chloride and chromium (III) sulphate, were prepared. The concentration of heavy metal ion was 100 [mg/dm^3]. 1.000 [g] of each hydrogel samples was placed into 100 [cm^3] PP container on the magnetic stirrer. 100.0 [cm^3] of metal ion solution was then added. Plastic containers were closed and hydrogel and salt mixtures were stirred for six days.

For measuring Cr^{3+} ion concentration 100 [µL] of Cr^{3+} ions solution was mixed with 1.00 [cm^3] of 10 % NaOH and 1.00 [cm^3] of 10 % H_2O_2 solution. The reaction was carried out in 10 [cm^3] volumetric flasks. After 2-3 minutes flasks were filled to mark with distilled water. The absorbance of created chromate ions CrO_4^{2-} was measured in 2.0 [cm] length optic glass cuvettes at 388 [nm]. Mercury ions were determined by reaction at pH=5.3 with dithizone-chloroform solution. The test solution – 100.0 [µL] was mixed with 1.00 [cm^3] concentrated acetate buffer solution. Than 5.00 [cm^3] of dithizone-chloroform analytical reagent was added and 10.00 [cm^3] of redistilled water. The mixtures were shaken in closed test tubes for 120 second. The top layer (water) was sucked off by vacuum pump and the absorbance of the solution was measured in 1.0 [cm] length cuvette at 482 [nm]. The colour of solution changed from deep green, violet to light green-yellow.

Table 2. Initial pH value of water mixed with crosslinked chitosan hydrogels

Sample	pH value	Observation
0	7.67	Cloudy solution
1	2.91	Swollen light brown block
2	3.83	Swollen light brown block
3	3.64	Swollen dark brown block
4	3.72	Swollen dark brown block

Aluminium ions were determined by mixing 50.0 [µL] of tested solution with autintricarboxylic acid ammonium salt solution. The colour of complex was pink-red. The reaction was carried out after adding 1.00 [cm^3] of concentrated acetate buffer at pH=5.30. The absorbance of complex was stable after 5 minutes after mixing reagents. The measurements were made in 2.0 [cm] length optic glass cuvette at 530 [nm]. On the first day the concentration of metal ion was measured only in clean standard solutions of heavy metal ions.

Table 3. Increment of the mass of dried chitosan hydrogel samples

Sample	Day 0 mass [g]	Day 7 mass [g]	Increment of mass [%]	Day 30 mass [g]	Increment of mass [%]
0	0.098	2.50	2250	-	-
1	0.181	2.41	1330	3.20	1770
2	0.122	4.41	1620	8.15	6680
3	0.406	5.16	1270	8.20	2020
4	0.374	3.61	970	5.63	1510

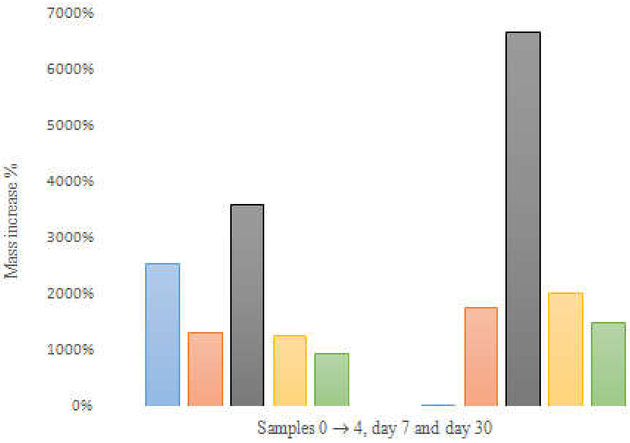

Figure 5. Swelling degree of chitosan crosslinked hydrogels after 7 days (left) and 30 days (right) of conditioning in distilled water

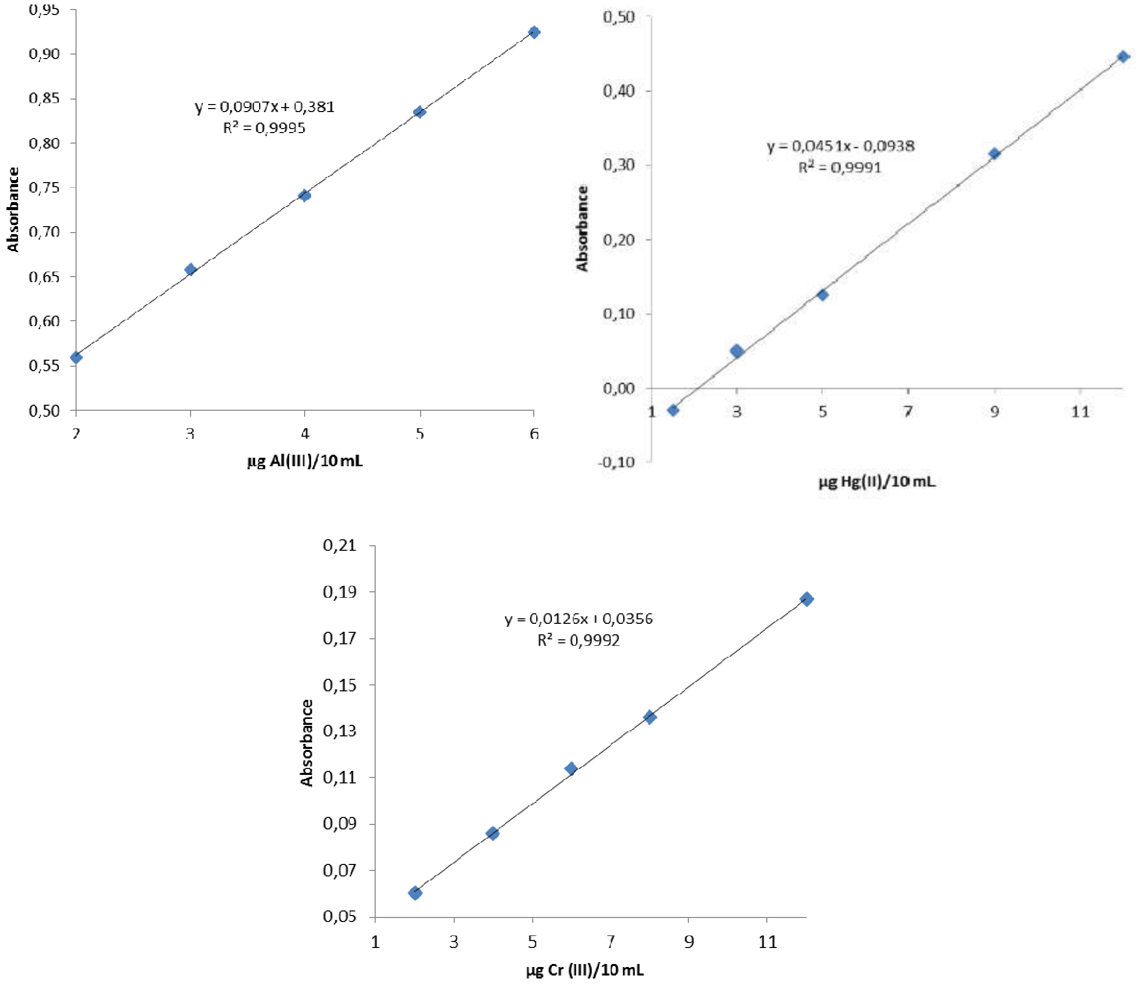

Figure 6. Calibration curves for spectrophotometric quantitative analysis

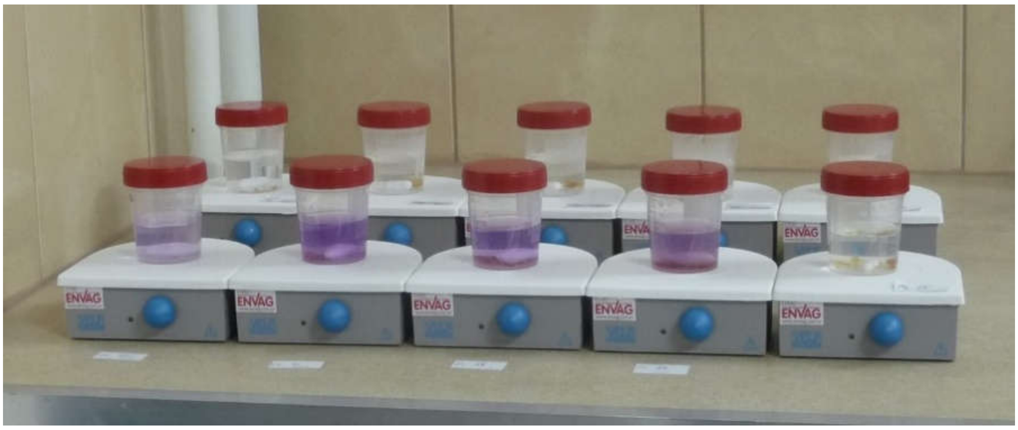

Figure 7. Mixtures of chitosan hydrogels and heavy metal ions solutions

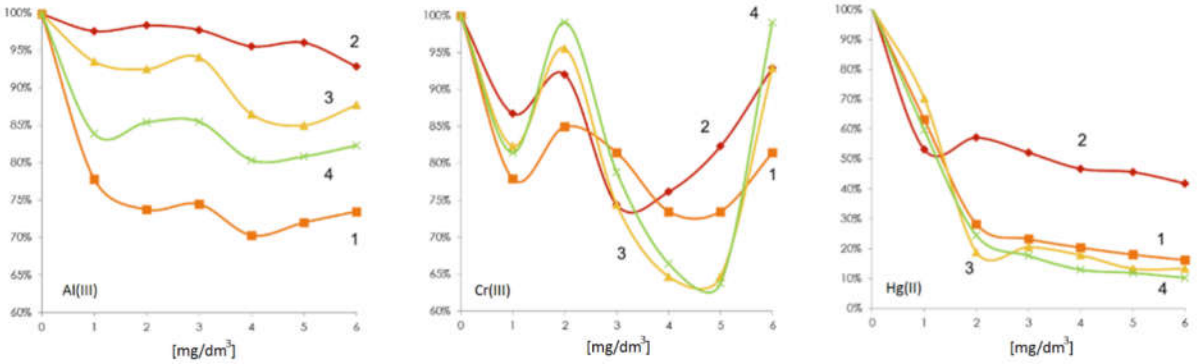

Figure 8. The amount of heavy metal remained in solution during six day period of measurements. 1.000 [g] of different chitosan hydrogel was absorbing heavy metal ion from 100.0 [cm^3] 100.0 [mg/dm^3] solutions

Table. 4. Comparison of sorption capacity and amounts of heavy metal ion adsorbed on hydrogels after 6 days

Sample number	Wet polymer [g]	[mg] of Al ion adsorbed and mass % of metal ion in hydrogel	mass % of Al ion in dry polymer	[mg] of Cr ion adsorbed and mass % of metal ion in hydrogel	mass % of Cr ion in dry polymer	[mg] of Hg ion adsorbed and mass % of metal ion in hydrogel	mass % of Hg ion in dry polymer
1	1,0	1,35 0,14 %	1,8 %	0,95 0,10 %	1,3 %	4,20 0,42 %	5,6 %
2	1,0	0,35 0,04 %	1,3 %	0,35 0,04 %	1,3 %	2,90 0,29 %	1,1 %
3	1,0	0,60 0,06 %	0,8 %	0,35 0,04 %	0,4 %	4,35 0,44 %	5,5 %
4	1,0	0,90 0,09 %	0,9 %	0,05 0,01 %	0,0 %	4,50 0,45 %	4,3 %

In the next days 100.0 [µL] or 50.0 [µL] of each tested solution was retrieved to analysis. Concentration of all reagents was selected experimentally. All calibration curves A, B and C respectively, are presented in the Fig. 6. As it was written, all samples were mixed in closed polypropylene containers on magnetic stirrers (Fig. 7). Condensed water on the walls before measurements was coupled with all mass of the solution.

RESULTS

From the measurements turned out that sorption of heavy metal ions is different and may be reversible (Fig. 8, A – aluminium ions, B – chromium ions, C – mercury ions respectively).

The concentration of aluminium ions was decreasing during four days. The best results have been achieved for hydrogels with the highest amount of EDTA acid (crosslinker). Samples with the lowest concentration had average from all samples heavy metal sorption capacity. The worst results were obtained for sample number 2, which had the highest swelling degree and was very soft. For chromium ions the results were different. Samples with the highest amount of EDTA acid were adsorbing the chromium in the smallest quantities. The samples with higher amount of aspartic acid adsorbed ions comparatively and the best results were achieved after 5 days. After that time strongly reversible process started and almost all of the amount of ions adsorbed was released. Mercury ions were adsorbed irreversibly. Like in the first example hydrogel number 2 behaved differently, but all other hydrogels have similar kinetics and sorption capacity. Also the mercury ions were adsorbed with the highest efficiency. From comparison in Table 4 it can be observed that the sorption capacity per gram of dry chitosan hydrogel for mercury ions is even 5.6%. Much worse results were achieved for aluminium and chromium ions adsorption.

DISCUSSION

The chitosan hydrogel synthesis under microwave radiation was fast and efficient. Products after reaction precipitated from the mixture and gray solid masses were obtained. The reaction carried out under classical heating sources was useless for hydrogel production. After soaking in water the volume of the hydrogels increased even 70 times. Hydrogels were able to adsorb heavy metals from water solution. Sorption for Cr(III) ion was reversible, for Al(III) ion was not very efficient but for mercury ions after two days the concentration in solution containing 100.0 [mg/dm^3] decreased even 70%. After sorbent drying it is possible to accumulate at least 5.6% by mass of Hg(II) ion after six days of water treatment.

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