ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 16, No. 5/6 2009

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INVESTIGATION OF HEAVY METAL SORPTION BY POTATO TUBERS

BADANIE SORPCJI METALI CIĘŻKICH PRZEZ BULWY ZIEMNIACZANE

Abstract: In the paper a potential application of potato tubers for the removal of heavy metals from aqueous solutions was investigated. Sorption of Cu^{2+}, Fe^{3+} and Pb^{2+} was studied for different salts in order to determine the influence of counter anions on the cation uptake by the investigated adsorbents. Potatoes in the form of raw and dried potato cubes and the peels were soaked in 5 % aqueous solution of the following salts: copper(II) acetate, chloride and sulfate, iron(III) chloride and nitrate(V) and lead(II) acetate and nitrate(V). After sample wet mineralization with HNO_3 and $HClO_4$, the total metal content was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The inner structure of the applied sorbents was determined by using the scanning electron microscopy (SEM).

Sorption was found to be dependent on both the cation and the anion present in the solution. Acetate ions significantly enhanced the metal uptake from the solution. In all studied samples the uptake of Pb^{2+} was most effective in comparison with that for the other cations. Among the sorbents, the potato peels have taken higher, than it was obtained for the others, amount of metals, and the raw potato cubes were more effective compared with the dried ones. The metal uptake was positively correlated to the moisture and protein content as well as the amount of Ca^{2+} and K^{+} ions in the initial samples. It was also related to the inner structure of used potato materials. The obtained results should be useful in the recovery of the heavy metals from the environmental samples.

Keywords: biosorption from solutions, heavy metals, potato sorbents

Contamination of surface and groundwaters by harmful substances, in particular the metal ions originated from the industrial effluents, is a commonly known problem. Metallic ores, their by-products and other minerals are widely utilized in different kinds of industries, so there are many industrial sources of such environmental pollution. Moreover, metal ions could penetrate the biological systems from the salt solutions used

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in agriculture, food processing or just in everyday life applications. Heavy metal cations are known to be toxic to plants, animals and human beings. Thus, they must be removed from wastewaters coming from mining, metallurgy, petroleum refining, chemical or tanning industry, etc. Furthermore, for the economic sake, metal ions should be recovered and used again in the industrial processes. Recently, many methods, like: ion exchange, reverse osmosis, membrane filtration, solvent extraction, coagulation and adsorption by various sorbents, are widely applied for metal ion removing in wastewater purification [1]. These methods are rather complicated, time consuming and expensive due to high costs of the operations and materials. It is therefore necessary to find alternative low-cost technology of separation of metallic pollutants from sewage waters. Many examples of usage of the agricultural by-products and biomass for the industrial effluent treatment are available in the literature. A range of materials have been already examined for this purpose. These include cotton bolls [2], *Sphagnum* peat [3], sugar beet pulp [4], lentil, rice and wheat shells [1], maize cobs [5], wood sawdust [6, 7], carbon derived from agricultural wastes [8, 9], just to mention a few. However, the new inexpensive, environmental friendly and locally available adsorbents of contaminations are still needed.

Potato production is one of the most important agriculture sector in Poland. Potato industry by-products, such as potato peels and the low-quality potato crops, are commonly utilized as animal foodstuff or the substrate in industrial processing [10]. However, the waste quantities cause problems with their disposal and utilization. According to literature, some trials were taken in the aim of using the potato waste products for microbial reduction of chlorate(VII) [11], as an antioxidant reagents [12, 13] or in the biofuels production [14, 15]. It was already reported, that potato starch due to anionic character could easily absorb heavy metal cations [16]. Thus, potatoes tubers containing starch should exhibited the same properties. To our knowledge, they have not been used until now for heavy metal removal from aqueous solutions.

Metal sorption by biomaterials, in particular by waste products, is of an empirical nature because of their complicated chemical composition and the structure influencing the process. Various parameters, such as a dosage and the adsorbent properties, contact time, an initial ion concentration, pH and temperature of the solution, could be important for optimization of the sorption process [1–9]. There are only a few reports about the influence of accompanying anions on the heavy metal ion uptake by biosorbents like starch [16] and algae [17].

The presented study was undertaken in order to evaluate the ability of raw potatoes and their by-products, such as potato peels and dried potato cubes, to absorb the metal cations from aqueous solution as well as to determine the counter anion effect on the sorption efficiency.

Material and methods

Commercially available potatoes (*Solanum tuberosum* L., 'Irga' cv.), their peels and dried potato cubes were used in the investigations. The potato tubers were carefully washed with tap water following by deionized water for removing surface impurities, then peeled and cut into cubes (of the side size about 5 mm). The peels were also cut into small pieces (approximately 5 mm × 5 mm × 1 mm). Samples of 50 g of both the raw potato cubes and the peels and 10 g of dried potato cubes were mixed with 100 cm^3 of 5 % aqueous solutions of copper(II) salts: $Cu(CH_3COO)_2$, $CuCl_2$, $CuSO_4$, iron(III) salts: $FeCl_3$, $Fe(NO_3)_3$, and lead(II) salts: $Pb(CH_3COO)_2$, $Pb(NO_3)_2$ (POCh, Poland), and shaken at 37 ^oC for 24 h with an agitation speed 200 rpm. Then, the samples were filtered off, threefold washed with deionized water and next with 99.8 % ethanol (POCh, Poland) and dried in a dryer for 12 h at 105 ^oC. Afterward, samples were powdered in a grinder, mineralized with HNO_3 and $HClO_4$ (2:1, v/v) and analysed. The samples were prepared and analysed in duplicate.

The sample total metal content was determined by using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the JY 238 Ultrace Jobin Yvon Emission apparatus. Background content of the investigated heavy metals and the contents of calcium, phosphorus, potassium, magnesium, and sodium in the initial materials were also determined by the same method.

The total nitrogen contents in the initial samples were determined by the Kjeldahl method by using the Büchi 324 distilling apparatus. The results were converted into the protein contents [18]. Amount of starch in the samples, after their dissolving in calcium chloride solution, was measured by the polarimetric method [19]. The moisture content of the samples was calculated according to the percentage of the sample weight loss after drying at 105 ^oC for 12 h; the measurements were performed in duplicate.

Scanning electron microscopy images at different magnifications of the sample microstructure were taken with the scanning electron microscope SEM Jeol (JSM-5500LV).

Results and discussion

Metal ions were introduced to the solids as aqua complexes typical for aqueous solutions of the salts used for soaking of the potato materials. The cations could be accumulated due to interactions with inner water molecules of the sorbents as well as the oxygen or nitrogen atoms of their constituents, eg polysaccharides or proteins. Thus chemical composition and the moisture content of the material could very much influence the ion uptake.

The chemical characteristics of the sorbents before processing is presented in Table 1. The very low amounts of trace elements found in the samples, similar to those reported for potatoes by the other authors, could be classified as natural for this kind of material [20–22]. The same assumption concerns the starch and protein content of the samples typical for potato originated products [21, 23]. It should be noted, however, that the values obtained for the potato peels were a little bit higher than in the raw and dried potato cube case. Except for dried potato, the samples exhibited high moisture content.

Scanning electron microscopy was used for characterisation of the cells, the inner construction and surface morphology of the investigated adsorbents. The SEM micrographs shown in Fig. 1 revealed the structure differences of the samples.

Table 1

Chemical composition of potato sorbents used in the experiments (mean of two measurements ± standard deviation)

Product	Moisture	Starch	Protein	Ca	P	K	Mg	Na	Cu	Fe	Pb
	[%]	[% d.m.]*		$[mg \cdot g^{-1}$ d.m.]							
Raw potato cubes	76.04 ± 0.32	59.12 ± 0.76	9.31 ± 0.15	0.70 ± 0.01	2.52 ± 0.04	6.04 ± 0.05	1.23 ± 0.03	0.22 ± 0.02	0.02 ± 0.01	0.27 ± 0.04	0.02 ± 0.01
Dried potato cubes	5.90 ± 0.21	60.77 ± 0.03	9.46 ± 0.03	0.65 ± 0.01	2.25 ± 0.10	3.48 ± 0.19	0.99 ± 0.03	0.17 ± 0.01	0.03 ± 0.01	0.29 ± 0.05	0.02 ± 0.01
Potato peels	85.88 ± 0.23	40.32 ± 0.10	14.78 ± 0.01	2.15 ± 0.17	2.96 ± 0.06	17.80 ± 1.18	2.24 ± 0.05	0.29 ± 0.07	0.04 ± 0.01	0.34 ± 0.05	0.02 ± 0.01

* dry matter

Parenchyma tissue with globular starch granules outside of the cells and small intercellular spaces could be observed in the sample of raw potato cubes (Fig. 1a). Drying caused significant changes to the potato tissue. As could be seen in the Fig. 1b, dried potato cubes exhibited irregular, compact structure with destructed cell walls and poorly recognized starch grains as well as lower porosity than it was observed for raw potato [24]. In the potato peel case, the distinctive layers of phelloderm and phellogen containing the phellum (dead cells filled with air) and the others composed of cellulose, pectin, lignin and protein could be noticed (Fig. 1c). Such a variety of active components and extensive surface area of the sorbent could enhance the metal ion trapping into this material as it was actually confirmed in the study.

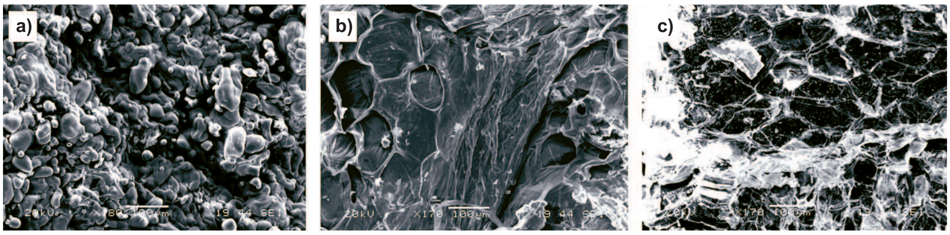

Fig. 1. SEM images of raw potato cube (a), dried cube (b) and potato peel (c)

The obtained results indicated sorption of Cu^{2+}, Fe^{3+} and Pb^{2+} ions by the all investigated potato sorbents (Fig. 2). The process efficiency was found to be dependent on both the cation and the anion present in the solution. In all studied samples the uptake of Pb^{2+} was most effective in comparison with that for Cu^{2+} and Fe^{3+} cations. The same was already noticed for potato starch [25].

Quantitative differences observed in the sorption efficiency could be caused by many factors. The results were strongly related to the moisture and protein content as well as the amount of Ca^{2+} and K^+ ions in the initial samples. It was somewhat surprising, that the starch content was found not to be the main factor influencing the process. The ion uptake was also dependent on the inner microstructure of used potato sorbents. The highest efficiency of the process was found for the potato peels. There might be several reasons for such results. The high moisture content seemed to be as much important as the layered structure and porosity of the peels causing favourable conditions for penetration the tissue by the hydrated metal ions. Moreover, the proteins, present in this material in significant amount, could also participate in binding of metal ions. An additional support might come from reasonable high concentration of the Ca^{2+}, K^+, Mg^{2+} and Na^+ cations which influenced the Cu^{2+}, Fe^{3+} and Pb^{2+} sorption by the cation-exchange mechanism [26].

Counter ions present in the solution noticeably influenced the content of particular cations in the sorbents. In all samples, acetate ions significantly increased the uptake, while sulfate ions were found to be least effective in the process. Similar results were obtained for starch soaked in copper salts [16]. The observed effect could be attributed to the anion hydration ability influencing amount of free water molecules available for

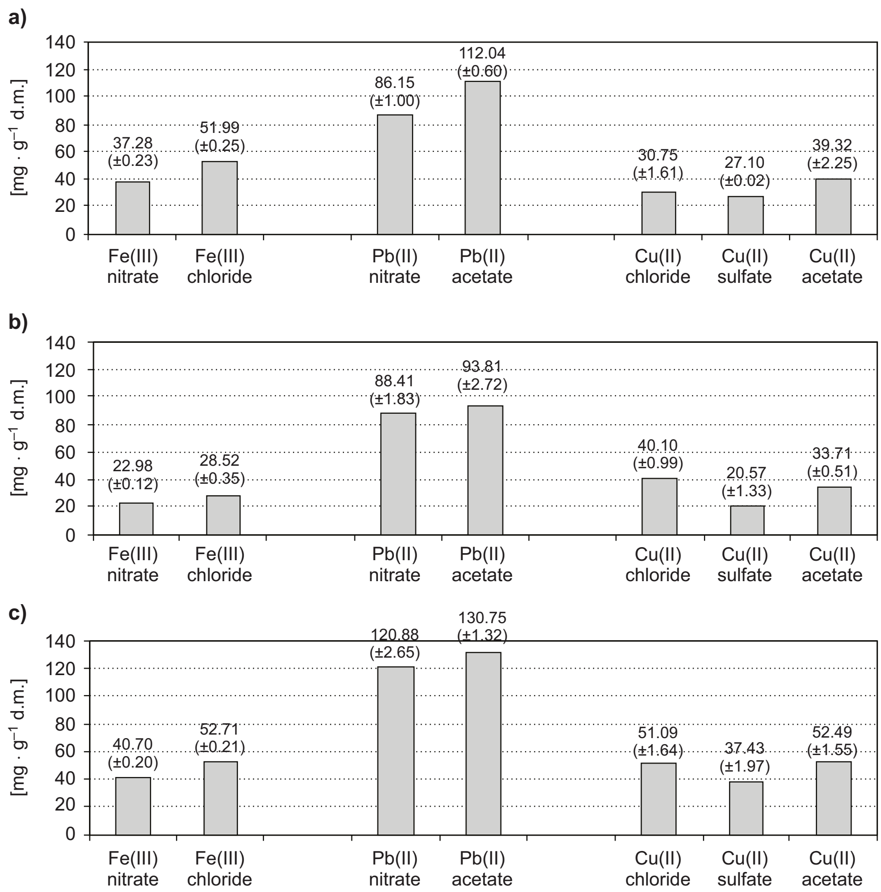

Fig. 2. Heavy metal content in raw potato cubes (a), dried potato cubes (b) and potato peels (c) (mean of two measurements ± standard deviation)

cation migration through the sorbent inner microstructure. Higher hydrated anions, like SO_4^{2-}, caused decreasing of amount of water molecules capable for cation hydration thus lowered amount of cations in the sorbent while the lower hydrated anions (like Cl^- or NO_3^-) acted in the opposite way. However, this regularity was not valid for acetate anions. In this case, probably, the anionic hydrolysis occurring in the solution slightly increased its pH value what could support cation binding to the OH^- and/or NH_2^- active groups of the sorbent components, like polysaccharide or proteins, and enhanced the sorption efficiency.

Conclusions

1. Potato tubers in the form of raw and dried potato cubes and potato peels, could absorb heavy metal ions from salt solutions.

2. Potato peels have taken more metals than other investigated sorbents, and the raw potato cubes were more effective compared to the dried ones.

3. The process was dependent on both the anion and the cation present in the solution. Uptake of Pb^{2+} was most effective in comparison with that for the other cations. Acetate ions significantly enhanced the metal uptake from the solution.

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BADANIE SORPCJI METALI CIĘŻKICH PRZEZ BULWY ZIEMNIACZANE

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Abstrakt: W pracy badano sorpcję metali ciężkich przez bulwy ziemniaczane oraz wpływ różnych anionów na wydajność tego procesu. Badano sorpcję Cu^{2+}, Fe^{3+} i Pb^{2+} z 5 % roztworów wodnych soli, takich jak octan, chlorek i siarczan(VI) miedzi(II), chlorek i azotan(V) żelaza(III) oraz octan i azotan(V) ołowiu(II). W roli sorbentów użyto surowe i suszone ziemniaki w postaci kostki oraz skórki ziemniaczane. Całkowitą zawartość metali w próbkach, po ich mineralizacji przy użyciu HNO_3 i $HClO_4$, oznaczono metodą ICP-AES. Wewnętrzną strukturę zastosowanych sorbentów określono przy użyciu skaningowej mikroskopii elektronowej (SEM).

Stwierdzono, że wydajność sorpcji zależy zarówno od rodzaju kationów, jak i od anionów obecnych w roztworze. Obecność jonów octanowych znacznie zwiększała pobieranie kationów z roztworu. Największą wydajność procesu, bez względu na zastosowany sorbent zaobserwowano dla jonów Pb^{2+}. Wśród sorbentów skórki ziemniaczane okazały się najbardziej efektywnym materiałem wiążącym badane kationy metali ciężkich, a najmniejszą wydajność uzyskano dla suszonej kostki ziemniaczanej. Zauważono pozytywną korelację pomiędzy ilością kationów metali związaną z danym sorbentem a jego wilgotnością, zawartością białka oraz ilością jonów Ca^{2+} i K^{+}. Ponadto, struktura wewnętrzna sorbentów była również czynnikiem wpływającym na efektywność procesu. Uzyskane wyniki wskazują, że bulwy ziemniaczane, a zwłaszcza skórki ziemniaczane mogą być przydatne jako biosorbenty do odzyskiwania metali ciężkich z próbek środowiskowych.

Słowa kluczowe: biosorpcja z roztworów; metale ciężkie; sorbenty ziemniaczane