Heavy metal ion accumulation on fly larva shells

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Fly larva shells, which are formed as a side product in the biological treatment of organic wastes, and chitin and chitosan produced from them are used as sorbents of heavy metal ions. Sorbents are characterised by determination of the content of main elements and pH-potentiometric titration. Free metal ions are absorbed best (up to 0.5–0.8 mmol g^{-1}) onto chitin and chitosan. The ability of chitin to absorb free metal ions decreases in the following order: Fe(III) > Cu(II) ≈ ≈ Pb(II) > Zn(II) .> Ni(II) > Mn(II), and that of chitosan decreases as follows: Cu(II) > Mn(II) > Ni(II) > Zn(II) > Pb(II) > Fe(III). The metal ion complexes are absorbed by fly larva shells up to 0.2–0.4 mmol g^{-1}. The ability to absorb metal ions and ligands depends on pH, concentration of metal ions in solution, and ligand species. Glycine has the retarding effect on the sorption of Ni(II) and Cu(II) ions, meanwhile EDTA enhances Cu(II) ion sorption. The obtained data show a promising potentiality of fly larva shells for the heavy metal removal from solutions containing strong complex agents.

Key words: fly larva shells, chitin, chitosan, heavy metal ions

INTRODUCTION

Most of heavy metals act as microelements for plants and animals. However, at high concentrations they become toxic. Living organisms contain both mechanisms to use heavy metals as nutrients and to protect themselves against the toxic effect of excess of metals. The mobility as well as the bioavailability and toxicity of metals are influenced by their chemical species. Most mobile species are soluble complex metal compounds. The use of metal complexes in industry is the main cause of enormous pollution of the environment by heavy metals.

The traditional techniques used for free metal ion removal are not suitable for complete metal removal from solutions containing metal complexes. The treatment processes of solutions containing metal complexes need additional or alternative methods such as membrane filtration, ion exchange, adsorption, which are expensive in comparison with precipitation methods. Effective technologies or sorbents for treatment of metal-contaminated waste waters are needed. For this purpose, natural materials available in large quantities, or certain waste products from industry or agriculture are suitable [1].

One of such products is fly (*Musca domestica*) larva shells, which are produced in rather large amounts as a waste product in the process of biological treatment of food industry wastes. These shells are composed mostly from chitin, poly[β-(1–4)-2-acetamido-2-deoxy-D-glucopyranosel], also called N-acetyl-D-glucosamine. In resent years various researches have drawn attention to the use of chitin-containing materials for treatment of wastewater contaminated with heavy metals [16, 17]. Chitin with a degree 75% deacetylation or above is called chitosan, poly[β-(1–4)-2-amino-2-deoxy-D-glucopyranosel], or D-glucosamine. Deacetylation degree is defined as the ratio of the number of amino groups in chitosan to the sum of amino- and acetamidogroups [10].

It must be said, that the sorption of free metal ions onto chitin and chitosan is thoroughly studied. However, we could find only one article [8] dealing with removal of Cu(II) complexes from wastewater with the aid of chitosan. The present work has been done to compare the ability of fly larva shells and recovered from them chitin and chitosan to absorb free metal ions as well as metal complexes. For investigations we have selected metal ions and metal ion complexes that are used in metal finishing industry and circuit board manufacture.

EXPERIMENTAL

Fly larva shells used for experiments were obtained from "Chitinas" organic waste treatment company (Vilnius). In order to ensure surface wetting, the raw material was treated with 4% NaOH for 20–24 h at room temperature and rinsed with water.

After such a treatment these shells were used further as a sorbent for heavy metal ions.

Chitin from fly larva shells was produced in the same way as from the crustacean exoskeletons. The key steps in the extraction of chitin from shells are the removal of proteins and minerals, such as calcium carbonate and phosphate, by treatment with alkaline and acidic solutions in turn [3, 7, 11]. In order to remove lipids and proteins, fly larva shells were treated with 4% NaOH for 2 h at 60 °C. Demineralization was carried out by using 5% HCl at 50 °C for 3 h. In both cases the ratio of shell material to the 4% NaOH or 5% HCl was 40 g per 1 l. Chitin after such a treatment is light brown in color. White chitin was obtained by treatment with 20% $(NH_4)_2S_2O_8$ in 5% H_2SO_4 solution for 2 h at 50 °C by constant mixing. After every operation the product was washed with deionized water until the pH of rinse water because neutral. Chitin was dried at 80 °C. Chitosan from chitin was recovered by deacetylation, using 45% NaOH for 4 h at 100 °C. After rinsing chitosan was dried at room temperature. Chitin and chitosan recovered in such a way are in the form of flakes 1–6 mm^2 in size.

The content of ash, carbon, nitrogen and phosphorus in these biopolymers was determined according to standard methods [12]. Incineration was carried out at 600 °C for 3 h, total nitrogen was determined by Kjeldahl method, organic carbon, after oxidation by chromic acid, organic and inorganic phosphorus and sulfur, by oxidation with H_2O_2 and dissolving in HCl.

The metal ion adsorption was investigated at room temperature in batch conditions by pouring metal ion-containing solutions onto sorbents. The load was 10 g of dry sorbent per 1 l of solution. pH was adjusted with NaOH or H_2SO_4 solutions and checked every day. In case of Pb(II) nitric acid was used as the pH adjuster. Though the main amount (about 90%) of metals is sorbed within the first 4–5 h, in most cases solutions were filtered and analyzed after 5 days to achieve complete sorption. Metal ions in solutions were determined by means of complexometric titration with EDTA and using appropriate indicators, Cu(II) was determined using iodide, small metal ion amounts were detected photometrically. Glycine concentration in solutions was determined complexometrically by use of the excess of Ni(II).

RESULTS AND DISCUSSION

The fly larva shells treated with NaOH, and the recovered chitin and chitosan have been used as sorbents for heavy metal removal from solutions. Chitin recovered from fly larva shells makes up 40–45% of the original weight of raw material for comparison, chitin recovered from the prawn *(Nephrops norvegicus)* shells accounts for approximately 16% [3]. The chemical composition of sorbents recovered from fly larva shells is tabulated in Table 1. Organic carbon and nitrogen are the essential elements of chitin. The decrease of nitrogen by treatment with alkali indicates the removal of proteins. Ashes indicate the content of inorganic components in fly larva shells. The shells contain calcium carbonate and phosphate. This is confirmed by the content of phosphorus. Organic phosphorus is present mostly in fatty compounds such as phospholipids. The proteins such as cerotins contain sulfur. The proteins, fatty compounds and inorganic compounds are removed by treatment with alkaline and acidic solutions [18].

pH-metric titration (Fig. 1) shows the high sorption capacity of chitosan for H^+ ions. It is due to the presence of surface -NH_2 groups (pH 6.3). The surface functional groups in chitin (mostly –OH and –NH–CH_3) have a low ability for interaction with H^+. The titration curve of fly larva shells is broad and ill-defined, thus reflecting the diversity of the functional groups. In fly larva shell chitin and chitosa are combined with other substances such as proteins, polysaccharides, lipids, pigments and inorganic materials, which contain additionally carboxylic, phosphatic, sulphide and other groups.

Sorption of free metal ions. Investigations have shown that fly larva shells treated with NaOH or both with NaOH and HCl do not absorb free metal ions such as Cu(II), Pb(II), Zn(II), Ni(II), Fe(III). These metal ions are absorbed only by chitin and chitosan. To avoid precipitation, the sorption experiments were carried out at different pH values for

Table 1. **Content of main elements in sorbents recovered from fly larva shells**

Sorbent	Ash, %	N, %	C, %	P, %		S, %	
				Total	Inorganic	Total	Inorganic
Raw material	9.2	8.2	31.7	0.85	0.75	0.32	0.12
Fly larva shell sorbent	3.1	7.8	36.5	0.5	0.5	0	0
chitin	0.1	6.9	41.3	0	0	0	0
chitosan	0,1	7.8	41.8	0	0	0	0

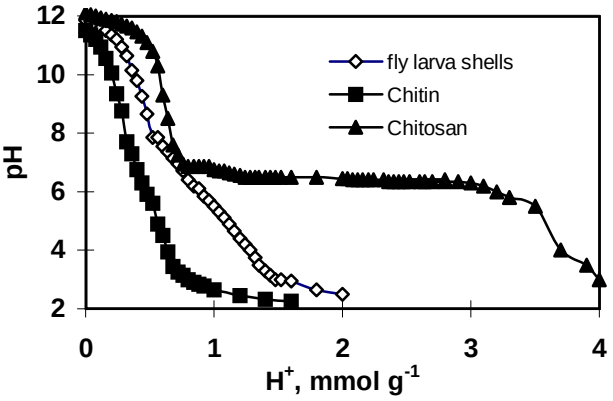

Fig. 1. pH metric titration of sorbents

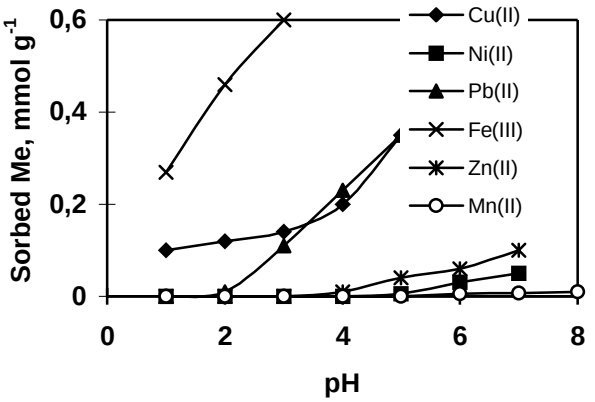

Fig. 2. pH influence on sorption onto chitin in 10 mmol · $\cdot l^{-1}$ metal ion solutions

every metal because of the different solubility products of these metal hydroxides. The sorption of free metal ions onto chitin (Fig. 2) strongly depends on pH. The sorbed quantities of metal ions sharply increase with an increase in pH. These quantities decrease in the following order: Fe(III) > Cu(II) ≈ Pb(II) > Zn(II) > Ni(II) > Mn(II). It is worth noting that this order correlates well with that of hydroxide solubility product. Metal ions which form less soluble hydroxides are absorbed more easily. Moreover, a similar order was obtained by using as metal ions sorbents humic substances [8], goethite (FeOOH) [5], various natural sorbents [13], silica gel-immobilized 8-hydroxyquinoline [2] and synthetic carboxylic ion exchanger [14]. All these sorbents contain hydroxyl or other oxygen-containing groups. This implies that the metal ions are bound with oxygen atoms onto sorbent surface into insoluble compounds similar to metal hydroxides. Metal ions from chitin surface are easily removed by diluted (1:4) HCl or HNO_3. After three such procedures the sorption ability of chitin does not change.

When chitosan is used as a sorbent (Fig. 3), the influence of solution pH on metal ions sorption is

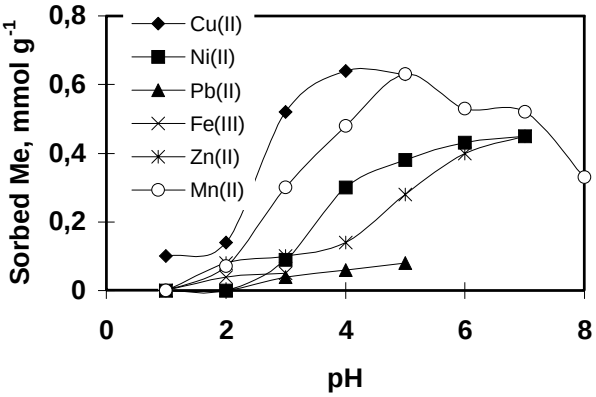

Fig. 3. pH influence on sorption onto chitosan in 10 mmol · $\cdot l^{-1}$ metal ion solutions

rather different. The sorption in most cases reaches the limit values with an increase in pH. The metal ions on chitosan are sorbed in the following order: Cu(II) > Mn(II) > Ni(II) > Zn(II) > Pb(II) > Fe(III). Chitosan is known as a good heavy metal ion sorbent. The chitosan–metal ion complex formation occurs through the amino groups functioning as ligands. The lone pair of electrons present in the nitrogen can establish dative bonds with transition metal ions. It partly explains the high sorption of Cu(II) and the low sorbtion of Fe(III).

The opinion that adsorption ability of chitosan is much higher than that of chitin can hardly be corroborated. Firstly, some of metal ions such as Fe(III) and Pb(II) are sorbed much better onto chitin, secondly, metals from chitosan cannot be removed by acids.

Sorption of metal complexes. Investigations were carried out with Ni(II)–glycine, Cu(II)–glycine and Cu(II)–EDTA complex solutions used for electroless nickel and copper plating and with spent electroless nickel plating.

Data in Fig. 4 show that the ability of fly larva shells to adsorb Ni(II) depends on pH and glycine concentration in the solutions. With increase in glycine concentration the residual concentrations of nickel ions in solutions increase. The most complete removal of nickel takes place in mildly acidic (pH 3–4) and alkaline solutions (pH 11–12). These peculiarities of such an influence of pH on adsorption of Ni(II) can be explained by changes in the composition of Ni(II)–glycine complexes depending on pH. In acidic solutions Ni(II) does not form complexes with glycine. In mildly acidic solution Ni(II) forms $NiGly^+$ complexes. The $NiGly_2$ complexes exist in solution at pH 5–10, and in alkaline solutions Ni(II) forms $NiGly^{3-}$ complexes [15]. The most complete removal of Ni(II) is achieved at lowest concentrations of Ni(II).

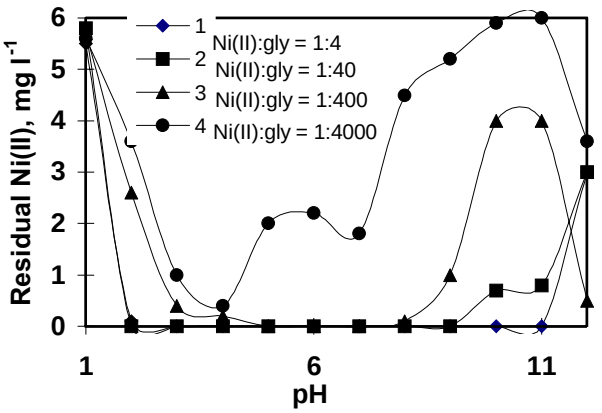

Fig. 4. Dependence of residual Ni(II) concentration in solution on pH and glycine. Ni(II)– 5.9 mg l^{-1} (0.1 mmol · l^{-1})

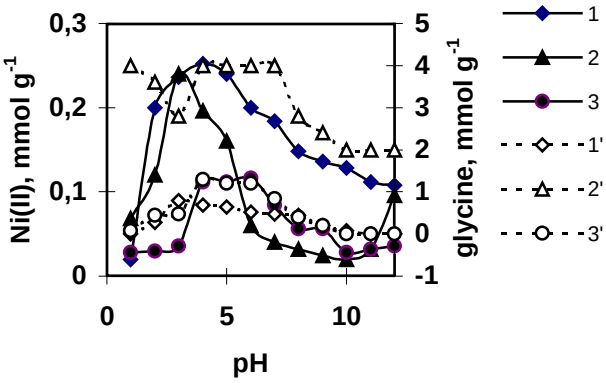

Fig. 6. Dependence of Ni(II) (*1, 2, 3*) and glycine (*1', 2', 3'*) sorption on pH onto fly larva shells. *1, 1'* – Ni(II) 10 and glycine – 4 mmol · l^{-1}; *2, 2,* – Ni(II) 10 and glycine 40 mmol · · l^{-1} *3, 3'* – Ni(II) 10 and glycine 40 mmol · l^{-1}

The sorption of Cu(II) in glycine solutions depends on pH and glycine concentration (Fig. 5). With increase in glycine concentration the sorption decreases, meanwhile the influence of pH in range 3–11 is negligible. Only at pH 11–12 the sorption increases. Cu(II) with glycine form only two complexes $Cu(gly^+)$ and $Cu(gly)_2$. Probably, the sorbent adsorbs the neutral complexes worse than those charged.

The sorption of glycine on fly larva shells takes place together with sorption of nickel ions (Fig. 6). The glycine sorption on fly larva shells is similar to that of nickel ions and depends strongly on pH and the concentration of glycine in the solution. The strongest sorption is in the pH range 3–5 for Ni(II) and pH 4–8 for glycine. The sorption of glycine is much higher than that of Ni(II) ions. The adsorbed quantities of glycine on fly larva shells exceed the quantities of nickel ions 10–20 times. The sorption ability of chitin containing biopolymers for organic compounds is well known [9]. The prevailing sorption of glycine on fly larva shells explains partly the inconsiderable absorption of Ni(II) ions without ligands. The Ni(II) sorption capacity of fly larva shells is rather high and exceeds remarkably the sorption capacity of other biosorbents [4, 6].

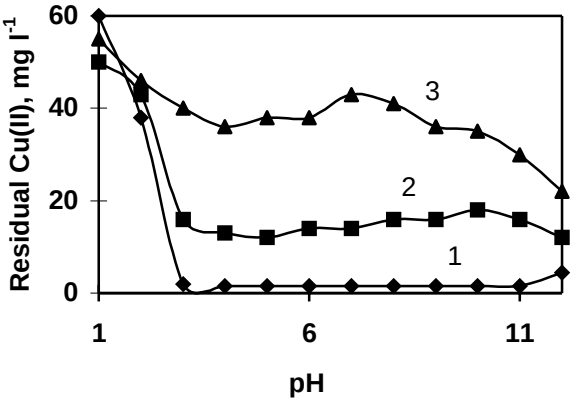

Fig. 5. Dependence of residual Cu(II) concentration in solution on pH and glycine · l^{-1} (Cu(II) –6.4 mg l^{-1} (0.1 mmol · l^{-1}). *1* – Cu(II):glycine = 1:5; *2* – Cu(II):glycine = 1:50; *3* – Cu(II):glycine = 1:500

A comparison of the effect of sorbents recovered from fly larva shells on Ni(II) and Cu(II) is documented in Table 2. Cu(II)–glycine is sorbed by all sorbents recovered from fly larva shells. Chitin binds less Cu(II) in glycinic solutions. Chitosan in this case is a weak sorbent for Cu(II). The pH range 5–8 is most suitable for sorption. However, the sorption of Cu(II) in EDTA solutions on recovered chitin and chitosan is very low. The sorption of free metal ions onto chitin and chitosan is high (0.4–0.6 mmol g^{-1}). The amounts of NaOH used for sorption correspond to the quantities of metal sorbed. The metal complex sorption on sorbents recovered from fly larva shells considerably differs from the sorption of free metal ions. The results show that with an increase in glycine concentration the sorption ability for Ni(II) ions as well as for glycine decreases. Cu(II) and Ni(II) ions in glycine solutions are sorbed best by fly larva shells (up to 0.4 mmol g^{-1}). During the sorption of metal complexes the amounts of NaOH used for adjusting pH are small, implying different sorption mechanisms for free metal ions and for metal ion complexes. Free metal ions have valence electrons, which can directly interact with the nitrogen or oxygen lone pair of electrons of the functional groups. Unexpected are the results of free metal sorption onto fly larva shells. These shells do not absorb free metal ions, though they are composed mostly from chitin and contain partly the same functional groups. Obviously the sorption mechanism onto fly larva shells is more complicated. The sorption of ligands exceeding the sorption of metals 10–20 times and the inconsiderable change in solution pH after sorption suggest that the surface functional groups act with the ligand of metal complexes,

Table 2. **Quantities of metals collected by sorbents at pH 4 and the used amount of NaOH, mmol g^{-1}**

Metal ion	Fly larva shells		Chitin		Chitosan	
	Metal	NaOH	Metal	NaOH	Metal	NaOH
Cu(II)	0	0	0.34	0.7	0.64	1,3
Ni(II) (pH 6)	0	0	0.09	0.2	0.42	0.8
Cu(II):glycine = 1:5	0.2	0.05	0.06	0.1	0.09	0.02
Cu(II):glycine = 1:50	0.11	0.06	0.03	0.01	0.06	0.04
Cu(II):glycine = 1:500	0.007	0	0	0	0	0
Cu(II):EDTA = 1:50	0.12	0.02	0	0	0.02	0
Cu(II):EDTA = 1:500	0.28	0.05	0.002	0	0.04	0
Ni(II):glycine = 1:4	0.4	0.05	0.01	0	0	0
Ni(II):glycine = 1:40	0.2	0.01	0.	0	0	0

thus forming multiple surface complexes. Such an assumption is corroborated by a different influence of ligands EDTA and glycine, containing different functional groups, on sorption by fly larva shells.

So, our study shows that fly larva shells seem to be a promising sorbent for sorption of heavy metal complexes. They are capable of removing rather high amounts of toxic heavy metals from wastewater containing ligands that are severe contaminants in practice. Free metal ions can be removed with chitin and chitosan produced from fly larva shells.

CONCLUSIONS

Chitin and chitosan recovered from fly larva shells act as sorbents of free metal ions (up to 0.6–0.8 mmol g^{-1}). The sorption ability of chitin decreases in the order Fe(III) > Cu(II) ≈ Pb(II) > Zn(II) .> Ni(II) > Mn(II) and correlates with the solubility of these metal hydroxides. The sorption capacity of chitosan decreases in the order Cu(II) > Mn(II) > Ni(II) > Zn(II) > Pb(II) > Fe(III) and is related to surface complexation by amino groups.

The metal ion complexes are absorbed best by fly larva shells. The sorption capacity and the extent of removal of metal ions from complex solutions depend on the concentration of ligand, pH and the complex species. The sorption ability of this biosorbent is sufficient to use in practice (up to 0.3–0.4 mmol g^{-1}) for decontamination of spent metal complex solutions. The sorption of metal complexes onto fly larva shells is explained by forming multiple surface complexes.

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SUNKIŲJŲ METALŲ SORBAVIMAS MUSIŲ LERVŲ IŠNAROMIS

S a n t r a u k a

Organinių atliekų biologinio apdorojimo procese susidarantis šalutinis produktas – musių lervų išnaros ir iš jų išskirti – chitinas ir chitozanas buvo panaudoti sunkiųjų metalų jonų sorbcijai. Sorbentai apibūdinti nustatant jų elementinę sudėtį ir pH-metrinu titravimu. Laisvieji metalų jonai sorbuojami tik chitinu ir chitozanu (iki 0,5–0,8 mmol g^{-1}). Sorbcinis chitino pajėgumas metalams išsidėsto šia tvarka: Fe(III) > Cu(II) ≈ Pb(II) > > Zn(II) .> Ni(II) > Mn(II), o chitozano – Cu(II) > > Mn(II) > Ni(II) > Zn(II) > Pb(II) > Fe(III). Musių lervų išnaros sorbuoja tik metalų kompleksus iki to 0,2–0,4 mmol g^{-1}. Sorbcinės savybės priklauso nuo metalo bei ligando kilmės ir jų pH. Glicinas trukdo Ni(II) ir Cu(II) jonų sorbcijai ant musių lervų išnarų, o EDTA didina Cu(II) sorbciją. Gauti duomenys rodo, kad musių lervų išnaros yra perspektyvus sorbentas pašalinti sunkiųjų metalų kompleksus iš nuotekų.