APPLICATION OF CHITIN CONTAINING SORBENTS FOR TREATMENT OF WATER SOLUTIONS

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Abstract. The objective of this work was to study the sorption properties of chitin containing sorbents (ShCS) which were prepared from fungus mycelium of *Aspergillus niger* – waste of biotechnological production of citric acid. These sorbents were used for removing heavy metals (Cu(II), Zn(II), Cr(VI), Cd(II), Pb(II)) from water solutions. For comparison chitosan containing sorbents (ChaCS) from *Aspergillus niger*, which are prepared according to the Muzzarelli method, were used. The influence of the degree of deacetylation (DD) and size of particles on the sorption properties of ChCS and ChaCS was shown. Molecular modeling of chelating complex Pb(II) – chitin was realized by the method of molecular mechanics MM+.

Keywords: chitin; chitosan; sorbent; mycelium; fungus, biomass; *Aspergillus niger*; citric acid; heavy metals, waste

1. Introduction

Last years the concern of scientists and contributors to chitin, chitosan and chitin containing compounds has increased. It is connected to their widespread occurrence in nature, particular properties, and also feasibility in many areas of a national economy. They are widely used as sorbents for sorption of the ions of heavy metals, soluble dyes and petroleum from water

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solutions.[1,2] The raw sources for obtaining chitin containing products are the shell of crabs, lobsters, shrimps, and also green water-plants, funguses.

The researchers of department of chemistry of the Cherkassy State Technological University developed an ecologically safe method of obtaining chitin containing sorbents (ChCS) from fungus mycelium of *Aspergillus niger* which differs by "soft" conditions of processing initial biomass. The aim of this work was the analysis of the physical and chemical characteristics of ChCS and also of their sorbate properties in relation to ions of heavy metals. In earlier works, based on an elemental analysis, it was established that ChCS comprises 31% chitin, 65% glucan, 2.5% melanin and 1.5% proteins.[3,4]

2. Experiment

Insoluble chitin containing sorbents were obtained from waste received during biotechnological production of citric acid. The waste is biomass of *Aspergillus niger*. The biomass was consecutively treated by a hot (60 °C) 1% NaOH water solution for 90 minutes, washed by distilled water, 1 M HCl solution and finally by organic solvent. The finished product was dried at 40°C for one hour. The degree of deacetylation (DD) of ChCS is 0,8%. ChCS, grinded by a ball mill to the 100-200 mesh size of particles, was used as a raw material for obtaining chitosan containing sorbents (ChaCS) by a known method.[5] This method includes the treatment of an initial raw material by a 40% NaOH water solution for 4 hours at a temperature of 118 °C. Such conditions of treatment were chosen as the most favorable for obtaining chitosan containing sorbents with good sorption characteristics and with a degree of deacetylation of 96%. The degree of deacetylation was determined based on the sorbent infrared spectra (IR) using the following equation:[6]

$$DD = \left[1 - \left(\frac{A_{1655}}{A_{3450}}\right)\frac{1}{1,33}\right] \cdot 100$$

where A_{1655} and A_{3450} are absorbency values at 1655 and 3450 cm^{-1} for the amide I and hydroxyl bands, respectively.

Modelling of chelating complex Pb(II) – chitin was realized by the method of molecular mechanics MM+[7] using the HyperChem program.

In this work the sorption of ions of heavy metals (Cu(II), Zn(II), Cr(VI), Cd(II), Pb(II)) on ChCS in static conditions was studied; 0.02 g of sorbent (ChCS or ChaCS) were shaken in a 0.125 mM solution (100 ml) of the metals salts for 1 hr at 20 °C and pH = 6,8. After filtration, the analysis was carried out by flame atomic absorption spectrometry. The sorption capacity q (mg/g) was calculated from:

$$q = \frac{(C_{in} - C_{eq}) \cdot V}{m}$$

where C_{in} is the initial metal concentration in solution (mg/L); C_{eq} is the equilibrium concentration (mg/L); V is the sample volume (L); and m is the sorbent weight (g).

For an estimation of the selective sorbate ability of ChCS and ChaCS, the distribution factor K_d was determined from:

$$q = \frac{(C_{in} - C_{eq}) \cdot V}{C_{eq} \cdot m}$$

3. Results and Discussion

It is known that chitin extracts metals ions from water solutions, forming chelating complexes. However, practically no information exists on which functional groups are involved in this process. In our molecular modeling representation, different atoms of oxygen and nitrogen from two chitin chains, as well as H_2O and Pb^{2+} were involved. Optimization was carried out for four possible structures. The most probable is a complex that consists of the lead ion between two chitin chains, where in the Pb^{2+} coordination participate the ring oxygen (O-5′) and the oxygen of the C-3 hydroxyl (Fig.1). This chelating complex is stable with the minimal energy of conformation of 349.4 kJ/mol. These data agree with those obtained in chitin-cadmium complexation in the wall of a *Neurospora crassa* cell, grown under conditions of Cd-toxicity.[8]

For the assessment of sorbents elective to extract the metals ions, the distribution coefficient K_d was calculated (Table 1).

TABLE 1. Distribution coefficient for ChCS and ChaCS

Sorbent	K_d, mL/g				
	Cu (II)	Zn (II)	Cr (VI)	Cd (II)	Pb (II)
ChCS	2000	410	348	610	2000
ChaCS	49500	500	5750	816	9462

The K_d values shown in Table 1 for the sorbents under study are compatible with chelating sites of a poly-amphoteric nature.

For ChCS: Pb (II) = Cu (II) > Cd (II) > Zn (II) > Cr (VI);

For ChaCS: Cu (II) > Pb (II) > Cr (VI)> Cd (II)> Zn (II).

We think that this can be explained by the fact that the composition of the sorbents includes amino, carboxyl and hydroxyl groups, which will form stable chelating complexes with the metals ions.

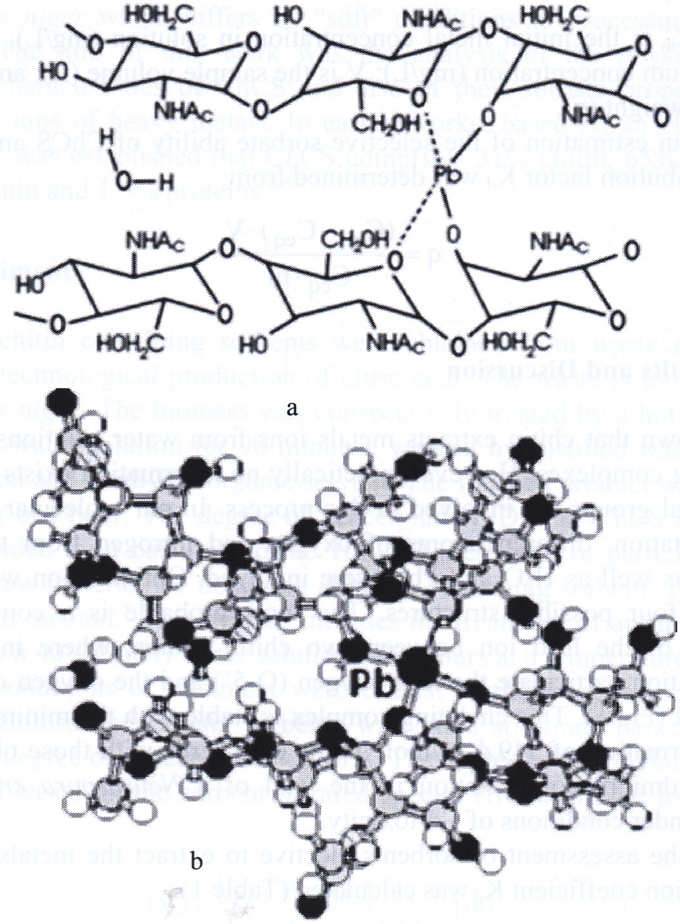

Figure 1. Chelating complexes chitin-lead: a – before optimization; b – after optimization:
● - Pb; ▨ - N; ◉ - C; ○ - H; • - O.

The sorption ability of the chitincontaining sorbents for Cu(II), Zn(II), Cr(VI), Cd(II) and Pb(II) ions, obtained with samples of sorbents with different particle sizes after a 1-h contact, are presented in Table 2.

The particles size influences the sorption ability of the sorbents. The decrease of the particles size is accompanied by an increase of the sorption ability of the sorbents for all metals studied. This fact can be ascribed to an increase of the active surface of the sorbents and by the larger accessibility of the metals to the functional groups.

Increasing the degree of deacetylation (DD) of the sorbents contributes to an increment of their sorption ability, especially for Cr (VI) ions. These results can be explained by the increase of the number of pores within the structure of the sorbents and to a larger access of the metals to the amino groups. The values for the removal of Cr(VI) ions with ChaCS are larger because they complex easily with amino groups than the other metals.

TABLE 2. Dependence of the sorbents sorption ability on the particles size and DD

Sorbent	DD,%	Particle size, μm	q, mg/g				
			Cu(II)	Zn(II)	Cr(VI)	Cd(II)	Pb(II)
ChCS	0,8	710-850	22,4	10,4	3,7	22,4	61,8
		355-500	25,6	13,6	5,1	26,9	80,3
		150-250	32,0	18,2	6,8	38,0	103,6
ChaCS	96	710-850	27,5	11,7	11,3	31,4	88,6
		355-500	30,4	15,6	12,8	35,3	107,1
		150-250	36,8	20,5	15,8	43,1	130,8

4. Conclusions

In this work it is shown that the biomass of the *Aspergillus niger* fungus mycelium, a waste from the biotechnological production of citric acid, may be used for the preparation of chitin-containing sorbents, by a method suggested by the authors; they can also be used for the preparation of chitisan-containing sorbents by previously known methods. These sorbents from *Aspergillus niger* can be an alternative to animal chitin and chitosan for the removal of metal ions from water solutions. It is known that the sorption of metals on chitin and chitosan is accompanied by the formation complexes. Modeling and quantum-chemical computations of these complexes showed that the most probable is a complex which consists of the metal ion between two chitin chains and also that the ring oxygen (O-5′) and the oxygen of C-3 hydroxyl participate in the Me^{2+} coordination. The sorption ability of the sorbents for Cu(II), Zn(II), Cr(VI), Cd(II) and Pb(II) ions is dependent on the degree of deacetylation and on the particles size.

As shown in our earlier works[3,4] ChCS and ChaCS are good petroleum and soluble dyes sorbents from water solutions. Economically and ecologically it is more favourable to use ChCS since, in their production process, the biomass is processed using lower concentration chemical solutions at a temperature of about 60 °C.

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