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BIOSORPTION OF METALS FROM GEOTECHNOLOGY SOLUTIONS

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Different microorganisms studied. As biosorbents emerge different microorganisms: bacteria, micromycetes, fungi, yeasts (baker's, beer and forage), active silts and microalga. As native sorbents studied active carbon and chitines, chitisan. Flotation biomass from the liquid, so named biosorbtive flotation we consider as promising. Scientific and practical urgency of problem consists in revealing an intercoupling between the sorption of non-ferrous metals by the biomass and its floatability, determination of optimum parameters for regulation flotation biomass, loaded by metals. An ability to sorption metals from solutions possess all microorganisms - bonding of metals is realized to the account of different mechanisms (ion exchange, complexing, reducing, formation low soluble compounds). Adsorptive capacity of microorganisms end efficiency of metals recovery determined. For instance, maximum Cu and Ag recoveries were about 100% from100 ml solutions 1 g/l/ on 10 g biomass. Floatability of sorbents greatly depends on sorption metals on their surface: mostly metals activated flotation, most of synthetic sorbents displayed pure floatability in ether cases. Biosorbents floated with greater ability. The concentration of metals (or removal toxic inorganic ions) by microorganisms with following flotation can become industrial process both for a cleaning sewages, and for a recovery of metals. There is much reason for making broad study and further development of that field of research with control of metal contents in solution by Ecotest apparatus with ion-selective electrodes on Cu, Ag, Ni, Co etc.; control of both - solution and solids (sorbents, minerals) with Spectroscan G roentgen-fluorescence spectrometer.

Keywords: biosorbents, flotation, parameters, biosorption, metals

INTRODUCTION

Biosorption methods have got sufficiently broad consideration on recent international conferences [Groudev et al., 2003, Matis et al., Volesky 1994]. Their high efficiency is shown on the example of sorptions of precious metals (Table 1) .

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Table 1. Sorption of precious metals by some microorganisms [Matis et al., 2001]

Metals	Sorbents	Sorption mgg-1
Microalga		
Au	Sargassum natas	420
Au	Micrococus luteus	30 min - 177 2 hours - 253
Au	Chlorella vulgaris	120
Au	Chlorella pyrenoiclosa	140
Pd	Granules of AMT Bioclamtm	462
Pt		102
Fungi		
Au	Aspergillus niger	176
Au	Phizopus arrhizus	100-164
Biopolymers		
Au	Chitosan	150
Ag	Chitosan	100

EXPERIMENTAL WORK

We studied sorption of metals on a number of both synthetic and native sorbents, on biomasses from the classes of fungi, yeasts, actinomycetes, alga. Than the biomasses were flotated by using ordinary laboratory conditions. The flotation characteristics of biomasses were greatly changed after the saturation of biomasses by metals ions. An increase of biomass hydrofobicity allows effectively separate biosorbents from solutions [Nebera, Solozhenkin 2002]. The comparison of synthetic sorbents (AM, AMP, AV 17, ANKB) with others biosorbents has been done. Also, natural sorbents such as: chitin, chitosan, active carbon have been investigated.

Much work is denoted toward native materials: chitines, chitosan, pine barc, sawdust as a sorbent of metals. Pine barc (Pinus pinaster, Aiton) after its chemical or biochemical processing was suitable for cleaning effluents from oil products and other organic materials [Skriabina et al., 2002, Sangalov et al., 1999]. From the number of biosorbents studied fungi, alga, bacteria, yeast were frequently used. Their sufficiently high efficiency, often exceeding the capacity of synthetic ion-exchange resins, has been reflected from our work [Taboada et al., 2003]

The strategy of laboratory studies was concluded in mixing a metal ion solution (50 ml) with sorbents (8-10 g) in the conical flasks (100 ml of volume). The flasks were shook (frequency 100 min-1 amplitude 10 mm). The analysis of contents of metal in solution before and after sorptions - have been done using ion-selective electrodes. The instrument Ecotech Akvilon and Spectroscan G for the roentgen-fluorescent analyze of sorbents were used. The sorption isotherms and distribution factors have received, also a sorption kinetic was determined.

RESULTS

The variable values in flotation experiments were: pH and the consumption of flotation reagents (sodium oleate, dodecylammonium cloride (DA). On the example flotation of sorbents loaded by copper, installed sufficiently high efficiency of biosorbents in the interval pH 5-11 (Fig. 2).

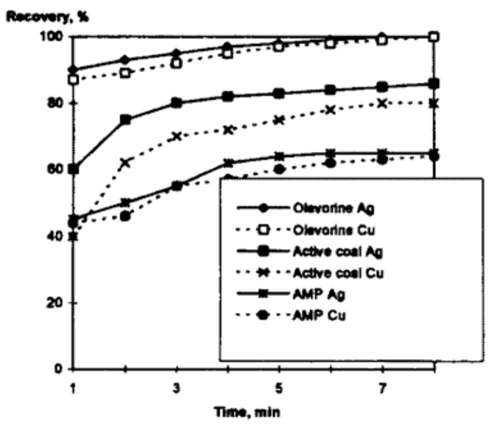

Fig. 1. Comparative sorption of Cu and Ag on different sorbents (AMP – synthetic anionic sorbents)

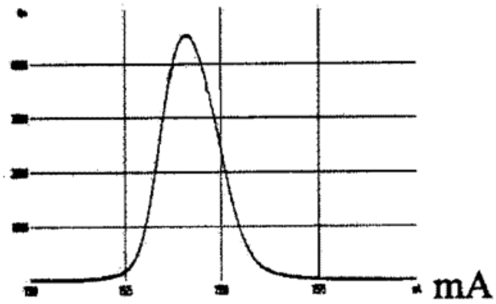

Fig. 2. The results of the analysis of Cu on biosorbent olevorine (20 mg/kg of sorbent, that corresponds to fig. 1 data): "sps" - pulses per sec; mA- a wavelength, milliangstrem

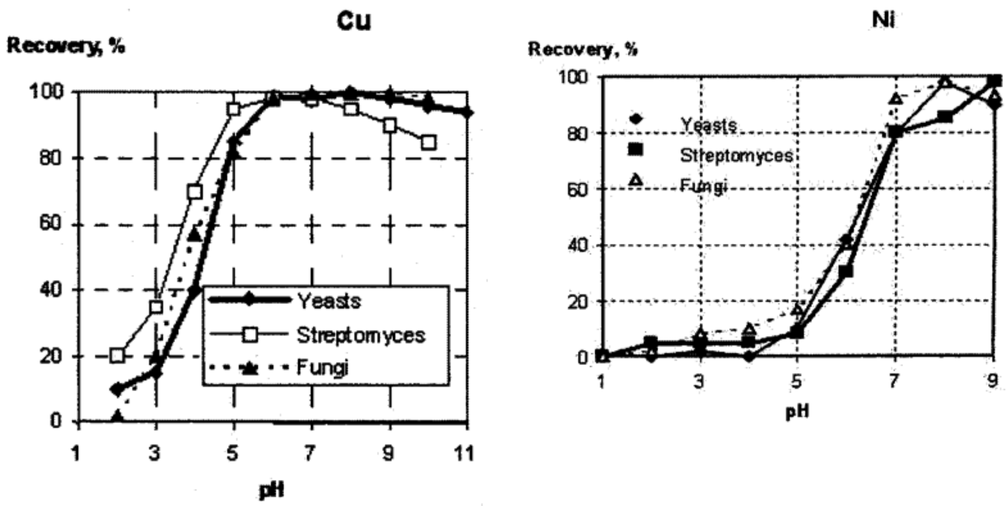

Fig. 3. Biosorbtion Cu, Ni at different pH

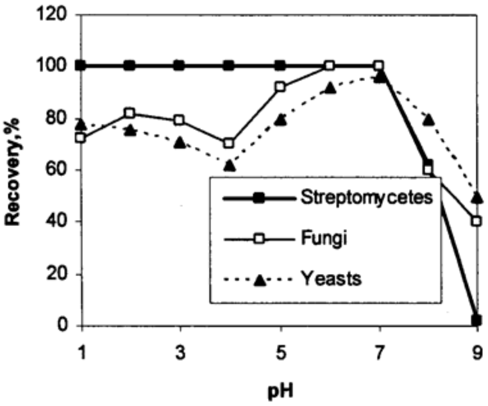

Fig 4. Flotation of biomasses epending on pH with dodecylamines (DA). Concentration of biomass, DA 3x10-4 M

Fig. 1 data show the unique biosorbtive ability of the olevorine (bacterial biomass, received from active silt at Mosvodostok firm, responsible for cleaning Moscow effluents [Tcherenkov 2004]) to silver and copper in comparison to the synthetic resins and active coal. Fig.2 presents the possibility selectively separate copper from nickel with different biosorbents under different pH ambiences. Under pH 5 copper adsorbed well and nickel adsorbed more effectively at higher pH (over pH 7).

The adsorptive capacity of microorganisms of different systematic groups in number of events exceeds 40% from the dry weight of biomass. Maximal Au loading on cells M. luteus reached 45 % from the dry biomass. High level of Au recovery reached, when using a biomass from departures an different alga biomasses. Sea brown algae Sargassum natas sorbed up to 4mg Au/g biomasses in 2 hours. Bacteria Micrococus luteus adsorbs 177 mg Au/g and 253 mgs Au/g biomasses after 30 min. and 2 hours respectively . Granules of AMT Bioclam sorbed 462 mg Pd and 102 mg Pt. Chlorella vulgaris accumulated up to 120 mg Au/g masses, Chlorella pyrenoiclosa - over 140 mg Au/g. Au sorption by Aspergillus niger fungi formed 176 mg Au/g, but fungi of Phizopus arrhizus sorbed 100-164 mg Au/g. Chitosan can take up 150 mg Au/g from $HAuCl_4$ solution under pH 3.3-4.2 at the recovery up to 99.5 % (Table.1).

The sorption kinetics of metal ions by the cells of microorganisms were high. The ion saturations were obtained at 20-60 min of the time period. Metal ions can convert in the colloidal particles of free metal or its non-soluble compounds (this can be explained uncommonly greater adsorptions values).The biomass of A. niger is an adsorption efficient of silver ions from the solutions which the concentration was 2.5 mg/l Ag. The sorption ability was up to 10% silver from the weight of dry biomass. The influence of pH values within 5-7 range do not observed on the silver biosorption. From studied biosorbents olevorin has shown high efficiency. Olevorin is a microbial mass isolated from active silt of water filter tank (Fig. 3). Its adsorptive capacity ability exceeded the factors showed by both active carbon and synthetic sorbent AMP.

The heavy metals removing by ion-exchange resins usually sensitive to the presence of Ca^{2+}, Mg^{2+} and Na^+ ions, but fungus biomass, does not adsorbed them in a good supply. Thereby, the fungi biomass can be more efficient than ion-exchange resins, in the presence of relatively high concentrations of Ca2+, Mg2+ and Na+.

The adsorption of metal ion on both non-specific and specific sorbents depends on pH. pH can be influenced on the metal ions accessibility in solution and on the adsorption centers onto the surface.

The acid conditions do not promote catins adsorption. However, the sorption under low pH is connected with the competition of metal cations and H+-ions on the cell surfaces. A significant increase of adsorption of each metal was observed under pH above 7 and it was reached a maximum under pH 10, approximately. In alkaline condition, the metals were precipitated in the form of non-soluble hydroxides onto the surfaces of cells. Interesting example of efficient cleaning of uranium-containing vine waters by driving them through mud ponds with rich vegetation and microflora were a field of studies by Sofia Mining Geological Institute [Groudev, et al., 2003].

The installation for bacterial heap leaching of copper from sulfide ore, belongs to Union Myanmar, works on Kyay Sin Taung deposit. The bioleaching of copper is following the extraction of Cu from the leached solution of copper by the solvent extraction process. This installation reached good results. The practical application of our results could be in cleaning returned solutions from Fe, Ca, Al and other metals.

For the model studied of sorbents, the biomasses containing of protein 58% and baker's yeast (Saccharomyces cerevisiae), chitin, chitosan (from "Bioprogress") and chitosan from the Union of Myanmar, active coal, turf, as well as granulated biosorbents (Biochemistries Institute RAS) and olevorin- a microbial biomass produced from silt of water cleaning were used. The Cu sorption capacity was 47.9 mgg-1 under pH 4 for 5 min contact and 94.9 mgg-1 after 1 hour contact at pH 4.

Table 2. Cu sorption kinetics

Time, min.	Adsorption capacity, mg/g sorbent				
	ANKB-10	SG-10	Chitosan2	Biomass	Yeasts
0	0	0	0	0	0
5	21	10	42	24	12
10	28	14	65	29	19
20	35	16	70	33	22
30	39	18	73	36	26
45	42	20	75	38.9	28.3
60	44	21	76	41.3	31.5

Chitin sorbents can be useful for the cleaning water solution from all heavy metals, radionuclides, bacteria, organic admixtures, and other compounds. High adsorptive features, low ash and cutting prices of chitin and chitosan allow for the application. The potential possibilities of using these sorbents in hydrometallurgical processes for the separations of valuable metals from technological or natural solutions were considered [Mineral proc.,2003, Wodolazov et al. 2000].

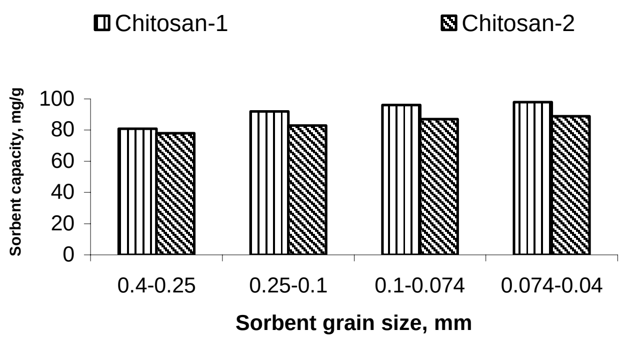

Fig 7. The effect of sorbent grain size on the Cu. sorption capacity

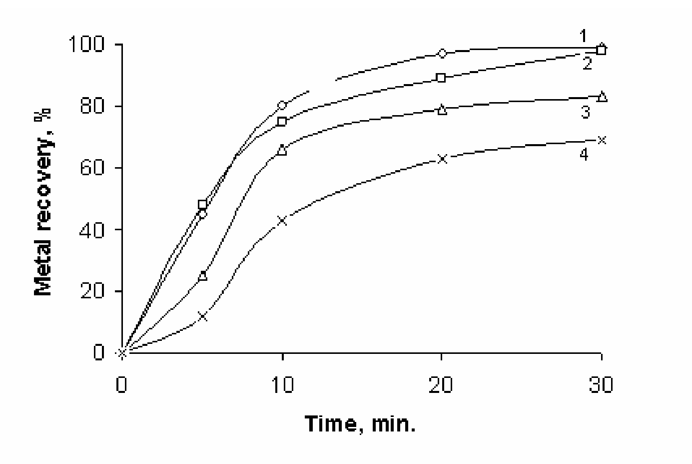

Fig 8. Kinetics of Fe ions adsorption: 1 - AMP; 2 SG - 10; 3-biomass; 4- ANKB-10

The results of calcium adsorption onto sorbents such as KU -2, SG-10, ANKB-10, and turf are presented in Fig. 8. The initial concentration of CaCl2 was 50 g/l. KU-2 possessed a high capacity 282.8 mgml-1 at a time of mixing 5 min, in contrast to other less efficient sorbents. The biosorbent possesses a high capacity, at the concentrations of Cu ions in an initial solution equals 300 mgml-1and the time of adsorption of 90 min, it was 41.25 mgg-1, but for yeasts the capacity was 22 mgg-1 under the same conditions. The velocity of Cu sorption on the biosorbent was high. The working capacity of sorbent achieves 14.02 mgg-1 at the recovery equals 93.46%. The influence of pH on the sorption of Cu was important. Under low pH, the sorption on yeasts was satisfy. For this biosorbent, under pH 5 and 3 and the 60 min contact time, the Cu recoveries were 99.0 and 97.7 %, respectively. The adsorptive capacity 14.85 and 14.6 mgg-1 respectively. For comparison, the adsorption capacity of yeasts was 74.3 mgg-1and the Cu extraction recovery was 74.3% under pH 5. The results of Cu extraction from sewages using both biosorbents, can be used for other plants.

Table 3. Kinetics of Pb sorption

Sorbents (7 ml).	Adsorption capacity mgml-1	Recovery, %.	Time, min.
Active carbon	0.71	4.4	5
Chitosan-2	6.8	42.2	
KU-2	10.14	63.1	
ANKB-10	14.10	87.7	
Turf	15.51	96.5	
Active carbon	3.10	19.33	15
Chitosan-2	8.2	51.0	
KU-2	14.6	91.1	
ANKB-10	16.01	99.6	
Turf	15.8	98.4	
Active carbon	4.14	25.7	30
Chitosan-2	10.9	67.8	
KU-2	14.64	91.1	
	16.07	100.0	
ANKB-10	15.9	99.07	
Turf			
Active carbon	4.9	30,8	60
Chitosan-2	14.1	87.7	
KU-2	14.64	91.1	
ANKB-10	-	-	
Turf	15.9	99.3	
Active carbon	5.6	34.89	90
Chitosan-2	14.8	92.0	
KU-2	-	-	
ANKB-10	-	-	
Turf	16.07	100.0	

The capacity and kinetics of adsorption depend on the size grains of sorbents, an ambiences pH, and the concentrations of metals in the solutions.

The ion adsorption depends on the grain size of sorbents and the time of mixing (Table 3). The most high capacity 118.57 mgml-1 was observed for -0.5 mm grain size of sorbent and the extraction was 83.0 % at the concentration of solution equals 2 g/l and time of adsorption equals 120 min. A high velocity of adsorptions was observed. The extraction of lead has obtained 100% at the time of mixing of solution with the sorbent, equals 5 min. The high adsorptions velocity was observed at the time period from 0 to 30 min, then the adsorption kinetic was slow.

The influence pH ambiences on the sorption and extraction of lead (II) on the brown coal (size fraction of -0.5 mm) from the solution which the concentration of lead (II) was 2 g/l, are presented in Table 4. The high adsorptive capacities equal 118.57 and 120.0 mg/ml at the time of adsorptions equals 120 min and pH 4 and 5 were obtained. The extraction of lead (II) has been 64.9% and the capacity of sorbent was 92.7 mg/ml under pH of 3.

The results of biosorptive extractions of metals from solutions and cleaning solutions using microorganisms show a possibility for the change the synthetic resins by biosorbents as well as in steady-state and dynamic conditions. The sufficient time of adsorption falls within 20-30 min. The capacity and kinetics of adsorption depended on pH, the concentrations of metals in solution and others conditions. A perspective using of chitin sorbents, yeasts and others microorganisms for removing Cu and other heavy metals from mine water and an application of sorbents for the conversion of productive geotechnological solution seem more realistic.

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Szereg mikroorganizmów i naturalnych substancji jest zdolnych do adsorpcji jonów metali z roztworów. Jako naturalne biosorbenty można używać chitynę i chitosan oraz węgiel drzewny. Badania biosorpcji na różnych mikroorganizmach i na równych naturalnych sorbentach zostały przeprowadzone. Na ich podstawie wytypowano szereg biosorbentów jako potencjalny materiał do zastosowania w oczyszczaniu ścieków z hałd mineralnych. Badania przeprowadzono nad flotacją biomasy uzyskanej po biosorpcji jonów metali. Otrzymane wyniki wskazują, że flotacja biomasy po adsorpcji jonów metali była bardzo dobra. Przykładowo, uzyski Cu i Ag były bliskie 100%, prowadząc adsorpcje za pomocą 10g biomasy z 100 ml roztworu tych jonów. Na podstawie przeprowadzonych doświadczeń starano się poznać korelację między wynikami adsorpcji jonów a wynikami flotacji biomasy. Uzyskane w pracy wyniki stwarzają przesłanki dla zastosowania tego procesu dla oczyszczania ścieków przemysłowych i odzysku z nich cennych metali.