SORPTION OF Co^{2+}, Zn^{2+}, Cd^{2+} AND Cs^{+} IONS BY ACTIVATED SLUDGE OF SEWAGE TREATMENT PLANT

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Abstract: Sludges are byproducts of sewage treatment process. Land application of sewage sludge is one of the final steps of waste water treatment, but solubilization of toxic metals restricts this method of sludge disposal. In our paper cobalt, zinc, cadmium and cesium sorption by suspension of non-treated activated sewage sludge (14 g/dm^3, dry wt.) from waste water spiked with $^{60}CoCl_2$, $^{65}ZnCl_2$, $^{109}CdCl_2$ or $^{137}CsCl$ were determined in laboratory experiments at 20°C. Activated sludge supplied by the municipal sewage treatment plant in Zeleneč (Trnava region, Slovakia) showed high efficiency to sorb Co^{2+}, Zn^{2+}, Cd^{2+} and Cs^{+} ions from waste water pH 6-7. The process can be characterized by the concentration equilibrium (C_{solid}/C_{liquid}) typical for sorption processes. Efficiency of the sorption increased in the order Cs < Co < Zn < Cd. Metal sorption process was not inhibited by pretreatment of the sludge with 0.2% formaldehyde or thermal inactivation at 60°C, what confirms that the process was not dependent on metabolic activity of the sludge. Cobalt, zinc, cadmium and cesium were easily removable from the sludge by washing with diluted HCl, EDTA or water solutions of the corresponding metal ions, but with low efficiency by deionized water.

Key words: activated sludge, sorption, cobalt, zinc, cadmium, cesium, radiotracer analysis

1. Introduction

Several physico-chemical methods were used for removal of heavy metals from industrial liquid wastes, such as ion-exchange, chemical precipitation, chemical reduction and adsorption. There are still some problems associated with these methods since these are cost-expensive and they themselves can produce other wastes, which will limit their industrial applications. Among the available treatment processes, the application of biological sorbents is the most promising due to the following reasons: requirement of chemicals for the treatment process is reduced, low operation costs, eco-friendly and cost-effective alternative of conventional techniques and high efficiency at low levels of contaminations.

Sludge of municipal waste water treatment plants are produced in huge amounts and generally represent one of the main problems of European countries (FYTILI and ZABANIOTOU, 2008). Many experimental studies are applied worldwide to determine the extractable trace metals in sludge to assess the bio-available metal fraction and the potential mobility of trace metals from polluted sludge (ALVAREZ *et al*., 2002; FUENTEZ *et al*., 2004; IAQUINTA *et al*., 2006). However, the activated sludge can be considered also as a biosorbent capable to bind toxic metals from liquid wastes of industrial origin.

In our previous papers we described sorption characteristics of Co, Zn and Cd binded by dry biomass of lichen *E. prunastri* (PIPÍŠKA *et al.*, 2008) and moss *R. squarrosus* (PIPÍŠKA *et al*., 2010) biomass. The objective of this study was to obtain quantitative data of cobalt, zinc, cadmium and cesium sorption by non-treated activated sludge of the municipal wastewater treatment plant.

2. Materials and methods

2.1 Sorption and desorption experiments

Activated sludge supplied by a municipal sewage treatment plant in Zeleneč (Trnava region, Slovakia) was kept in refrigerator at 4°C for 30 d and used for experiments. Suspension of activated sludge pH 6.9 pre-concentrated by centrifugation contained 14.0 g/dm^3 biomass (dry wt.). In batch experiments, the test tubes with 1 ml of activated sludge suspensions in waste water were spiked with $^{60}CoCl_2$, $^{65}ZnCl_2$, $^{109}CdCl_2$ or $^{137}CsCl$ (0.5-50 mmol/dm^3) and shaken at 20°C. In time intervals, the biomass was separated by centrifugation (20 min at 12 000 × g), supernatant was removed and sediment was used for radiometric determination of sorbed metals.

In desorption experiments, the biomass after metal sorption was separated (20 min at 12 000 × g) and resuspended by wortexing for 30 min in 1.0 ml deionized water, 0.1 M EDTA, 0.1 M HCl, 0.5 mM $CoCl_2$, 0.5 mM $ZnCl_2$, 0.5 mM $CdCl_2$ or 0.5 mM CsCl. Concentration of metals in biomass was estimated by similar way as in the sorption experiments. Biomass dry weight was estimated by drying for 24 h at 60 °C.

The prediction of Co, Zn, Cd and Cs speciation in the solution as a function of pH was performed using the Visual MINTEQ (version 2.53) program.

2.2 Radiometric analysis

The gamma spectrometric assembly using the well type scintillation detector 54BP54/2-X, NaI(Tl) (Scionix, the Netherlands) and the data processing software Scintivision 32 (ORTEC, USA) were used for ^{60}Co, ^{65}Zn, ^{109}Cd and ^{137}Cs determination in sediment of sludge and supernatant fluids at the energy of γ- photons [keV]: ^{60}Co- 1173.24, ^{65}Zn – 1115.52, ^{109}Cd – 88.04, ^{137}Cs – 661.62. Counting time 600 s allowed obtaining data with measurement error <2 %, which do not reflect other sources of errors. Standardized solutions of $^{65}ZnCl_2$ (50 mg/dm^3 $ZnCl_2$ in 3 g/dm^3 HCl), $^{60}CoCl_2$ (20 mg/dm^3 $CoCl_2$ in 3 g/dm^3 HCl), $^{109}CdCl_2$ (50 mg/dm^3 $CdCl_2$ in 3 g/dm^3 HCl), $^{137}CsCl$ (20 mg/dm^3 CsCl in 3 g/dm^3 HCl) were obtained from The Czech Institute of Metrology (Prague, Czech Republic).

3. Results and discussion

3.1 Metal sorption

Sorption experiments showed that non-treated activated sludge is able to bind high amounts of cobalt, zinc, cadmium and cesium (Fig. 1). At C_0 = 50 mmol/dm^3,

sorptions Q (μmol/g; dry wt.) 611, 995, 1076 and 374 for cobalt, zinc, cadmium and cesium respectively, were observed. However, at the initial concentration C_0 = 50 mmol/dm^3, the system was not saturated, and higher Q_{max} values can be expected.

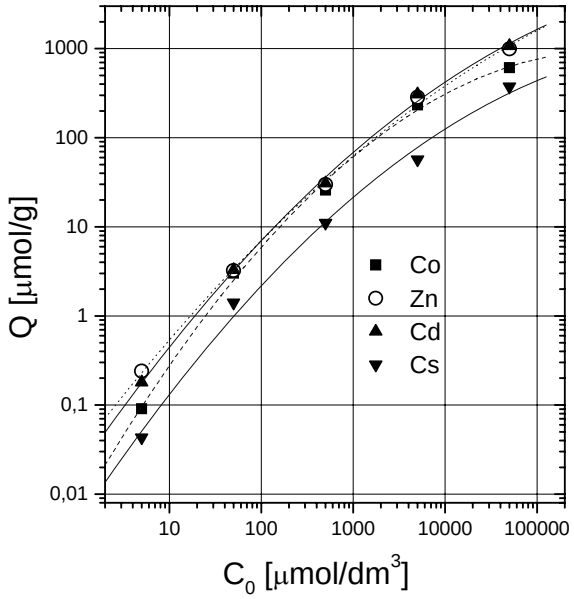

Fig. 1. Cobalt (-■-■-■-), zinc (-o-o-o-), cadmium (-▲-▲-▲-) and cesium (-▼-▼-▼-) uptake Q (μmol/g; dry wt.) by non-treated activated sludge in dependence on the initial $CoCl_2$, $ZnCl_2$, $CdCl_2$ and CsCl concentration. Specific radioactivity in solutions [Bq/mL]: ^{60}Co – 195; ^{65}Zn – 156; ^{109}Cd – 192 and ^{137}Cs – 172. Data after 1h reaction at 20°C. Biomass concentration 14.0 g/dm^3 (dry wt.). Data are the arithmetic mean of three replicates.

3.2 The role of metabolic activity

Broad consortium of vital aerobic microbial population in activated sludge can participate in metal uptake driven by metabolic processes. On the other hand, dead microbial biomass and polymers such as proteins and polysaccharides can also bind metals on the basis of sorption processes or complexing. Experiments showed that treatment of activated sludge by formaldehyde or thermal inactivation at 60°C had minimal effect on cobalt, zinc, cadmium and cesium uptake (Fig. 2). It means, that metal uptake is not dependent on metabolic activity and physico-chemical processes play decisive role in cobalt, zinc and cadmium binding by non-treated activated sludge.

The sorption of metals is attributed to the bacterial cell wall (FEIN 2006; VULLO *et al*., 2008) and to the exopolymeric substances (PAL and PAUL, 2008), which contain a large number of negatively charged functional groups such as carboxyl, phosphate and sulphate (WINGENDER *et al*., 1999). Exopolymers can be expected

to buffer metal ion concentrations over wide ranges of concentrations and pH (BHASKAR and BHOSLE, 2006). Comprehensive data dealing with metal binding by activated sludge can be found in papers (MILNE *et al*., 2003; GUIBAUD *et al*., 2009).

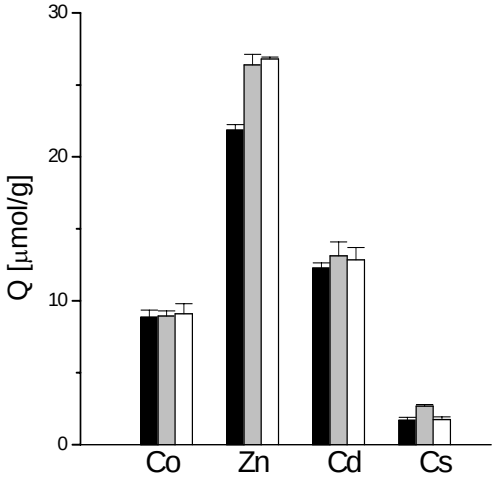

Fig. 2. Uptake of cobalt, zinc, cadmium and cesium Q (μmol/g; dry wt.) by non-treated activated sludge --■--, formaldehyde-treated sludge (0.5%, 30 min at 20°C, under wortexing) --▒--, and thermally treated sludge (30 min at 60°C) --□--. Specific radioactivity in solutions [Bq/mL]: ^{60}Co – 198; ^{65}Zn – 150; ^{109}Cd – 167 and ^{137}Cs – 162. Sorption 1 h under agitation at 20°C. Reaction conditions see Fig. 1.

3.3 The role of pH

Acidic pH region is not typical for municipal waste waters as well as activated sludges. It is generally known, that metal cation biosorption is diminished below pH 4 (PIPÍŠKA *et al.*, 2010). In acidic pH region species of cobalt and zinc exist as Me^{2+} cations, and cesium as Me^{+} cation (Fig. 3).

In the case of cadmium the main ionic form within pH 4 -8 beside Cd^{2+} is $CdCl^{+}$ with the ratio approx 60 to 40 (Fig. 4). Above pH 7 more complex ionic equilibrium takes place, in dependence of the concentration of anion such as chloride, carbonate and phosphate.

The concentration of $Cd(OH)_3^-$ anion is increasing above pH 9. During the sorption of metals by sludges from alkaline liquid wastes besides sorption of Me^{2+} cations, also the existence of other than ionic metal forms with different solubility in water have to be taken into consideration. This fact is in agreement with our observations that sorption efficiency of activated sludge increases above pH 8 (not shown). Strong sigmoidal pH dependence of Cd^{2+} sorption by polysaccharides of activated sludge with inflection point at pH 8.6 was described by GUIBAUD *et al*. (2009).

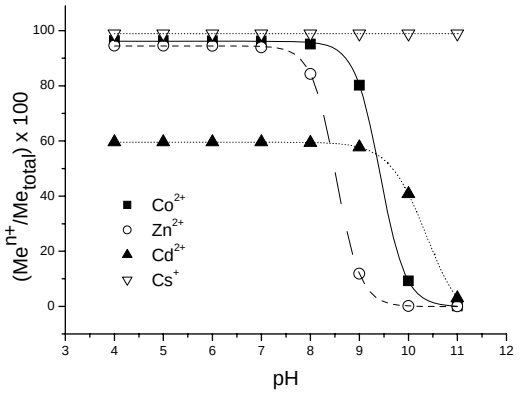

Fig. 3. Molar fraction of Co^{2+}, Zn^{2+}, Cd^{2+} and Cs^{+} in dependence on pH of synthetic waste water (IAQUINTA *et al.,* 2006) at 25°C and C_0 1.0 mmol/dm^3. Calculated by speciation program Visual MINTEQ ver. 2.53.

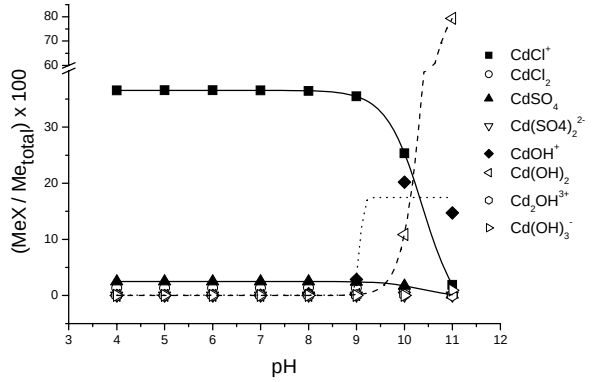

Fig. 4. Speciation forms of cadmium in dependence on pH of synthetic waste water (IAQUINTA *et al.,* 2006) at 25°C and C_0 1.0 mmol//dm^3. Calculated by speciation program Visual MINTEQ ver. 2.53.

3.4 Desorption

High percentage of Co, Zn, Cd and Cs can be desorbed from the sludge by one step washing with $CoCl_2$, $ZnCl_2$, $CdCl_2$ and CsCl solutions respectively, as well as with EDTA and HCl solutions (Tab. 1; Fig. 5B).

At the same time only 6, 2 and 7 per cent of sorbed cobalt, zinc and cadmium, respectively, can be solubilized by washing the activated sludge with deionized water. It means that for releasing of the above mentioned metals certain, ionic force is necessary for replacing metal ions from binding sites. Cesium was easily removable from the sludge even with deionized water. Generally, Cs^{+} ions show the highest mobility in biological systems resembling behavior of K^{+} ions.

Cadmium showed the highest affinity to the sludge and the lowest extractability with mineral acids and salt solutions (Fig. 5A, B). The explanation of this

phenomenon will require a more detailed study oriented toward speciation of cadmium in individual components of the sludge flocks.

Table 1. Removable portion of metals from activated sludge by single step washing of sludge with 0.1 M HCl, 0.1 M EDTA or 0.5 mM $CoCl_2$, $ZnCl_2$, $CdCl_2$ or CsCl. Specific radioactivity in solutions [Bq/mL]: ^{60}Co – 205; ^{65}Zn – 158; ^{109}Cd – 160 and ^{137}Cs – 146. Calculations based on volume radioactivity of supernatant washing liquid.

Parameter	Co	Zn	Cd	Cs
Sorbed Q (μmol/g; dry wt.) *	26±0.7	30±0.9	31±1.1	11±0.2
Removed with water [%]	6	2	7	36
Removed with 0.5 mM salt [%]	46	50	15	72
Removed with 0.1 M HCl [%]	81	91	30	83
Removed with 0.1 M EDTA [%]	90	92	73	81

* Biosorption from C_0 = 0.5 mmol/dm^3 solutions at biomass concentration 14.0 g/ dm^3 (dry wt.).

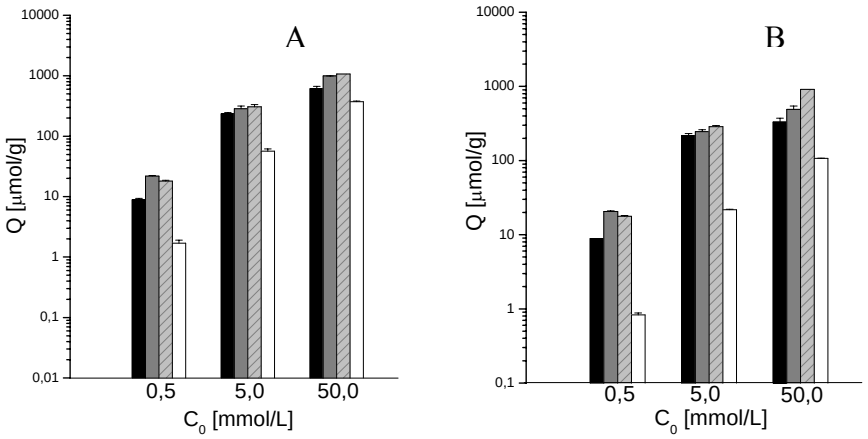

Fig. 5A. Cobalt (-■-), zinc (-▒-), cadmium (-▒-) and cesium (-□-) uptake Q (μmol/g; dry wt.) by non-treated activated sludge in dependence on the initial $CoCl_2$, $ZnCl_2$, $CdCl_2$ and CsCl concentration. Specific radioactivity in solutions [Bq/mL]: ^{60}Co – 195; ^{65}Zn – 156; ^{109}Cd – 192 and ^{137}Cs – 172. Data after 1h reaction at 20 °C. Biomass concentration 14.0 g/dm^3 (dry wt.).
Fig. 5B. Remaining metal uptake after 30 min washing of the sludge with $CoCl_2$, Zn Cl_2, Cd Cl_2 or CsCl solution. Data are the arithmetic mean of three replicates.

According to HSIAU and LO (1998), sequential extraction revealed that the percentages of the heavy metals of organically bound form and exchangeable form in chemically fixed sludge samples were in the order of Cu > Pb > Cr > Zn.

However, mobility of cesium can be diminished by supplementing of activated sludge with clay materials or bentonites. In that case, cesium released from activated sludge will be bound irreversibly on clay minerals and will not be bio-available or leachable under natural conditions and even under more drastic conditions such as with alkali or acid solutions. Clays (DYER *et al*., 2000) and bentonites (see e.g.

GALAMBOŠ *et al.*, 2010; ZÁVODSKÁ and LESNÝ, 2006) are well known sorbents for irreversible cesium binding, as well as for binding many heavy metals and metalloids.

Activated sludge disposes much higher capacity for metal sorption calculated for unit biomass, than the content of metals contained in municipal waste waters. It means that the sludge biomass is not saturated and can be used as sorbent for reversibly sorption of the metals from other liquid wastes.

Table 2. Sorption capacities (mg/g, dry wt.) of naturally occurring sorbents. According to BAILEY *et al*. (1999), modified.

Sorbent	**Cs**	**Co**	**Zn**	**Cd**	**Pb**	**Hg**
Bark				32	182	400
Modified cotton						1000
Chitin						100
Chitosan				558	796	1123
Clay				16.5	58	
Microbial biomass				28	116	
Lignin			95		1865	150
Modified wool				87	135	632
Moss				46.7		
Peat				5.1	230	16.2
Seaweed				215	344	
Xanthate				33.3	18	1.2
Zeolite				84.3	155.4	150.4
Lichen biomass [(1)]		5.7	7.3			
Moss biomass [(2)]		7.2	12.2	19.4		
Green algae [(3)]		14.5				
Activated sludge[(4)]				24.5		
Activated sludge [(5)]	50	36	65	121		

(1) PIPÍŠKA *et al*. 2008; (2) PIPÍŠKA *et al*., 2010; (3) HORNÍK *et al.*, 2008; (4) CHOI and YUN, 2006; (5) This paper.

In Tab. 2, the sorption capacity (Q) values of activated sludge obtained in this paper are compared with Q values of other sorbents published. As we can see, activated sludge showed the sorption capacity comparable with other low-cost sorbents and therefore the sludge could be used for lowering concentration of toxic metals originating from industrial effluents, subsequently dewatered or incinerated.

4. Conclusions

The non-treated activated sludge from aerobic phase of municipal waste water treatment plant contains the whole spectrum of metals. However, the sorption capacity of the sludge is much higher than actual concentration of heavy metals in treated waste waters. Sludge can be used as an efficient sorbent for the removal of heavy metals from industrial liquid wastes. Sorption capacity of activated sludge studied for Co, Cd,

Zn and Cs from 0.5 mmol/dm^3 solution was 36, 65, 121 and 50 mg/g (dry wt.), respectively. The ability of non-treated activated sludge to sorb Co^{2+}, Zn^{2+}, Cd^{2+} and Cs^{+} metal ions is based mainly on physical processes not dependent on the metabolic activity of the sludge microflora. Recovery of the metals by washing with diluted HCl, EDTA and salt solutions decreases in the order: Cs > Co = Zn > Cd. The obtained data stress the potential of surplus production of activated sludge as a sorbent for binding of toxic and radiotoxic metals and metaloides from liquid industrial wastes. The next treatment of the sludge will depend on the concentration of sorbed metals and their toxicity. Incineration will be one of the ways for final treatment.

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