SORPTION CHARACTERISTICS OF ACTIVATED SLUDGE FOR Co-Zn BINARY SYSTEM

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Toxic and radiotoxic metals of liquid wastes are sorbed by the sludge of Waste Water Treatment Plants (WWTPs) with a high efficiency.. Sludges with low toxic metals concentrations can be temporally stored or utilized as soil conditioners in agriculture. Other possible and economically acceptable way is repeated utilization of the sludge as heavy metals sorbent. Since effluents can contain several metals, it is necessary to study the simultaneous sorption of two or more metal ions and also to quantify the mutual effect of one metal on the other. In the present study, we have undertaken the study on the sorption characteristics of Dried Activated Sludge (DAS) from industrial WWTP for sorption Co^{2+} and Zn^{2+} ions from their binary aqueous system in batch experiments using radiotracers ^{60}Co and ^{65}Zn technique. Values of maximum sorption capacity (Q_{max}) of DAS at pH 6 calculated from extended Langmuir adsorption isotherm were 247 ± 15 μmol g^{-1} for Co^{2+} and 479±32 μmol g^{-1} for Zn^{2+} ions. Results revealed that the sorption capacity of DAS for both the metals increases with increased initial concentration in the range 100 – 4000 μmol dm^{-3} $CoCl_2$ and $ZnCl_2$, respectively. Presence of Zn^{2+} ions as co-ions caused more significant decrease of Co^{2+} uptake in binary Co-Zn system than vice versa. Experimental data Co and Zn sorption in binary system were well described by extended Langmuir model and affinity parameter *b* indicate higher affinity of DAS to Zn^{2+} in comparison with Co^{2+} ions. Prediction of total Co-Zn sorption by DAS using extended Langmuir model was less suitable due to dissimilarity of Q_{max} value of DAS for Co^{2+} and Zn^{2+} in single systems.

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Introduction

Industrial effluents treated with wastewater treatment plants (WWTPs) contain high amounts of organic matter and pollutants including metals such as Co, Cd, Zn etc.[1] Toxic metals of liquid wastes are sorbed by the sludge of WWTPs with a high efficiency. Liquid part of sludge is being dispersed to an aqueous recipient but solid part is processed for the next disposal (e.g. temporally storing, landfilling, incineration). The increased amount of sewage sludges (which are not having a tendency to settle) are a global environmental problem.

Sludges with a low toxic metals concentration can be temporally stored or utilized as soil conditioners in agriculture processes. Activated sludges produce high amounts of extracellular polymeric substances (EPS) which are metabolic products of bacteria accumulated on the cell surface.[2] EPS as soil beneficial substances are mainly composed from polysaccharides, proteins and humic substances, containing high concentration of ionizable functional groups.[3] The matrix of extracellular polymers is involved in the processes of microbial aggregation in flocs, stabilization of biofilms, water retention and uptake of exogenous organic compounds.[4] Organic polymers play also crucial role in the sorption process of heavy metals by biomass of activated sludge. Composition of activated sludge as a consortium of bacteria, microalgae, fungi and protozoa and metal sorption characteristics varies depending on type of waste waters and technology used. Reversibility of metals binding represents the condition of metals entry to the food chain.

Other possible and economically acceptable way is repeated utilization of the sludge as heavy metals sorbent. Biological materials have effective sorption capacity and cheaper regeneration cost as compared to conventional sorbents and ion-exchange resins.[5] For instance, diverse variety of microorganisms were used extensively for toxic and radiotoxic metals sorption and accumulation studies.[6] Bivalent metal ions such as Co^{2+} and Zn^{2+} can be removed from aqueous solutions not only by inorganic sorbents, such as zeolites but also by sorbents prepared from microbial biomass.[7-8] Adsorption and precipitation on sorbent surface are predominant in the process of metal uptake. Only small fraction of Me^{2+} ions is localized intracellularly.[8] The bio-sorption is largely attributed to the binding of metals onto the bacterial cell surface due to the presence of active functional binding sites.[9] Moreover, sorption in multicomponent systems is complicated, because of the possible interactions among the metals. Different adsorption characteristics of metal ions as one of the major sorption process parameter can affect metal positions on surface binding sites of sorbents. Competitive effect of metal components can be evaluated by many statistics and mathematics tool.[10] Marešová et al.[11] used extended Langmuir type equations to describe the sorption of Co^{2+} and Sr^{2+} in binary system by sorbent prepared from moss biomass. On the basis of that, the objective of our study was to investigate sorption characteristics of DAS from industrial WWTP for sorption Co^{2+} and Zn^{2+} ions from their binary aqueous system. To obtain reliable experimental data, radiotracer technique with $^{60}CoCl_2$ and $^{65}ZnCl_2$ was used. Binary equilibrium isotherm data of Co-Zn system were described using extended Langmuir model.

Experimental

Material

Samples of activated sludge were obtained from aerobic phase of WWTP in Enviral Inc, the plant producing bioethanol (Leopoldov, Slovak Republic). After washing twice in deionised water, the sludge was oven dried at 90 °C for 72 h, ground and sieved. Powdered dried activated sludge (DAS) of particle size <450 µm was used for metal sorption studies.

Standardized $^{60}CoCl_2$ solution (5.181 MBq cm^{-3}; 20 mg dm^{-3} $CoCl_2$ in 3 g dm^{-3} HCl) and $^{65}ZnCl_2$ solution (0.8767 MBq cm^{-3}; 50 mg dm^{-3} $ZnCl_2$ in 3 g dm^{-3} HCl) were obtained from the Czech Institute of Metrology. Chemicals used were of analytical reagents grade.

Sorption experiments

Batch sorption experiments were carried out by suspending of DAS biomass (2.5 g dm^{-3} d.w.) in 8 cm^3 water solutions of $CoCl_2$and $ZnCl_2$ in variable molar concentration range 100 - 4000 µmol dm^{-3} in molar ratios 2:1, 1:1, 1:2 spiked with $^{60}CoCl_2$ (65 kBq dm^{-3}) and $^{65}ZnCl_2$ (63 kBq dm^{-3}. The reaction pH was adjusted to 6.0 ± 0.1 with 0.1 mol dm^{-3} NaOH and 0.1 mol dm^{-3} HCl. Flasks were agitated on reciprocal shaker (120 rpm) at 22 °C and samples were taken for equilibrium study. Biomass was filtered out, washed twice in deionised water and radioactivity of both activated sludge and liquid phase was measured. All experiments were performed thrice. Presented data are arithmetic mean values. The metal uptake was calculated as:

$$Q_{eq} = (C_0 - C_{eq})\frac{V}{M} \quad (1)$$

where Q is the uptake (µmol g^{-1}), C_0 and C_{eq} are the liquid-phase concentrations of metal at initial and equilibrium (µmol dm^{-3}), V is the volume (dm^3), and M is the amount of dried bio-sorbent (given in grams).

Analytical equipments

The gamma spectrometric assembly using 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 and ^{65}Zn determination in DAS and supernatant liquids at the energy of γ- photons: ^{60}Co - 1173.24 keV and ^{65}Zn – 1115.52 keV.

Determination of initial cobalt and zinc content in sorbent was made by atomic absorption spectrometry (ETAAS) device ShimadzuAA-6300 (USA) with an electrothermal atomization equipment Shimadzu GFA-EX7i using a Shimadzu autosampler ASC6100 and background correction method of Smith-Hieftje, after decomposition samples of high-pressure digestion mineralization equipment DAH406 Berghof (DE).

Sorption isotherm models

Analysis of sorption equilibrium data was done using extended Langmuir adsorption isotherms equations:

$$Q_{eq}(Me_1) = \frac{Q_{max Me_1} b_{Me_1} C_{eq}(Me_1)}{1 + b_{Me_1} C_{eq}(Me_1) + b_{Me_2} C_{eq}(Me_2)} \quad (2)$$

$$Q_{eq}(Me_2) = \frac{Q_{max Me_2} b_{Me_2} C_{eq}(Me_2)}{1 + b_{Me_1} C_{eq}(Me_1) + b_{Me_2} C_{eq}(Me_2)} \quad (3)$$

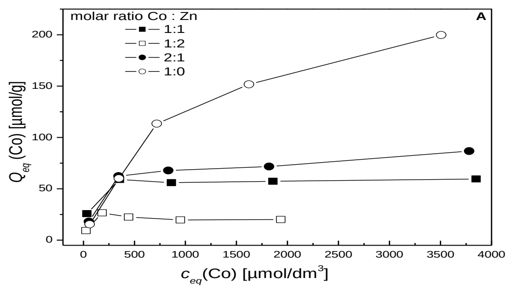
$$b_{Me_1} = \frac{1}{K_{Me_1}} \quad \text{and} \quad b_{Me_{21}} = \frac{1}{K_{Me_2}}$$

where $c_{eq}(Me_1)$ and $c_{eq}(Me_2)$ represent concentration of metals in equilibrium and Q_{maxMe1} and Q_{maxMe2} represent the maximum sorption capacity for both metal present in reaction solution, b_{Me1} and b_{Me2} represent affinity constants of Langmuir model for both metals and K_{Me1} and K_{Me2} are constants of equilibrium for surface binding sites of sorbent available for metals Me_1 and Me_2.

To calculate maximum sorption capacity of the sorbent and the corresponding parameters of adsorption isotherms ORIGIN 8.0 Professional (OriginLab Corporation, Northampton, USA), GraphPad PRISM 5.0 (GraphPad Software Inc., USA) and Table Curve 3D 4.0 (Systat Software, Inc., Chicago, USA) were used.

Results and discussion

In comparison to the single metal solutions sorption in binary systems is complicated, because of possible interactions among the metals.



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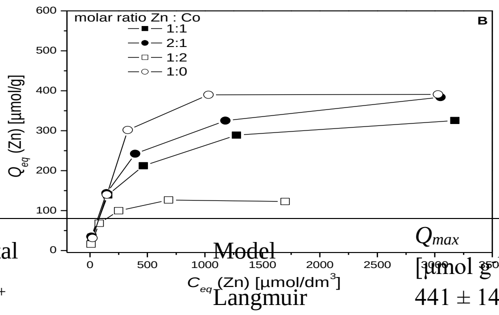

Figure 1. Cobalt (A) and zinc (B) sorption from binary system Co-Zn at variable initial molar [Co]: [Zn] ratios by dried activated sludge (2.5 g/dm^3, d.w.) at 22°C and pH 6.0.

Metal	Model	Q_{max} [µmol g^{-1}]	*B* [L µmol^{-1}]	*K* [L g^{-1}]	*1/n*	R^2
Zn^{2+}	Langmuir	441 ± 14	0.0045 ± 0.0015	-	-	0.96394
	Freundlich	-	-	40.6 ± 15.31	0.29 ± 0.10	0.81961
Co^{2+}	Langmuir	256 ± 9	0.0010 ± 0.0001	-	-	0.99353
	Freundlich	-	-	4.29 ± 1.36	0.48 ± 0.04	0.96704

Table 1. Comparison of Langmuir and Freundlich equilibrium parameters (±SD) for Co^{2+} and Zn^{2+} sorption by dried activated sludge from single system at pH 6 obtained by non-linear regression analysis [10]

Table 2. Extended Langmuir isotherm parameters for Co^{2+} and Zn^{2+} sorption in binary Co-Zn system by dried activated sludge calculated by non-linear regression analysis.

Sorption	Q_{max} [µmol g^{-1}]	b_{Co} [dm^3 µmol^{-1}]	b_{Zn} [dm^3 µmol^{-1}]	R^2	*RMSE*
$Q_{max\ Co}$	247 ± 15	0.001 ± 0.0002	0,005 ± 0,001	0,975	8,15
$Q_{max\ Zn}$	479 ± 32	0.002 ± 0.001	0,004 ± 0,001	0,949	32,89

Sorption of cobalt and zinc ions by dried activated sludge from binary Co-Zn system increased with an increasing initial concentration of both metals in the range of 0 – 4 000 µmol dm^{-3} $CoCl_2$ and $ZnCl_2$, respectively. Obtained results are shown in Fig. 1A, B. The presence of co-ion in solution caused significant decrease of uptake of primary ion. Zn^{2+} as co-ion caused the decrease about 85% of Co^{2+} ions sorption from 200 µmol g^{-1} to 25 µmol g^{-1} d.w. of sludge. The competitive effect of zinc increased with increasing of its solution concentration. On the other hand Co^{2+} as co-ion in sorption of Zn^{2+} ions caused decrease about only 68% from 390 µmol g^{-1} to 125 µmol g^{-1} d.w. of sludge. At equimolar concentration of both metal ions (ratio 1:1) maximum sorption capacity of activated sludge was 325 µmol g^{-1} for zinc and 60 µmol g^{-1} for cobalt. For a description of Co^{2+} and Zn^{2+} sorption equilibrium in single-component systems was more suitable Langmuir adsorption model (Table 1).

Experimental data from two-component system (Co-Zn) were fitted and evaluated by extended Langmuir competitive model.[11] For determination of sorption equilibrium of Co^{2+} and Zn^{2+} ions we used Eqs. 3 and 4. Parameters of extended Lanqmuir model for single and binary metal uptake calculated by non-linear regression analysis are shown in Table 2.

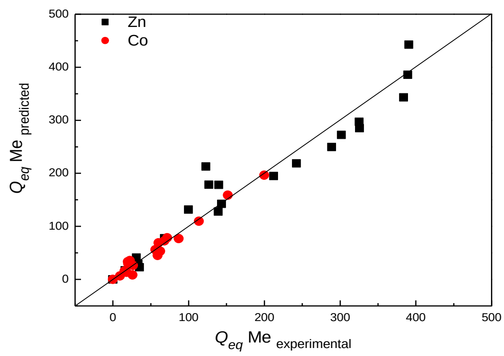

Fig. 2. Comparison of experimentally observed data with predicted data obtained using the extended Langmuir model.

The degree of affinity is expressed in the form of the parameter *b*, which is the Langmuir constant. The relationship between value and its affinity for metal sorbent is proportional, based on Arrhenius equation to express energy of sorption process. Parameter b_{Zn} is higher than b_{Co} that indicates higher affinity of sorbent prepared from activated sludge to zinc ions in comparison with cobalt ions in sorption process from binary system Co-Zn.

The correlation between predicted and experimental values of metal sorption by DAS is shown in Fig. 2. Since most of the points are distributed around the line, this indicates that equation used described the sorption data well. The adequacy of model was also compared by coefficient of determination and by RMSE (Table 2). It is evident that extended Langmuir model fits the data well.

The extended Langmuir model can be represented by adsorption isotherms in 3-D space (Fig. 3 A,B). X and Y axes represent the concentrations of cobalt and zinc in equilibrium (C_{eqCo} , C_{eqZn}), while the Z axis represents plotted value of sorbed cobalt and zinc (Q_{eq}). Experimental sorption values of metal uptake are presented as individual points.

The Fig. 3 shows that at higher concentrations of the metal ions, binding sites of sorbent can be easily saturated what is presented by the plateau of sorption surface. This adsorption model is suitable and has a high efficiency for the description and prediction of single metal sorption. For determination of binary metal sorption, the method has proved to be less effective. It is mainly due to the different values of maximal sorption capacities of Co^{2+} and Zn^{2+} ions. Extended Langmuir model is suitable for description of metal cations sorption processes for which parameters (Q_{max}) are approximately similar.[11] The sorption capacity of activated sludge for zinc was higher about 50% as compared to cobalt sorption.

This difference in affinity of sorbent for Me^{2+} ions could be because of different physico-chemical characteristics of metal ions.[12] Remenárová et al.[13] showed different sorption capacity of DAS for Cd^{2+} and Zn^{2+} ions. Metal ions can be classified according to covalent index that reflects different ligand affinities.[14]

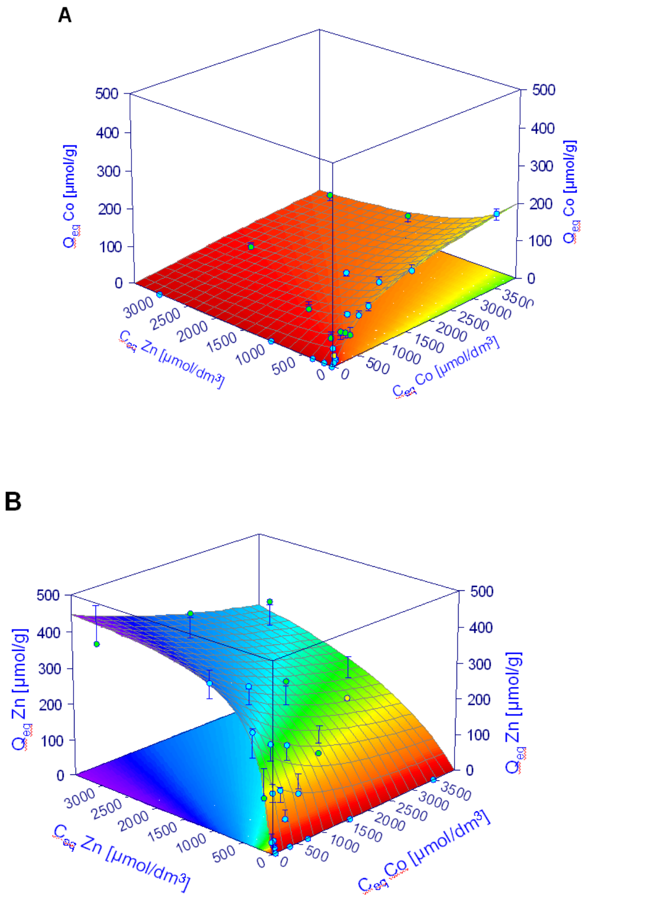

Fig. 3. 3-D sorption isotherm surfaces of Co^{2+}-Zn^{2+} binary system: (A) Co^{2+} sorption (μ mol g^{-1}); (B) Zn^{2+} sorption (μ mol g^{-1}). The sorption surfaces are predicted by the competitive Langmuir model (Eqs. 2 and 3) and the points present experimental data obtained at pH 6 and 22 °C. Error-bars represent 90% confidence interval.

Higher affinity of reactive sites on sludge surface for zinc ions in binary sorption system is also related to the covalent index, ionic radius and electronegativity (Table 3). Ionic index is responsible for the preference of the metal ion binding to the oxygen ligands. Co^{2+} ion has higher value of covalent index that indicates a covalent binding to the active sites of sulfo and nitro functional groups.

Table 3. Physico-chemical properties of Co^{2+} and Zn^{2+} ions

Properties	**Co^{2+}**	**Zn^{2+}**
Atomic weight	58.93	65.39
Ionic radius *r* (pm)	72	74
Electronegativity (Pauling) X_m	1.88	1.65
Covalent index ($X_m^2r^{-1}$)	2.5	2.04
Ionic index (z^2r^{-1})	5.4	5.4

Conclusion

Sorbent prepared from DAS from industrial WWTP has an ability to remove cobalt and zinc from binary aqueous system. Experimental data of batch metal sorption were obtained using radiotracer technique with ^{60}Co and ^{65}Zn.

Values of maximum sorption capacity (Q_{max}) of DAS at pH 6 calculated from extended Langmuir adsorption isotherm were 247±15 μmol g^{-1} for Co^{2+} and 479±32 μmol g^{-1} for Zn^{2+} ions. Results revealed that the sorption capacity of DAS for both metals increases with an increase in initial concentration in the range 100 – 4000 μmol/dm³ $CoCl_2$ and $ZnCl_2$, respectively. Presence of Zn^{2+} ions as co-ions caused more significant decrease of Co^{2+} uptake in binary Co-Zn system than vice versa. Experimental data Co and Zn sorption in binary system were well described by extended Langmuir model and affinity parameter *b* indicate higher affinity of DAS to Zn^{2+} in comparison with Co^{2+} ions. Prediction of total Co-Zn sorption by DAS using extended Langmuir model was less suitable due to dissimilarity of Q_{max} value of DAS for Co^{2+} and Zn^{2+} in single systems. Determination of binding mechanisms of cobalt and zinc from binary system to active sites of sludge surface as content variable microbial mass will require detailed study for further storage or disposal this material. Zinc and cobalt as metals included to the borderline class bind to the residues of histidine and free amino groups of proteins.

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