Anaerobic Sulphate-Reducing Microbial Process Used for Sorbent Preparation

Jana JENČÁROVÁ[1], Alena LUPTÁKOVÁ

[1] Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovakia; email: jencarova@saske.sk

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Abstract

The presence of metals in waters represents today typical anthropogenic pollution. Their increased content, originating in various industry sectors and previous mining activity, is undesired. High concentrations of metals are hazardous for all living organisms. They may accumulate to toxic levels, cause many disorders and diseases and ecological damage under certain environmental conditions. Sulphate-reducing microbial process utilization is one of the options to prepare applicable sorbent which removes metal ions from solutions. This sorbent is created as a consequence of sulphate-reducing bacteria metabolism in anaerobic environment. It is considered to be able to remove many metals from solutions, such as Zn, Cd, Pb, Cu, Ni, As.

Keywords: anaerobic bacteria, sorbent, metals, adsorption isotherms

Introduction

Wastewaters containing metals in considerable amounts originate mainly from metal finishing, electroplating, metallurgy, mining, chemical and battery manufacturing processes. Heavy metals are well-known toxic elements and their discharge into receiving waters can have undesired effect on human health or the environment. Since they are not biodegradable, they tend to accumulate in living organisms and cause numerous diseases and disorders (Senthilkumaar et al., 2000). Wastewaters coming from various industries are often acidic and typically characterized by a significant content of soluble metals, such as zinc, copper, cadmium, lead, iron, nickel, arsenic, mercury, chromium. Therefore, there is a need to treat these waters before being discharged into the environment.

Accumulation of metal ions by microorganisms has received attention due to its potential applications in environmental protection and recovery of toxic or strategic heavy metals. The removal of metals via adsorption over solid adsorbents, e.g. activated carbons and others is one of the convenient methods used.

It can be alternate by biosorption, which utilizes various natural materials of biological origin, including bacteria, fungi, yeast and algae (Wang and Chen, 2009; Volesky, 2004; Ahalya et al., 2003; Chen et al., 2000). Biosorbents possess metal-sequestering properties and can be used to decrease the concentration of metal ions in solution to low levels. Biosorption is either metabolism independent, such as physical or chemical sorption onto the cell wall, or metabolism related, such as transport, internal compartmentalization, and extracellular precipitation by metabolites (Gadd, 1993).

Several studies revealed that iron sulphides synthesized by sulphate-reducing bacteria (SRB) are useful as adsorbents and can decrease concentrations of common wastewater and acid mine drainage cations to low levels (Zhou et al., 2017; Mullet et al., 2004; Watson et al., 2001). The most widely metabolic pathway of SRB – overall dissimilatory reduction – is the complete reduction of sulphate to hydrogen sulphide through a series of intermediate reactions (Rivers Singleton, 1993). The end product, hydrogen sulphide, can react with metal ions to form insoluble metal sulphides or reduce soluble toxic metals, often to less toxic or less soluble forms (Tebo, 1995). Then, sulphide production by SRB has implications for bioremediation of heavy metal pollution by exploitation of adsorption or precipitation.

The objective of this work was to create sorbent samples by bacteria cultivation, realize sorption experiments and interpret obtained results by using adsorption isotherms.

Materials and methods

Growth media and conditions

Bacteria were grown in selective nutrient medium for SRB cultivation – Postgate's C. Medium contains the following, per liter of distilled water - 0.5g KH_2PO_4, 1g NH_4Cl, 4.5g Na_2SO_4, 0.2g sodium acetate, 2g $MgSO_4.7H_2O$, 0.1g $CaCl_2.H_2O$, 2g sodium lactate, 1g yeast extract, 0.1g sodium thioglycollate, 0.1g ascorbic acid, 0.5g $FeSO_4.7H_2O$ and resazurin (Postgate, 1984). Cultures of SRB were maintained at 30°C under anaerobic conditions.

Source of inoculum

Sulphate-reducing bacteria were isolated from mineral spring Gajdovka (Košice, Slovakia). This water was classified as potable, natural, mineralized water with pH 7–8 and strong H_2S odour.

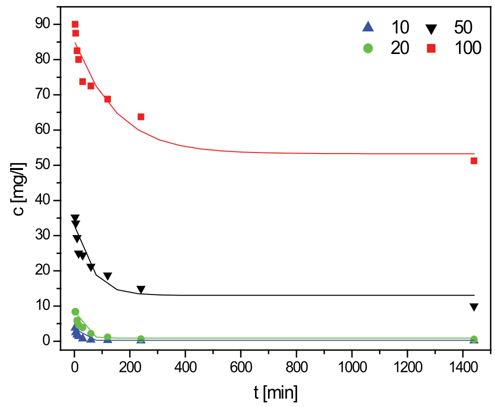

Fig. 1. Kinetics of cadmium sorption by biogenic sorbent

Rys. 1. Kinetyka sorpcji kadmu za pomocą sorbentu biogenicznego

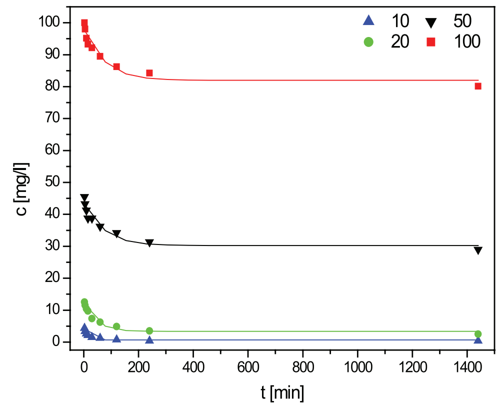

Fig. 2. Kinetics of zinc sorption by biogenic sorbent

Rys. 2. Kinetyka sorpcji cynku za pomocą sorbentu biogenicznego

Sorbent creation

The precipitates in form of biogenic iron sulphides were created by SRB activity in Postgate's C medium modified by $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$ addition. Sorbent production was performed in glass bottles containing 10 vol. % of bacteria inoculum under anaerobic conditions 10 months at 30°C. Dry samples were studied by EDX, SEM and XRD analyses (Jenčárová et al., 2015).

Model solutions

Stock solutions with metal (zinc, cadmium) ions concentration 1 g/l were prepared by dissolving the $ZnSO_4.7H_2O$ and $3CdSO_4.8H_2O$ (p.a. grade) in distilled water. Model solutions for sorption experiments with different initial concentrations of metal ions (10–100 mg/l) were made from prepared stock solutions.

Sorption studies

Kinetics measurements were carried out in plastic Erlenmeyer flasks using mechanical laboratory shaker for 24 hours. The sorbent dose 1 g/l was contacted with 100 ml model solution of a known concentration (10, 20, 50 and 100 mg/l) of Zn^{2+}/Cd^{2+}. The concentration of metal ions from model solution was determined at known time intervals. The pH of solutions before sorption experiments was adjusted at pH 5.8 ± 0.1 with 0.01M NaOH and 0.01M HCl. Experiments were realized at room temperature. The analysis of zinc and cadmium ions was performed by AAS.

Results and discussion

The precipitates created in a consequence of microbial process of sulphate-reduction by SRB were used for sorption experiments. Biogenic iron sulphides were applied in dosing 1 g/l. Model solutions contained concentration of cadmium and zinc ions 10, 20, 50 and 100 mg/l.

Figure 1 and 2 illustrate results of sorption kinetics measurements within 24 hours. It is visible that sorption processes were most remarkable during initial minutes. The metals cations from model solutions with low initial concentration (10 and 20 mg/l) were adsorbed well and the equilibrium was attained very quickly. Zinc sorption from solution (Fig. 2), especially with higher initial concentration (50 and 100 mg/l), was significantly slower and after 24 hours did not reach the values of cadmium, not half. From these findings we can state that sorbent samples showed better affinity for cadmium than for zinc. It was also confirmed by maximum sorption capacity calculated for the sorption study by initial metal concentration 100 mg/l, when this value achieved 22 mg/g for zinc. Maximum sorption capacity of cadmium was 62 mg/g.

The results of the sorption experiment conducted in this study were fitted with the Langmuir and Freundlich adsorption models. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species.

Langmuir isotherm relates metal uptake per unit weight of adsorbent (qe) to the equilibrium adsorbate concentration in the bulk fluid phase (ce). This model is based on the assumption that maximum adsorption (qmax) occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{q_{\max} b c_e}{1 + b c_e} \tag{1}$$

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites

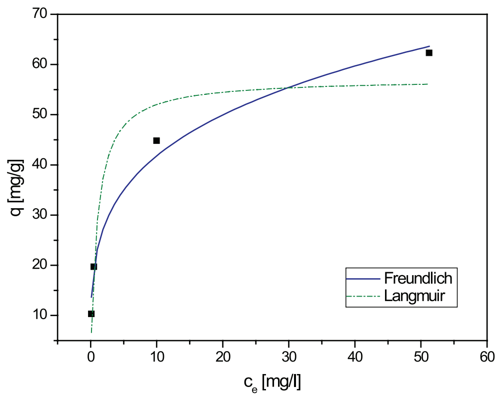

Fig. 3. Adsorption isotherms for Cd^{2+} sorption by biogenic sorbent

Rys. 3. Izoterma adsorpcji jonów Cd^{2+} za pomocą sorbentu biogenicznego

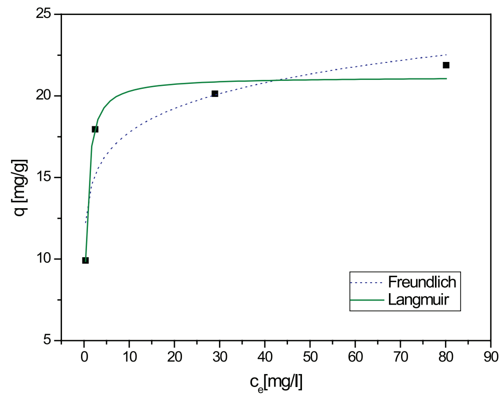

Fig. 4. Adsorption isotherms for Zn^{2+} sorption by biogenic sorbent

Rys. 4. Izoterma adsorpcji jonów Zn^{2+} za pomocą sorbentu biogenicznego

Tab. 1. The sorption isotherms coefficients

Tab. 1. Współczynnik Vedat dla izotermy sorpcji

Metal	**Langmuir isotherm**			**Freundlich isotherm**		
	q_{max}	**b**	**R^2**	**K**	**1/n**	**R^2**
Zinc	21. 17	2.30	0.99	13.66	0.11	0.84
Cadmium	57.17	1.01	0.94	23.11	0.25	0.99

with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of metal adsorbed per unit mass of adsorbent (q_e) and the concentration of the metal at equilibrium (c_e):

$$q_e = Kc_e^{1/n} \quad (2)$$

K and n are empirical constants, they characterize system and are indicators of the adsorption capacity and adsorption intensity, respectively (Kumar and Kirthika, 2010).

Figure 3 and 4 show fitting the experimental points obtained in cadmium and zinc sorption by biogenic iron sulphides with Langmuir and Freundlich isotherm. They indicate that Freundlich isotherm fits Cd^{2+} removal from model solutions a little bit better than Langmuir isotherm. Langmuir model is more suitable to describe the sorption of Zn^{2+}. The Langmuir and Freundlich constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 1.

The values of R2 from 0.94 to 0.99 indicate that the sorption process is satisfactorily described by the selected isotherm models. The maximum sorption capacity for zinc according to Langmuir model was 21.17 mg/g, for cadmium 57.17 mg/g, respectively. This corresponds to values of maximum sorption achieved in the experiments. The constant K (Freundlich model), related to the sorption capacity also confirmed higher value for cadmium. Freundlich model for Zn^{2+} sorption has limited application with a regression coefficient R2 0.84. The calculated parameters introduced in Table 1 present that the sorbent is more suitable for Cd^{2+} removal from model solutions what was also showed by results of kinetics study.

Conclusion

The utilization of sulphate-reducing bacteria in order to prepare biogenic sulphides can be an alternative for wastewaters treatment to remove heavy metals ions. Laboratory experiments showed that this sorbent is able to eliminate zinc and cadmium ions from aqueous solutions. The process of metal ions sorption was described by Langmuir and Freundlich model. The correlation coefficient shows that the sorption process of zinc could be described by the Langmuir equation. Cadmium sorption can be described by both models, there is small variance between them. Results of kinetics study confirm that sorbent samples showed better affinity for cadmium than for zinc. Maximum sorption capacity for cadmium reached 62 mg/g.

Acknowledgements

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Mikrobiologiczny beztlenowy proces redukcji siarczanów do przygotowania sorbentu

Obecność metali w wodach stanowi obecnie typowe zanieczyszczenie antropogeniczne. Ich podwyż-szona zawartość, pochodząca z różnych sektorów przemysłu i wcześniejszej działalności górniczej są niepożądane. Wysokie stężenia metali są niebezpieczne dla wszystkich żywych organizmów. Zawartość metali przekraczająca poziom toksyczności powoduje wiele zaburzeń i chorób oraz szkód ekologicz-nych. Wdrożenie procesów mikrobiologicznych jest jedną z opcji przygotowania sorbentu do usuwania jonów metali z roztworów. Sorbent powstaje w wyniku metabolizmu bakterii redukujących siarczany w środowisku beztlenowym. Sorbent taki jest w stanie usunąć z roztworów takie metale jak Zn, Cd, Pb, Cu, Ni, As.

Słowa kluczowe: bakterie beztlenowe, sorbenty, metale, izotermy adsorpcji