

KRYSTYNA KOSIŃSKA\*, TADEUSZ MIŚKIEWICZ\*\*

## PRECIPITATION OF HEAVY METALS FROM INDUSTRIAL WASTEWATER BY *DESULFOVIBRIO DESULFURICANS*

Wastewater from leather tanning, electroplating, organic dye production and non-ferrous metallurgy was treated in a batch anaerobic bioreactor of the total volume of 2.7 dm<sup>3</sup> using *Desulfovibrio desulfuricans* for the removal of Cr<sub>total</sub>, Cu(II), Fe(II), Ni(II) and Zn(II) as metal sulfides. Except the tannery effluent, the wastewater samples were supplemented with an appropriate quantity of swine manure in order to enrich them with simple organic compounds and biogenic elements (N and P), and thus upgrade the sulfate reducing activity of *D. desulfuricans*. The metal removal efficiencies obtained varied from 85.2% to 98.96%.

### 1. INTRODUCTION

Toxicity of heavy metals to any living organisms has been widely acknowledged. Owing to their specific nature and multidimensional interactions, heavy metals pose a serious hazard to the environment even at low concentrations, and their toxic impact may persist over a long period. There is reliable evidence regarding a rise in the toxicity of heavy metals when they are oxidized or reduced. Ni(II), for example, is less toxic than Ni(IV), and the toxicity of As(III) is lower compared to that of As(V). What is more, heavy metals cannot be chemically or biologically degraded, thus they tend to accumulate, which may cause their content in the food chain to increase dangerously, with serious implications for the consumer's health and even life. In the light of these observations, it is not surprising that the issue of heavy metal contamination has taken on a sense of significance in environmental pollution control, and that it has been given the status of high priority on the list of problems requiring immediate solution.

High concentrations of heavy metals, which noticeably exceed the toxicity threshold for living organisms, are detected, *inter alia*, in mine drainage waters and in indus-

---

\*Institute of Environmental Protection – National Research Institute, Division in Wrocław, Wyrbrzeże Wyspiańskiego 39E, 50-370 Wrocław, Poland.

\*\*Department of Bioprocess Engineering, Wrocław University of Economics, ul. Komandorska 118/120, 53-345 Wrocław, Poland; e-mail: tadeusz.miskiewicz@ue.wroc.pl

trial effluents. To reduce these concentrations, various methods have been developed and examined for applicability. In the majority of instances, these are physicochemical methods involving ion exchange, precipitation, coagulation-flocculation, flotation, membrane filtration and electrodeionization [1, 12, 23, 31]. It is essential to note, however, that the weaknesses inherent in physicochemical methods (their low efficiency, large quantities of sludge produced and high costs involved) severely limit the range of their application. These shortcomings have directed the attention of environmental scientists to alternative methods which have been extensively studied in recent years. Particular consideration has been given to biological methods, specifically to biosorption by non-living biomass [2, 9–11, 24, 26, 29, 30, 32–34, 39]. It is also the application of growing cells [27], including sulfate reducing bacteria (SRB), that has aroused much interest in recent times [4, 6, 7, 16, 25, 28, 36].

SRB are obligate anaerobes that oxidize simple organic substances by utilizing sulfate as a terminal electron acceptor. Sulfate reduction favours the formation of sulfide that occurs in the form of water-soluble anions ( $\text{HS}^-$  at neutral pH and  $\text{S}^{2-}$  at high pH), which react with heavy metal ions and precipitate them as sulfides. Most of the sulfides are stable under anaerobic conditions. The use of SRB for the anaerobic treatment of industrial effluents laden with heavy metals is of benefit not only because of the extent of removal that can be achieved in this way. SRB reduce sulfate, oxidize organic pollutants, and produce alkalinity, which lowers pH, thus providing favourable conditions for the enhancement of SBR activity. An additional benefit derived from the use of SRB is that valuable metals can be easily recycled from the sulfide precipitates.

The manifold possibilities offered by the use of biological sulfate reduction have spurred many investigators to examine the applicability of the process to the detoxification of various heavy-metals-laden industrial effluents. However, most attention has been focused so far on heavy metal removal from acid mine drainage water [i.e. 13–15, 18]. Other industrial effluents have not received due consideration although the concentrations of heavy metals measured there do not very much differ from those observed in mine drainage water. This holds true primarily for the industrial effluents being subject of the present work, where the potential of *Desulfovibrio desulfuricans* to decontaminate heavy-metals-laden wastewater from leather tanning, electroplating, organic dye production and non-ferrous metallurgy was examined.

## 2. EXPERIMENTAL

*Experimental set-up.* The wastewater was treated in a batch anaerobic bioreactor of the total volume of  $2.7 \text{ dm}^3$ . Temperature of the biotreatment processes was maintained at  $38 \text{ }^\circ\text{C}$ . The bioreactor was seeded with  $0.5 \text{ dm}^3$  of inoculum and  $2.0 \text{ dm}^3$  of

wastewater supplemented with swine manure. The samples containing wastewater discharged by non-ferrous metallurgy were enriched with calcium lactate. When necessary, pH of the wastewater was adjusted with 0.1 M NaOH.

*Wastewaters.* The physicochemical parameters and heavy metal concentrations determined in raw wastewater samples are itemized in Table 1.

Table 1

Characterization of the industrial wastewater used in the experiments

Parameter	Wastewater from				Maximum concentration <sup>a</sup>
	Leather tanning	Electroplating	Organic dye production	Non-ferrous metallurgy	
COD, mg·dm <sup>-3</sup>	2284	530	749	49	–
SO <sub>4</sub> <sup>2-</sup> , mg·dm <sup>-3</sup>	1123	3787	2120	813	–
COD/SO <sub>4</sub> <sup>2-</sup>	2	0.14	0.35	0.06	–
pH	8.83	2.4	6	7.8	–
P-PO <sub>4</sub> <sup>3-</sup> , mg·dm <sup>-3</sup>	7.8	0.3	4.1	2.02	–
N-NH <sub>4</sub> <sup>+</sup> , mg·dm <sup>-3</sup>	183.5	10.9	82	2.55	–
Cd(II), mg·dm <sup>-3</sup>	0.056	0.183	trace	0.03	0.4
Co(II), mg·dm <sup>-3</sup>	0.24	0.399	trace	0.113	1
Cr <sub>total</sub> , mg·dm <sup>-3</sup>	1.26	125.6	trace	0.041	1
Cu(II), mg·dm <sup>-3</sup>	0.049	32.95	4.9	0.91	1
Fe(II), mg·dm <sup>-3</sup>	5.1	129.98	5.2	0.29	–
Ni(II), mg·dm <sup>-3</sup>	0.302	218.04	trace	0.184	1
Pb(II), mg·dm <sup>-3</sup>	0.12	1.67	trace	0.177	1
Zn(II), mg·dm <sup>-3</sup>	0.172	250	0.74	3.25	5

<sup>a</sup>Maximum permissible concentrations of heavy metals for treated effluents that are to be discharged into municipal sewerage systems in Poland [37].

The wastewater samples examined, except those containing tannery effluents, required enrichment with simple organic compounds and biogenic elements (N and P). For this purpose, use was made of the liquid effluent from industrial pig farming (swine manure). The manure was characterized by the following physicochemical parameters: COD (chemical oxygen demand in mg·dm<sup>-3</sup>) – 2940, concentrations of SO<sub>4</sub><sup>2-</sup>, N-NH<sub>4</sub><sup>+</sup>, and P-PO<sub>4</sub><sup>3-</sup> – 250, 410 and 81.5 mg·dm<sup>-3</sup>, respectively; alkalinity as CaCO<sub>3</sub> – 1900 mg·dm<sup>-3</sup>, and a pH – 7.7. The tannery effluent had to be neutralized because of the low pH (2.4). The parameters of the wastewater being treated in the bioreactor, upon upgrading the COD to SO<sub>4</sub><sup>2-</sup> ratio, neutralization and inoculation, are itemized in Table 2. The heavy metal concentrations given in the table are those exceeding the maximum permissible concentrations specified for treated industrial effluents that are to be discharged into municipal sewerage systems [37] (Table 1).

Table 2

Characterization of the wastewater after upgrading the COD/SO<sub>4</sub><sup>2-</sup> ratio, neutralization and inoculation

Parameter	Wastewater from			
	Leather tanning	Electroplating	Organic dye production	Non-ferrous metallurgy
COD, mg·dm <sup>-3</sup>	1800	2853	1520	1438
SO <sub>4</sub> <sup>2-</sup> , mg·dm <sup>-3</sup>	900	2583	585	560
COD/SO <sub>4</sub> <sup>2-</sup>	2	1.1	2.6	2.6
pH	8.75	6.67	7.48	7.56
Cd(II), mg·dm <sup>-3</sup>	trace	trace	trace	trace
Co(II), mg·dm <sup>-3</sup>	trace	trace	trace	trace
Cr <sub>total</sub> , mg·dm <sup>-3</sup>	0.938	trace	trace	trace
Cu(II), mg·dm <sup>-3</sup>	trace	0.48	0.7	0.55
Fe(II), mg·dm <sup>-3</sup>	trace	trace	3.65	trace
Ni(II), mg·dm <sup>-3</sup>	trace	38.5	trace	trace
Pb(II), mg·dm <sup>-3</sup>	trace	trace	trace	trace
Zn(II), mg·dm <sup>-3</sup>	trace	7.32	1.15	1.95

*Inoculum.* The inoculum was a mixed anaerobic culture dominated by the species *Desulfovibrio desulfuricans*, which was isolated from hydrosulfuric curative waters of the spa Busko Zdrój in Poland and had the volume of 0.5 dm<sup>3</sup> in each experiment. The total solids (TS), volatile solids (VS), mineral solids (MS), COD, SO<sub>4</sub><sup>2-</sup> and alkalinity of the inoculum were (g·dm<sup>-3</sup>) 91, 28, 63.7, 0.1, 0.02 and 2.7 as CaCO<sub>3</sub>, respectively. pH of the inoculum was 7.9. The composition of the growth medium for *D. desulfuricans* and the method of fabrication of inoculum have been described elsewhere [20].

*Analyses.* The raw wastewater, inoculum and biotreated wastewater were analyzed for pH, COD, SO<sub>4</sub><sup>2-</sup>, N-NH<sub>4</sub><sup>+</sup>, P-PO<sub>4</sub><sup>3-</sup>, alkalinity, TS, VS and MS using standard methods [3]. Heavy metals were determined with an AAS-30 Carl Zeiss Jena flame atomic absorption spectrometer. Samples for analyses were collected daily and filtered through a filter paper. Metal assays and other measurements were conducted in triplicate. The experimental error was within 5% of the mean throughout.

### 3. RESULTS

Chromium, a characteristic heavy metal contaminating wastewater from tanning operations [30, 35], dominated in the tannery effluent used for the purpose of our study, and it was the only heavy metal whose concentration exceeded the maximum permissible value (Table 1). There was no need to enrich the tannery wastewater sam-

ples with sulphate or organic compounds since the value of the COD to  $\text{SO}_4^{2-}$  ratio failed to be higher than 0.8. The variations in  $\text{Cr}_{\text{total}}$  concentration observed in the tannery effluent during precipitation in the presence of *D. desulfuricans* are shown in Fig. 1.

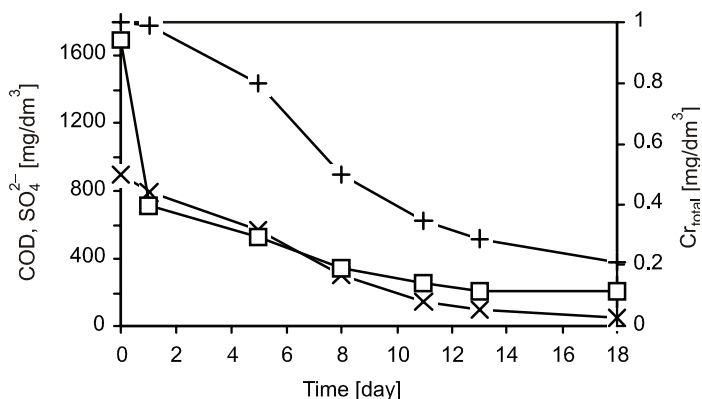


Fig. 1. Time dependences of the concentrations of  $\text{Cr}_{\text{total}}$  (□),  $\text{SO}_4^{2-}$  (×) and COD (+) in the tannery effluent treated using SRB

The concentration of  $\text{Cr}_{\text{total}}$  was reduced rapidly to the value of  $0.398 \text{ mg}\cdot\text{dm}^{-3}$  during the first 24 h of the 18-day process. Then it noticeably decreased to stabilize at the value of  $0.116 \text{ mg}\cdot\text{dm}^{-3}$  from the 13th day further on. The  $\text{Cr}_{\text{total}}$ ,  $\text{SO}_4^{2-}$  and COD removal efficiencies amounted to 87.6%, 88.9% and 78.7%, respectively. The concentrations of  $\text{SO}_4^{2-}$  and COD persisting in the effluent from the biotreatment process amounted to  $99.9 \text{ mg}\cdot\text{dm}^{-3}$  and  $383.4 \text{ mg}\cdot\text{dm}^{-3}$ , respectively.

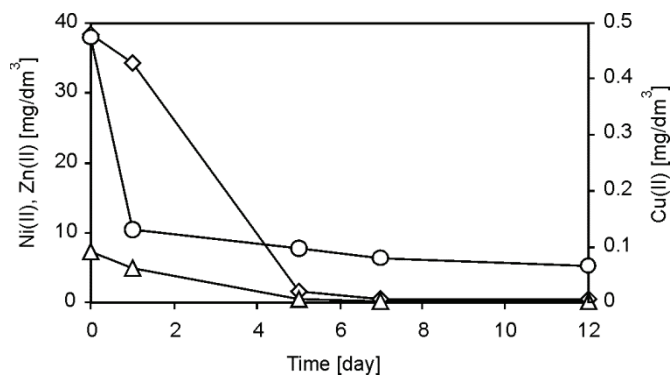


Fig. 2. Time dependences of the concentrations of Cu(II) (○), Ni(II) (◇) and Zn(II) (△) in the wastewater from electroplating treated using SRB

The electroplating effluent ( $1.4 \text{ dm}^3$ ) was neutralized to pH of 6.67 and enriched with swine manure ( $0.6 \text{ dm}^3$ ). In the course of the biotreatment process which took 12 days, the wastewater samples were analyzed for Cu(II), Ni(II) and Zn(II), since solely these heavy metals displayed concentrations exceeding the maximum permissible values for industrial effluents discharged into municipal sewerage systems (Table 1). Relevant data are shown in Fig. 2. Decrease in the concentrations of dissolved Zn(II), Ni(II) and Cu(II) amounts to 97.53%, 98.96% and 85.42%, respectively. The efficiency of  $\text{SO}_4^{2-}$  and COD after biological reduction attained totals 97.13% and 91.24%, respectively. The concentrations of  $\text{SO}_4^{2-}$  and COD persisting in the effluent from the biotreatment process were  $74 \text{ mg}\cdot\text{dm}^{-3}$  and  $250 \text{ mg}\cdot\text{dm}^{-3}$ , respectively.

The samples collected at the plant producing organic dyes included decolorized overall production wastewater with a poor content of organic compounds. Enrichment was attained by adding  $0.7 \text{ dm}^3$  of swine manure to  $1.3 \text{ dm}^3$  of the wastewater from organic dye production. Of the heavy metals under analysis, only Cu(II) and Zn(II) were found to occur in the raw dye effluent at concentrations exceeding the maximum permissible values (Table 1). The wastewater samples were also analyzed for the presence of Fe(II), although no maximum permissible concentrations had been established in Poland for this heavy metal in the industrial effluents that are to be discharged into the sewerage system. The concentration of Fe(II) in the wastewater samples was found to be high, which prompted the authors of this paper to investigate the potential of *D. desulfuricans* for the removal of this heavy metal. Figure 3 shows the patterns of decrease in the concentrations of the investigated heavy metals during the 6-day bioprecipitation process. Thus, the extent of reduction obtained *via* this route totalled 95.89%, 96.86% and 94.61% for Fe(II), Cu(II) and Zn(II), respectively. The concentrations of these heavy metals persisting in the treated effluent amounted to  $0.15 \text{ mg}\cdot\text{dm}^{-3}$ ,  $0.022 \text{ mg}\cdot\text{dm}^{-3}$  and  $0.062 \text{ mg}\cdot\text{dm}^{-3}$ , respectively.

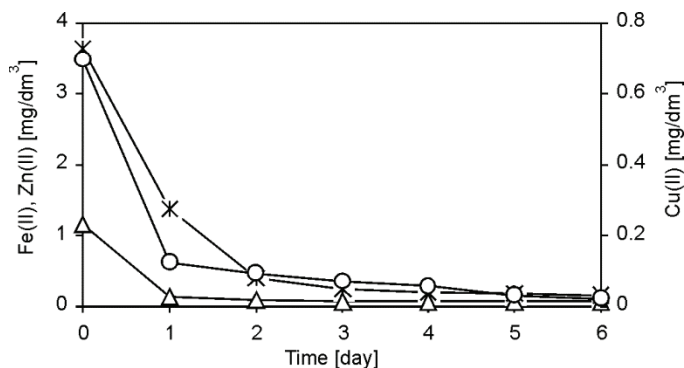


Fig. 3. Time dependences of the concentrations of Cu(II) (O), Fe(II) (\*) and Zn(II) (Δ) time in the wastewater from organic dye production treated using SRB

Upon inoculation, the content of organic substances in the wastewater samples occurred in excess ( $1520 \text{ mg}\cdot\text{dm}^{-3}$ ) over the content of  $\text{SO}_4^{2-}$  ( $585 \text{ mg}\cdot\text{dm}^{-3}$ ). It was, however, assumed that such a quantity of sulfate would suffice to remove heavy metals from the wastewater. The efficiency of the removal attained (which is higher than 94%), as well as the concentration of  $\text{SO}_4^{2-}$  persisting in the effluent from the biotreatment process (which amounts to  $28 \text{ mg}\cdot\text{dm}^{-3}$ ), indicates that there was no deficit in sulfate. As a result of the biotreatment process, the extent of reduction in the concentrations of  $\text{SO}_4^{2-}$  and COD totalled 95.2% and 26.32%, respectively. The concentration of COD persisting in the effluent amounted to  $1120 \text{ mg}\cdot\text{dm}^{-3}$ .

Since the wastewater from non-ferrous metallurgy was deficient in readily available carbon and biogenic elements for SRB growth, the samples were enriched with 6 g of calcium lactate as a carbon source and with  $0.15 \text{ dm}^3$  of swine manure as a source of biogens. The replacement of a large part of the effluent from industrial pig farming by lactate prevented the raw wastewater being excessively diluted. The maximum permissible concentration was found to be exceeded only in the case of Zn(II) (Table 2). The pattern of Zn(II), COD and  $\text{SO}_4^{2-}$  reduction in the course of the 12-day biotreatment process is shown in Fig. 4. The precipitation of zinc terminated after 48 h of the biotreatment process, and its concentration in the liquid phase stabilized at the level of  $0.1 \text{ mg}\cdot\text{dm}^{-3}$ . This means that 94.77% of the heavy metal penetrated into the precipitate. The reduction in the concentrations of  $\text{SO}_4^{2-}$  and COD continued to the end of the 12th day; their concentrations persisting in the effluent from the biotreatment process totalled  $33 \text{ mg}\cdot\text{dm}^{-3}$  and  $108 \text{ mg}\cdot\text{dm}^{-3}$ , respectively.

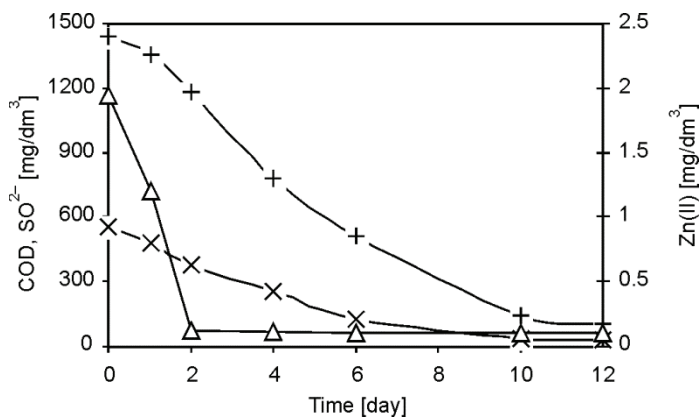


Fig. 4. Time dependences of the concentrations of Zn(II) ( $\Delta$ ), COD (+) and  $\text{SO}_4^{2-}$  ( $\times$ ) in the wastewater from non-ferrous metallurgy treated using SRB

A close analysis of the plot describing the pattern Zn(II) concentrations during the precipitation process makes it clear that the concentration of dissolved Zn(II) began to increase gradually on the 6th day to reach the value of  $0.13 \text{ mg}\cdot\text{dm}^{-3}$  by the end of the process (after 12 days). Seemingly, this pattern is attributable to the desorption of Zn(II) from the surface of its sulfide. It is widely acknowledged that during biological sulfate reduction metals adsorb onto the surface of metal sulfides formed [17].

#### 4. DISCUSSION

The wastewater treated in the bioreactor showed lower concentrations of heavy metals (Table 2) than did the raw wastewater (Table 1). This is attributable to the dilution of raw wastewater in the bioreactor upon inoculation, neutralization and swine manure addition.

The choice of the industrial effluents for the purpose of the study was based on the assumption that they contain large quantities of sulfate and heavy metals. When heavy metals are to be removed from an industrial effluent using *D. desulfuricans*, a large quantity of sulfate in the wastewater is a requisite for maximizing the extent of removal. Biological sulfate reduction in *D. desulfuricans* cells is a source of  $\text{HS}^-$  and/or  $\text{S}^{2-}$  anions which react with heavy metal cations and precipitate them as sulfides (sparingly soluble or insoluble). Another requisite for enhancing the efficiency of heavy metal removal is the presence of simple organic compounds, which are electron donors in biological sulfate reduction. It seems therefore advisable to take into account the value of the  $\text{COD}/\text{SO}_4^{2-}$  ratio, which can be a control criterion for the biological hydrogen sulfide production [19, 38]. Choi and Rim [8] observed that the minimum value of the COD to  $\text{SO}_4^{2-}$  ratio, 0.67, sufficed to provide the maximum extent of sulfate reduction. We found in a previous work [21] that the *D. desulfuricans* cells used in the study reported on in this paper efficiently reduced sulfate and removed organic pollutants at a COD to  $\text{SO}_4^{2-}$  ratio of at least 0.8. As can be seen from the data in Table 1, it is only the effluent from leather tanning that shows the desired value of the  $\text{COD}/\text{SO}_4^{2-}$  ratio (2.0). In the current work, however, the  $\text{COD}/\text{SO}_4^{2-}$  ratio in every instance took a value higher than 0.8, since the assumption had to be made that not all of the organic compounds in the investigated industrial wastewater after supplementation with swine manure would be assimilated by *D. desulfuricans*. The idea of using this mode of wastewater enrichment has been derived from a previous work [22], where swine manure was found to be a rich source of simple organic compounds and biogenic elements for the *D. desulfuricans* cells applied in the present study. It is essential to note, however, that only the removal of heavy metals and the reduction in sulfate were sufficiently high. The effluent from the biotreatment process still contained large quantities of non-utilized organic pollutants, which suggests that the bioprecipitation of



heavy metals should constitute one of the unit processes in the treatment train for heavy-metal-laden industrial effluents.

The work reported here has substantiated some earlier findings about the high extent of heavy metal removal from industrial wastewater obtained with bacteria of the genus *Desulfovibrio* [16]. As for our present study, the separation of metal pollutants was very high in all of the effluents, ranging between 85.2% and 98.96%, and the concentrations of dissolved Cr<sub>total</sub>, Cu(II), Fe(II), Ni(II) and Zn(II) persisting in the effluent after the biotreatment process were lower than their maximum permissible values.

All the findings suggest that the potential of the SRB used for the removal of heavy metals from industrial wastes can be enhanced. It can therefore be expected that if a more efficient source of simple organic compounds than the pig manure is used, if the operating parameters of the bioreactor are optimized, and if the bioreactor works in a continuous mode, the metal bioprecipitation rate will increase.

When the SRB biomass is to be used for the removal of heavy metals from an industrial effluent, it is necessary to take into account their toxic influence on the bacteria of the genus *Desulfovibrio* [5]. In the study reported on in this paper heavy metals failed to exert a toxic effect on the SRB.

## 5. CONCLUSIONS

The use of biological sulfate reduction by *Desulfovibrio desulfuricans* for heavy metal decontamination of the wastewater from leather tanning, electroplating, organic dye production and non-ferrous metallurgy has been left in the literature without due consideration. This holds true primarily for the effluents from organic dye production and non-ferrous metallurgy. The present work shows that the use of *D. desulfuricans* provides a high extent of heavy metal removal from all of the effluents tested.

There is evidence to suggest that the potential of *D. desulfuricans* for the removal of heavy metals from industrial wastewater can be enhanced by replacing the swine manure with a more efficient source of simple organic compounds, by optimizing the operating parameters of the bioreactor, and substituting the continuous mode of operation for the batch mode.

The precipitation of heavy metals using *D. desulfuricans* should constitute one of the unit processes in the treatment train for the effluents examined.

## REFERENCES

- [1] ADHOUM N., MONSER L., BELLAKHAL N., BELGAIED J-E., J. Hazard. Mater., 2004, 112, 207.
- [2] AHLUWALIA S.S., GOYAL D., Bioresour. Technol., 2007, 98, 2243.
- [3] *Standard Methods for the Examination of Water and Wastewater*. 15<sup>th</sup> Edition, American Public Health Association, Washington 1975.
- [4] BOSHOF, G. DUNCAN J., ROSE P.D., Water Res., 2004, 38, 2651.

- [5] CABRERA G., PÉREZ R., GÓMEZ J.M., ÁBALOS A., CANTERO D., *J. Hazard. Mater.*, 2006, 135, 40.
- [6] CAO J., ZHANG G., MAO Z., FANG Z., YANG C., *Miner. Eng.*, 2009, 22, 289.
- [7] CHANG I.S., KIM B.H., *Chemosphere*, 2007, 68, 218.
- [8] CHOI E., RIM J.M., *Water Sci. Technol.*, 1991, 23, 1259.
- [9] CUI J., ZHANG L., *J. Hazard. Mater.*, 2008, 158, 228.
- [10] DEMIRBAS A., *J. Hazard. Mater.*, 2008, 157, 220.
- [11] DENG X., LI Q.B., LU Y.H., SUN D.H., HUANG Y.L., CHEN X.R., *Water Res.*, 2003, 37, 2505.
- [12] FENG X., WU Z., CHEN X., *Sep. Purif. Technol.*, 2007, 57, 257.
- [13] GIBERT O., DE PABLO J., CORTINA J.L., AYORA C., *Rev. Environ. Sci. Biotechnol.*, 2002, 1, 327.
- [14] GLOMBITZA F., *Waste Manage.*, 2001, 21, 197.
- [15] JIMÉNEZ-RODRIGUEZ A.M., DURÁN-BARRANTES M.M., BORJA R., SÁNCHEZ E., COLMENAREJO M.F., RAPOSO F., *J. Hazard. Mater.*, 2009, 165, 759.
- [16] JONG T., PARRY D.L., *Water Res.*, 2003, 37, 3379.
- [17] JONG T., PARRY D.L., *J. Colloid Interface Sci.*, 2004, 275, 61.
- [18] JOHNSON D.B., HALLBERG K.B., *Sci. Total Environ.*, 2005, 338, 3
- [19] KHANAL S.K., HUANG J.-C., *Water Environ. Res.*, 2005, 77, 3037.
- [20] KOSIŃSKA K., MIŚKIEWICZ T., ILNICKA-OLEJNICZAK O., *Environ. Prot. Eng.*, 1995, 21, 83.
- [21] KOSIŃSKA K., MIŚKIEWICZ T., *Biotechnol. Lett.*, 1999, 21, 299.
- [22] KOSIŃSKA K., MIŚKIEWICZ T., *Environ. Technol.*, 2000, 21, 585.
- [23] KURNIAWAN T.A., CHAN G.Y.S., LO W.-H., BABEL S., *Chem. Eng. J.*, 2006, 118, 83.
- [24] LESMANA S.O., FEBRIANA N., SOETAREDJIO F.E., SUNARSO J., ISMADJI S., *Biochem. Eng. J.*, 2009, 44, 19.
- [25] LUPTAKOVA A., KUSNIEROVA M., *Hydrometallurgy*, 2005, 77, 97.
- [26] MACK C., WILHELMI B., DUNCAN J.R., BURGESS J.E., *Biotechnol. Adv.*, 2007, 25, 264.
- [27] MALIK A., *Environ. Int.*, 2004, 30, 261.
- [28] MARTINS M., FALEIRO M.L., BARROS R.J., VERISSIMO A.R., BARREIROS M.A., COSTA M.C., *J. Hazard. Mater.*, 2009, 166, 706.
- [29] MUÑOZ R., ALVAREZ M.T., MUÑOZ A., TERRAZAS E., GUIEYSSE B., MATTIASSEN B., *Chemosphere*, 2006, 63, 903.
- [30] ONYANCHA D., MAVURA W., NGILA J.C., ONGOMA P., CHACHA J., *J. Hazard. Mater.*, 2008, 158, 605.
- [31] PANAYOTOVA T., DIMOVA-TODOROVA M., DOBREVSKY I., *Desalination*, 2007, 206, 135.
- [32] ROMERA E., GONZALEZ F., BALLESTER A., BLÁZQUEZ M.L., MUÑOZ J.A., *Bioresour. Technol.*, 2007, 98, 3344.
- [33] SAY R., DENIZLI, A., ARICA M.Y., *Bioresour. Technol.*, 2001, 76, 67.
- [34] SRIVASTAVA N.K., MAJUMDER C.B., *J. Hazard. Mater.*, 2008, 151, 1.
- [35] TARIQ S.R., SHAH M.H., SHAHEEN N., KHALIQUE A., MANZOOR S., JAFFAR M., *J. Hazard. Mater.*, 2005, 122, 17.
- [36] THABET O.B.D., BOUALLAGUI H., CAYOL J.-L., OLLIVIER B., FARDEAU M.-L., HAMDI M., *J. Hazard. Mater.*, 2009, 167, 1133.
- [37] Decree of the Minister of Building of 14 July 2006 (Dz.U. z 2006 r. Nr 136, poz. 964) (in Polish).
- [38] VELASCO A., RAMÍREZ M., VOLKE-SEPÚLVEDA T., GONZÁLEZ-SÁNCHEZ A., REVAH S., *J. Hazard. Mater.*, 2008, 151, 407.
- [39] WANG J., CHEN C., *Biotechnol. Adv.*, 2006, 24, 427.