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EFFECT OF HETEROTROPHIC BIOLEACHING ON EFFECIENCY OF AUTOTROPHIC BIOLEACHING OF METALS FROM TOXIC WASTE HEAPS IN ZLOTY STOK REGION

WPŁYW BIOŁUGOWANIA HETEROTROFICZNEGO NA EFEKTYWNOŚĆ BIOŁUGOWANIA AUTOTROFICZNEGO METALI Z TOKSYCZNYCH ZWAŁOWISK ZŁOTOSTOCKICH

Abstract: The results of two step bioleaching (autotrophic after heterotrophic) of mine wastes from heap "Jan" in Zloty Stok were presented. The results of the performed processes are very promising. 67 % of arsenic was extracted and exceedance of its permitted quantities in soil was reduced 3 times.

Keywords: biotechnology, bioleaching; bioreactor, heterotrophic bacteria, autotrophic bacteria, mineral wastes

Zloty Stok – a small town built at the feet of the Zlote Mountains is one of the most popular tourist centre in The Klodzko Land and is the place where the oldest gold mine in Poland is located. The first historical document mentioning the existence of the settlement and mining works in the surroundings of Zloty Stok goes back to 1273. Exploited deposits were mainly gold bearing arsenic ores: loellingite ($FeAs_2$) and arsenopyrite ($FeAsS$). The peak of gold mining in Zloty Stok fell for the 16th century when up to 150 kg of gold were recovered every year. The mine was closed in 1962 [1]. This seven centuries lasting exploitation of arsenopyrite deposits and smelting activities left surroundings of Zloty Stok mine with waste heaps containing high levels of metals, especially arsenic [2]. Considering this toxic waste heaps lying in the heart of the tourist

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region, remediation is inevitable and strongly recommended. By using bioleaching, the remediation method which allows metals recovery, there is possibility to turning waste heaps into unconventional ore deposits [2].

Study of bioleaching of sulphide minerals associated with metaloorganic and organic matter in case of copper shales showed that preliminary heterotrophic (neutral) bioleaching of the mineral material provides better efficiency of its further autotrophic (acid) bioleaching. Combination of this two processes allows for increasing the yield of metals in the leaching solution [3, 4]. The results were encouraging and suggested conducting similar two step bioleaching process in case of the mineral material from the waste heaps of Zloty Stok. To verify two step bioleaching efficiency in case of gold bearing arsenic ores two processes were performed and obtained results were compared: classical autotrophic bioleaching and two step autotrophic after heterotrophic bioleaching.

Experiment I

Test material was obtained from the waste heap "JAN", placed near road Zloty Stok – Ladek Zdroj. Samples from three characteristic places were taken. Material was crushed, sieved and averaged. Graining was 0.1–0.3 mm. Material contains: Ni – 151.0 ppm; Cu – 331.0 ppm; As – 4.54 %; Cd – 1.05 ppm; Cr – 71.7 ppm; Co – 22.8 ppm; Tl – 0.95 ppm and Pb – 62.0 ppm. Before bioleaching material was treated with 10N sulphuric acid in order to lower the pH level. After treatment chemical analyses were made. Material after pretreatment contains: Ni – 122.0 ppm; Cu – 310.0 ppm; As – 3.72 %; Cd – 0.36 ppm; Cr – 51.5 ppm; Co – 10.5 ppm; Tl – 0.59 ppm and Pb – 43.0 ppm.

The sample of pretreated mineral material (350 g) was placed in a tank bioreactor Biostat 5L with 3000 cm^3 2K solution and 500 cm^3 cultures of active strains of autochthonic autotrophic bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* in ratio 1:1 [5]. Process was performed 30 days at temperature 35 ^oC, pH = = 2. The system was constantly stirred (200 rpm) and aerated. At the end of the process material was flushed, dried and chemical analysis was made. The results were: Ni – 82.0 ppm; Cu – 253.0 ppm; As – 3.4 %; Cd – 0.26 ppm; Cr – 42.6 ppm; Co – 10.1 ppm; Tl – 0.52 ppm and Pb – 31.0 ppm.

Experiment II

The second process of bioleaching of the material from heap "JAN" was performed in two steps. In the first step the sample of prepared mineral material (350 g) was placed in tank bioreactor Biostat with 3500 cm^3 leaching medium consisted of mineral solution inoculated with selected active strains of heterotrophic bacteria *Bacillus lentu*, *B. latero-sporus*, *B. cereus* and *B. brevis* isolated from examined material [5]. These bacteria are known by their ability to oxidation of organic and metalorganic matter and their resistance to high arsenic concentrations. Process lasted 20 days, at temperature 25 ^oC, pH was in range (6.5–7.0). The system was constantly stirred (200 rpm) and aerated. At the end of the process chemical analysis of material was made. The results were: Ni – 121.0 ppm; Cu – 298.0 ppm; As – 2.95 %; Cd – 1.03 ppm; Cr – 79.1 ppm; Co – 18.0 ppm; Tl – 0.73 ppm and Pb – 62.0 ppm.

After heterotrophic bioleaching material was filtered, dried and subjected to standard pretreatment before autotrophic leaching. The chemical analysis of the pretreatment material was made. The results were: Ni – 113.0 ppm; Cu – 279.0 ppm; As – 2.2 %; Cd – 0.38 ppm; Cr – 55.9 ppm; Co – 11.4 ppm; Tl – 0.59 ppm and Pb – 34.2 ppm.

The sample of material (180 g) was placed in tank bioreactor Biostat with 1300 cm^3 2K solution and 500 cm^3 cultures of active strains of autochthonic autotrophic bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* in ratio 1:1 [4]. Process was performed 35 days at temperature 35 ^oC, pH = 2. The system was constantly stirred (200 rpm) and aerated.

At the end of the process chemical analysis of material was made. The results were: Ni – 82.0 ppm; Cu – 207,0 ppm; As – 1.5 %; Cd – 0.10 ppm; Cr – 39.8 ppm; Co – 10.1 ppm; Tl – 0.52 ppm and Pb – 32.5 ppm.

Results and discussion

The total amounts of extracted metals in the first experiment – autotrophic bioleaching of raw material – included chemical leaching during pretreatment and further autotrophic bioleaching are presented in Table 1.

Table 1

The total amounts of extracted metals

Element	Chemical leaching	Autotrophic bioleaching	Total leaching
	[%]		
Ni	19.20	32.8	45.70
Cu	6.40	18.4	23.60
As	18.00	8.6	25.10
Cd	68.57	21.2	75.24
Cr	28.20	17.3	41.60
Co	54.00	3.8	55.00
Tl	0.00	11.9	11.90
Pb	30.60	27.9	50.00

All of the monitored metals, except thallium, were found in the leachate after chemical pretreatment and all of them were found in the leachate after autotrophic bioleaching. The highest yield was obtained for nickel. The total extraction was: 75.24 % Cd; 55.0 % Co; 50.0 % Pb; 45.7 % Ni; 41.6 % Cr; 25.1 % As; 23.6 % Cu and 11.9 % Tl.

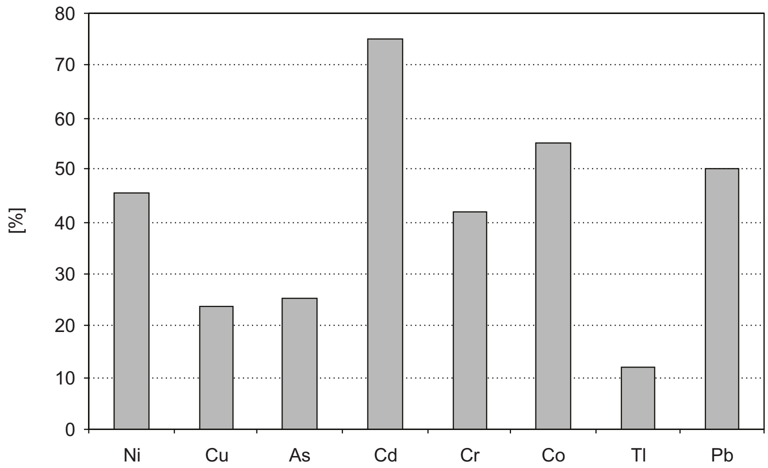

Fig. 1. The efficiency of autotrophic bioleaching of monitored metals from the raw material

The total amounts of extracted metals in the second experiment – autotrophic bioleaching of material after heterotrophic bioleaching – included chemical leaching in the middle stage are presented in Table 2.

Table 2

The total amounts of extracted metals

Element	Stage I Heterotrophic bioleaching	Stage II Chemical leaching	Stage III Autotrophic leaching	Total leaching
	[%]			
Ni	19.9	6.6	27.4	45.7
Cu	9.97	6.4	25.8	37.5
As	35.0	25.4	31.8	67.0
Cd	1.9	63.1	73.7	95.0
Cr	0.0	22.0	28.8	44.5
Co	21.0	36.7	11.4	55.0
Tl	0.0	0.0	11.9	11.9
Pb	0.0	45.0	5.0	47.6

The best yield was obtained for cadmium (95.0 %), arsenic (67.0 %) and cobalt (55.0 %). The yields of nickel (45.7 %), chromium (44.5 %) and copper (37.5 %) could also be considered as satisfying.

The heterotrophic bioleaching of chromium, thallium and lead was not observed while arsenic (35.0 %), cobalt (21.0 %) and nickel (19.9 %) has been leached very well. The chemical leaching of cadmium (63.1 %), lead (45.0 %) and cobalt (36.7 %) was significant, as well as autotrophic leaching of cadmium (73.7 %).

Comparison of the results of experiment I (autotrophic leaching) and experiment II (autotrophic leaching after heterotrophic) shows that heterotrophic leaching led prior to autotrophic had a positive impact on the results obtained in case of cadmium, copper and arsenic (Fig. 2.).

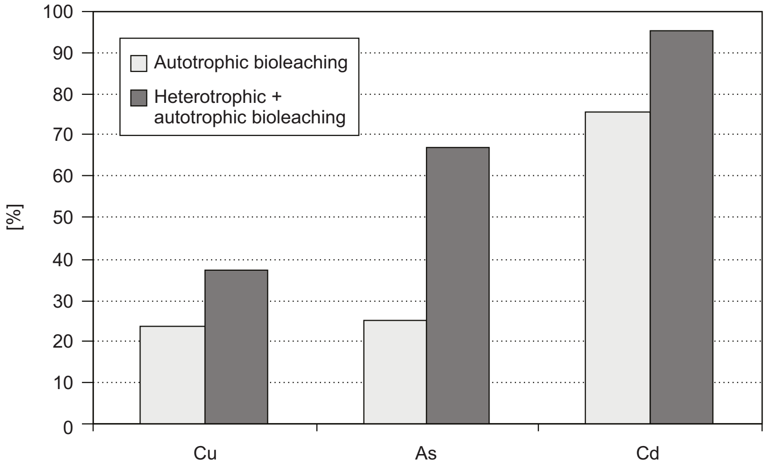

Fig. 2. Comparison of Cu, As and Cd extraction in autotrophic and heterotrophic + autotrophic bioleaching

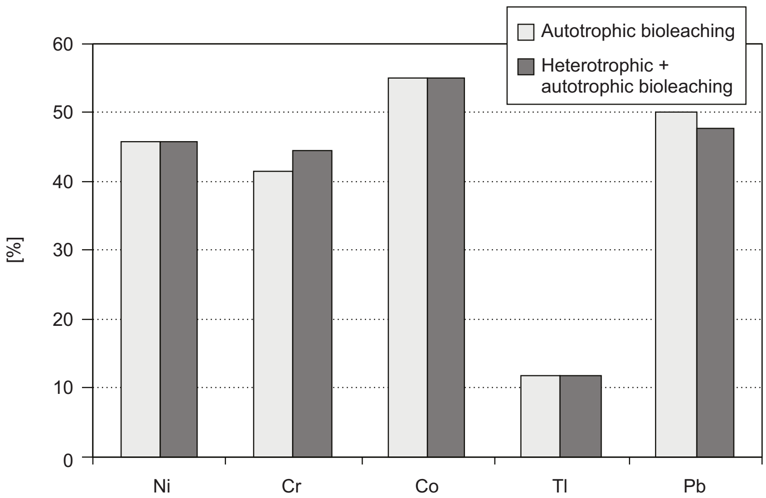

Fig. 3. Comparison of others metals extraction in autotrophic and heterotrophic + autotrophic bioleaching

Conclusions

The efficiency of recovery of the most toxic arsenic equals 67 % in experiment II and was almost three times better than in experiment I. Such a good extraction level is sufficient reason to introduce two step bioleaching as a remediation process for Zloty Stok waste heaps.

However the concentration of arsenic in the material from heap "Jan" was reduced from 45.4 g/kg (4.54%) to 15 g/kg (1.5 %) i.e. three times and exceeds the permitted quantities 300 times for the class C soils and 700 times for the class D soils, reduction of its concentration by 67 % can be considered as a success [6]. There are strong evidences that two step bioleaching can be more effective using tube bioreactors [2, 7, 8].

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Abstrakt: Przedstawiono wyniki badań dwuetapowego bioługowania (neutralnego i kwaśnego) odpadów pogórniczych zdeponowanych na hałdzie "Jan" w Złotym Stoku. Uzyskane wyniki dowiodły słuszności podjętych badań. Wyługowaniu uległo na przykład 67 % arsenu zawartego w materiale. Taki wynik spowodował, że przekroczenie dopuszczalnego poziomu zawartości arsenu w glebie zmalało trzykrotnie.

Słowa kluczowe: biotechnologia, bioługowanie, bakterie heterotroficzne, bakterie autotroficzne