SEMI-PASSIVE TREATMENT OF MINE WASTE WATER IN ANAEROBIC CONDITIONS

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ABSTRACT. In this study synthetic acid mine waters, similar to the naturally generated ones in mines, were treated by a passive system under anaerobic conditions. The constructed laboratory-scaled system consisted of three anaerobic chambers connected sequentially, each one with a volume of 15 l. Each chamber was filled with a mixture of 4.5 kg of solid organic substrate (cattle manure, sawdust and hay in a ratio 4:1:1) and 2 kg of limestone with particles size distribution of 5÷10 mm. The model solution contained SO_4^{2-} (3000 mg/l), Cu^{2+} (10 mg/l), Zn^{2+} (25 mg/l), Cd^{2+} (5 mg/l), As^{5+} (5 mg/l), Fe^{2+} (100 mg/l) and Mn^{2+} (20 mg/l). Passive and semi-passive treatment was conducted at a hydraulic retention time of 6 days. During the stage of semi-passive treatment, lactate was added as an additional carbon and energy source. The results demonstrated that the sulphate-removal efficiency from mine waste water by passive treatment was insignificant (approx. 9 %), while the addition of lactate at concentrations of 1, 2, 3 and 4 ml/l increased the removlal rate for sulphates as follows: 35.7 %, 67.1 %, 82.3 % and 98.3 %. In all studied regimes the ions of copper, iron, zinc, cadmium and arsenic were effectively removed (97 %-99.9 %). The rate of manganese removal was low (30 %). The results could serve as a basis for the establishment of pilot-scaled installations for semi-passive treatment of acid mine water in the studied manner.

Keywords: acid mine water, sulphate-reduction, semi-passive treatment

ПОЛУПАСИВНО ТРЕТИРАНЕ НА МИННИ ОТПАДЪЧНИ ВОДИ В АНАЕРОБНИ УСЛОВИЯ

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РЕЗЮМЕ. Проследено е пречистването на синтетични кисели руднични води, имитиращи генерираните в миннодобивната дейност в лабораторна инсталация за анаеробно пасивно третиране. Лабораторната инсталация е изградена от три последователно свързани анаеробни камери, всяка с обем 15 l. Всеки съд е запълнен със смес от 4.5 kg твърд органичен субстрат (говежда тор, дървени стърготини и сено в съотношение 4:1:1) и 2 kg варовик с размер на частиците 5÷10 mm. Третираният моделен разтвор съдържа SO_4^{2-} (3000 mg/l), Cu^{2+} (10 mg/l), Zn^{2+} (25 mg/l), Cd^{2+} (5 mg/l), As^{5+} (5 mg/l), Fe^{2+} (100 mg/l) и Mn^{2+} (20 mg/l). Проведено е пасивно и полупасивно третиране при осигурено контактно време от шест денонощия, като по време на стадия за полупасивно третиране в системата е добавен лактат като допълнителен източник на въглерод и енергия. Установено е, че ефективността на отстраняване на сулфати от водите при пасивно третиране е приблизително 9 %, а при добавяне на лактат в концентрации 1, 2, 3 и 4 ml/l сулфатите на изхода на инсталацията намаляват съответно с 35.7 %, 67.1 %, 82.3 % и 98.3 %. При всички изследвани режими ефективно се отстраняват йоните на тежките метали – мед, желязо, цинк, кадмий и арсен (97 % – 99.9 %). Степента на отстраняване на мангана е ниска – около 30 %. Получените резултати и направените от нас констатации, биха могли да послужат като основа за изграждане на пилотни инсталации, базирани на полупасивно третиране по установен начин.

Ключови думи: кисели руднични води, сулфат-редукция, полупасивно третиране

Introduction

The formation of acid mine water is a natural result of the exploitation of sulphide minerals, ores and coal deposits, abandoned mine sites and mining waste dumps. The negative environmental impact of acid mine drainage (AMD) water is due to its high content of heavy metals, toxic and radioactive elements. Discontinuance and mobility of mine wastewater generation is often difficult and even impossible task, and requires additional treatment of these waters. A passive treatment technology has typically been applied to the treatment of seeps from waste rock piles, acid mine drainage and tailings impoundments at abandoned mine sites. This technology can be also suitable at active mining operations as a means of effluent remediation from tailings ponds for off-site discharge. The systems of this type use completely natural and biological mechanisms to remove sulphate and heavy metals from mine wastewater. For acid mine waters that have a net acidity greater than zero, the treatment design needs to involve systems that add alkalinity. The most common inorganic source of alkalinity for passive AMD treatment is limestone ($CaCO_3$).

After the neutralisation of wastewater, depending on the flow rate and type of pollutants, the passive system may include aerobic or anaerobic treatment facilities (Skousen et al., 2019; Naidu et al., 2019).

Treatment of metal-containing wastewaters with sulphate-reducing bacteria (SRB) is quite promising as an alternative to chemical methods. The microbial sulphate reduction in passive treatment of mine water is carried out in anaerobic cells, anaerobic constructed wetlands, sometimes called 'bioreactors' and alkalinity producing system (RAPS), which is also referred to as a successive alkalinity producing system (SAPS) (Taylor et al., 2005). Under anaerobic conditions SRB use sulphate as a terminal electron acceptor for the organic compounds oxidation and produce hydrogen sulphide. Heavy metals are precipitated in the form of sulphides or carbonates. The systems can be suitable for acidic medium and can also function at sub-zero temperatures (Martínez at al., 2019). A few metals (Fe, Cu, Pb, Zn, Cd, Ni e.d.) are successfully

removed by anaerobic constructed wetlands, but manganese, arsenic and cyanides are better removed under aerobic passive systems than anaerobic ones (Fernandez-Rojo et al., 2019; Muhammad et al., 2015).

Although passive systems for improving water quality have certain advantages over natural processes, they are highly complex and susceptible to many factors such as flow rates, hydraulic retention time, rainfall, temperature variations and e.d. (Alsaiari, Tang, 2018). Solid substrates have a limited lifetime and have to be replaced or supplemented with liquid or gaseous substrates once the original substrate has been depleted. Many passive treatment installations require some periodic operation, such as carbon source addition or temperature control to sustain the desired processes and conditions. Under these conditions, they are referred to as semi-passive (Nielsen et al., 2018).

The main objective of the present study is to determine the influence of the amount of added lactate on the removal of sulphate, heavy metals and arsenic in the conditions of semi-passive treatment of mine wastewater.

Materials and methods

Design of laboratory installation

The anaerobic wetland consists of three cascade connected anaerobic cells - cuboidal containers with length 190 mm, width 150 mm and an altitude of 560 mm (Fig. 1). Each container is filled with a mixture of 4.5 kg solid organic matter (cow manure, hay and sawdust in the ratio 4:1:1) and 2 kg limestone (particles size 5-10 mm). Water enters in the first anaerobic cell by a PVC tube (50 mm diameter) reaching the bottom of the container. Thus, upstream of the treated water is provided and the volume of the substrate is optimally utilised. The outlet water from the first cell proceeds in the same way in the second cell. The effluent water from the second cell passes through a perforated PVC pipe (50 mm diameter) reaching the bottom of the third container.
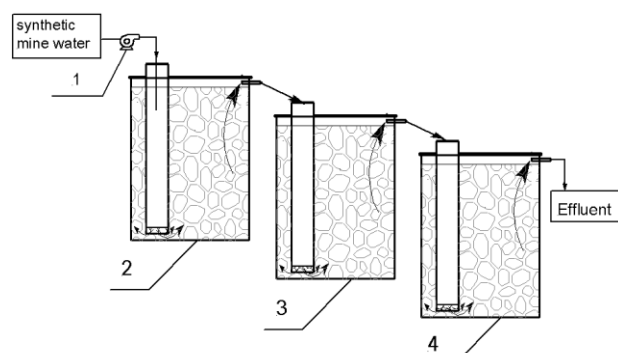

Fig. 1. Design of the laboratory installation: (1) peristaltic (roller) pump, (2, 3 and 4) anaerobic cell

The anaerobic cells were inoculated with mixed cultures of sulphate-reducing bacteria. The inoculum contains genera, belonging to the species *Desulfotomaculum*, *Desulfovibrium*, *Desulfomicrobium* and *Desulfobacterium.*

Process operation

Synthetic mine water containing iron and copper was treated through the so-constructed laboratory installation

during the period 2013-2017. Within this period, more easily degradable biopolymers were depleted and wastewater purification efficiency decreased to 10% of the initial results.

New research was carried out in 2018. The synthetic mine waters contain SO_4^{2-} (3000 mg/l), Fe^{2+} (100 mg/l), Zn^{2+} (25 mg/l), Mn^{2+} (20 mg/l), Cu^{2+} (10 mg/l), Cd^{2+} (5 mg/l) and As^{5+} (5 mg/l). The heavy metals and arsenic were imported in the form of $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$, $CdCl_2.2.5H_2O$ and K_2HAsO_4. The concentration of sulphates was adjusted to 3.0 g/l by the addition of Na_2SO_4 and $MgSO_4.7H_2O$. The pH of the synthetic mining water was adjusted to 4.6 by sulphuric acid. Passive and semi-passive treatment was performed by maintaining hydraulic retention time of 6 days. Lactate at concentrations of 1, 2, 3 and 4 ml/l was added as an additional source of carbon and energy during the semi-passive treatment stage.

Analytical methods

The pH and Eh were measured in key points of the laboratory installation. The sulphate concentration was determined using spectrophotometric method by $BaCl_2$. The total sulphide concentration was measured immediately after sampling using Nanocolor test 1-88/05.09. The organic substrate concentration was estimated by measuring the chemical oxygen demand (COD). The dissolved metal and arsenic concentrations were determined by ICP spectrophotometry.

Results and discussion

During the first three months, passive treatment of synthetic mine water was carried out. At this mode the pH of treated waste waters increased from 4.6 to 6.75, which is due to the chemical neutralisation with limestone and bicarbonate alkalinity production by sulphate-reducing bacteria (Fig. 2).
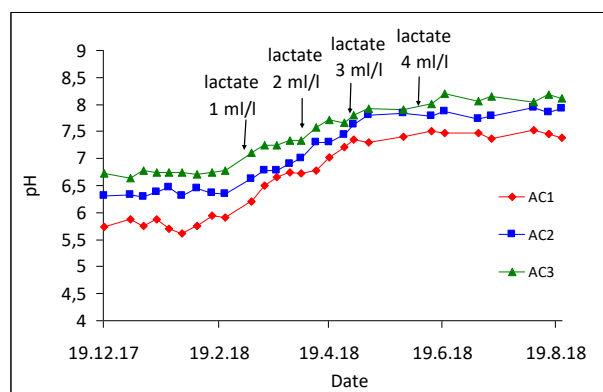

Fig. 2. Dynamics of pH during treatment of wastewater by laboratory installation

The concentration of sulphate at the outlet of the laboratory installation was very high – around 2715 mg/l, and the degree of sulphate removal was only 9% (Fig. 3).

The rate of microbial sulphate reduction under conditions of limitation of SRB with a source of carbon and energy was around 47.5 mg SO_4^{2-}/l/day. During this period the hydrogen sulphide was нош detected in the effluent from the three anaerobic cells. However, the ions of copper, iron, zinc, cadmium and arsenic were effectively removed (93-99%). Most

of the pollutants were precipitated in the form of sulphides, but part of the iron was also precipitated in the form of ferric hydroxides at condition of increased pH in the anaerobic cells.

The COD values at the effluent were in the range of 78 to 105 mg/l. This shows that due to hydrolysis of the hardly degradable organic polymers in the solid organic substrate, low molecular weight organic compounds, which are used as electron donors for sulphate-reducing bacteria, still entered into the solution.
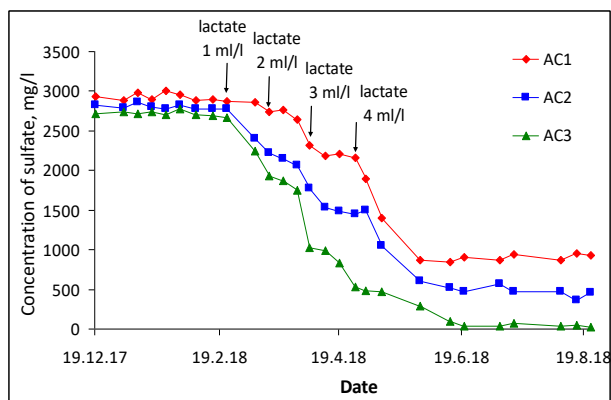

Fig. 3. Dynamics of concentration of sulphate during treatment of wastewater by laboratory installation

Semi-passive treatment of waste water was carried out over a period of 6 months. Sulphate-reducing bacteria oxidise simple organic compounds (such as lactate, acetate, butirate,

ethanol, glycerol, H_2 and other products of fermentations) with sulphate at anaerobic conditions. Lactate is one of the most preferred sources of carbon and energy for sulphate-reducing bacteria, performing incomplete oxidation of organic matter. For this purpose, lactate was added to the synthetic mine water in increasing concentration from 1 to 4 ml/l.

Data for basic chemical parameters of the effluents from anaerobic cells are presented in Table 1. The pH values of the effluent from the laboratory installation were higher than 7 for all tested regimes, due to the higher concentration of microbial produced HCO_3^- ions by the sulphate reduction (Table 1). There is a correlation between the increase in lactic acid concentration and the increase in pH in the effluents from anaerobic cells (Fig. 2). At the same time, with the increase in the concentration of the organic compound, strong reduction conditions were established due to the increased amounts of microbial produced hydrogen sulphide. The lowest values of Eh (-445 - -497 mV) were measured by adding lactate to the treated wastewater at a concentration of 4 ml/l.

The addition of lactate to the treated water resulted in an increase in the rate of microbial sulphate reduction (Fig. 3). The rate of the process was respectively 178, 336, 412 and 492 mg SO_4^{2-}/l.d at lactate concentrations of 1, 2, 3 and 4 ml/l.

We observed that the increase of concentration of lactate from 1 to 4 g/l led to an increase of the rate of the sulphate-reduction in a linear relation (Equation 1).

Table 1. *Values of basic parameters in the effluents from anaerobic cells*

Parameter	Effluents from anaerobic cells											
	Lactate – 1 ml/l			Lactate – 2 ml/l			Lactate – 3 ml/l			Lactate – 4 ml/l		
	AC1	AC2	AC3	AC1	AC2	AC3	AC1	AC2	AC3	AC1	AC2	AC3
pH	5.8±0.2	6.5±0.1	7.2±0.1	6.4±0.3	7.0±0.3	7.7±0.3	7.14±0.2	7.7±0.1	7.8±0.1	7.4±0.2	7.8±0.05	8.1±0.1
Eh, mV	-160 ±15	-250 ±18	-310 ±21	-320 ±19	-360 ±22	-410 ±19	-420 ±15	-447 ±21	-457 ±19	-454 ±21	-475 ±20	-479 ±18
SO_4^{2-}, mg/l	2864 ±25	2223 ±17	1930 ±30	2639 ±12	1485 ±25	986 ±27	2460 ±31	1324 ±25	531 ±32	910 ±27	360 ±26	50 ±15
H_2S, mg/l	4 ± 4	8 ± 5	11 ± 4	17 ± 9	78 ± 11	133± 5	337 ± 21	548± 9	690±16	488± 9	571± 11	716±21
Fe^{2+}, mg/l	21.45	0.341	0.114	5.74	1.31	0.091	2.56	1.08	0.10	1.33	0.08	0.07
Zn^{2+}, mg/l	0.278	0.123	0.076	0.198	0.031	0.02	0.125	0.025	0.006	0.110	0.017	0.005
Mn^{2+}, mg/l	10.23	7.43	4.67	11.09	8.54	5.96	11.54	9.43	5.78	10.99	8.97	6.06
Cu^{2+}, mg/l	0.021	0.019	0.013	0.018	0.015	0.012	0.009	0.007	0.005	<0.005	<0.005	<0.005
Cd^{2+}, mg/l	0.024	0.014	0.006	0.011	0.007	0.005	0.006	0.005	<0.005	<0.005	<0.005	<0.005
As^{5+}, mg/l	2.54	0.014	0.006	0.011	0.007	0.005	0.006	0.005	0.005	<0.005	<0.005	<0.005
COD, mg/l	500 ±18	115 ±25	87 ±20	1246 ±25	766 ±10	136 ±20	2253 ±5	1683 ±25	693 ±20	3723 ±15	2253 ±25	2073 ±20

Rate of sulphate-reduction, (mg/l.d) = 101.8 x Concentration of lactate, (g/l) + 100 (R^2 = 0.9648) (1)

The sulphate-reduction rates in natural and constructed wetlands reported in literature, range from 0.3 to 675 mg SO_4^{2-}/l/day. Most of the reported values are between 30 and 150 mg SO_4^{2-}/l/day. The results obtained show that the COD/SO_4^{2-} ratio significantly influenced the sulphate reduction, and the COD/SO_4^{2-} ratio can successfully control the rate of microbial sulphate reduction. In the present study the COD/SO_4^{2-} ratio was 0.33, 0.67, 1 and 1.33 with the addition of lactate at concentrations of 1, 2, 3 and 4 g/l, respectively. The results are

also a proof of the formation of a stable microbial community in each anaerobic cell within the whole period of operation.

As the rate of microbial sulphate reduction increases, higher concentrations of excess hydrogen sulphide are observed (Table 1). This favours the efficient precipitation of heavy metals and arsenic as insoluble sulphides. In all studied regimes the ions of copper, iron, zinc, cadmium and arsenic were effectively removed (97-99.9%). The removal of manganese in anaerobic conditions was low − around 30%, as the main mechanism of Mn removal was the sorption of this heavy metal from the solid organic matter.

The effluent from the third anaerobic cell contained low concentration of sulphates. However, excess amounts of H_2S, high value of COD, as well as Mn were determined in the effluent. The measured COD values of the outflow for laboratory installation were high because of the incomplete oxidation of lactate usually with acetate as an end product. This result shows that it is necessary to perform additional treatment of the wastewater. In the passive treatment, the removal of COD, excess hydrogen sulphide and manganese is done in aerobic wetlands. This oxidation step is necessary to remove COD and the excess of H_2S as elemental sulphur. Under oxidising conditions, the divalent manganese is oxidised to a tetravalent and precipitated in the form of MnO_2. At present, there are several types of constructed wetlands used for wastewater treatment (Vymazal, 2008). Free water surface systems are used in many countries. The vertical flow systems which are intermittently fed allow higher oxygenation of the bed.

Conclusions

The following conclusions can be drawn from this study:

Passive systems are attractive in the treatment of mine waste water, but over time, due to the depletion of organic material, the efficiency of water purification decreases. One solution to this problem is the application of semi-passive treatment with the use of lactate as a source of carbon and energy.

The addition of lactate to the treated water resulted in an increase in the rate of microbial sulphate reduction, and the highest rate 492 mg SO_4^{2-}/l.d being achieved was with the addition of 4 g/l of lactate.

The reduction of sulphates from 3000 mg/l to below 250 mg/l requires the addition of lactate at concentrations of 4 g/l.

The COD/SO_4^{2-} ratio significantly influenced the sulphate−reduction. It was also found that the COD/SO_4^{2-} ratio can successfully control the rate of microbial sulphate reduction.

Under anaerobic conditions of semi-passive treatment, the ions of copper, iron, zinc, cadmium and arsenic were effectively removed (97-99.9%), but the rate of manganese removal was low (30%).

The excess amounts of H_2S, high value of COD, as well as Mn, are determined in the effluent from anaerobic cells, which requires further treatment of the waters in oxidising conditions.

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