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TECHNICAL COMMUNICATION

Application of a Peat-humic Agent for Treatment of Acid Mine Drainage

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Abstract A peat-humic agent (PHA), derived by mechanical, chemical, and thermobaric treatment of peat from the Krugloe deposit (Novosibirsk region, Russia), is a good sorbent for potentially toxic elements, and can be used to neutralise acid mine drainage (AMD). A new AMD remediation method has been developed using this PHA with subsequent solid/liquid separation using haydite sand or activated carbon.

Keywords Acid mine drainage · Tailings · Pollution · Wastewater treatment

Introduction

The waste products of the ore mining and processing industry can be oxidized by atmospheric oxygen and microbial activity, forming acid mine drainage (AMD), with high concentrations of SO_4^{2-}, Fe, Zn, Cu, Cd, Pb, and other elements. Various agents such as limestone, lime, clay, activated carbon, zeolite, iron (III) hydroxide, fly ash, cellulose, and rice husks (Chockalingam and Subramanian 2006; Cravotta and Ward 2008; Gabr and Bowders 2000; Herrera et al. 2007; Kumar Vadapalli et al. 2008; Lee et al. 2004; Nogueira da Silveira et al. 2009; Pérez-López et al. 2007; Ríos et al. 2008; etc.), different protective screens (Doncheva and Pokrovskiy 1999; Ji and Kimb 2008; Kovalev et al. 2000; Maximovich and Blinov 1994; Maximovich et al. 1999; Sergeev et al. 1996; Zosin et al. 2004; etc.), and microbial populations (Benner et al. 2000; Elliott et al. 1998, Foucher et al. 2001; Kalina and Caetano Chaves 2003; Kim et al. 2000; Sandstrom and Mattsson 2001) have been used to minimise the technogenic influence of the mining and mineral processing industry. The aim of the present study was to investigate, at laboratory scale, the effectiveness of an alkaline peat-humic agent (PHA) as a sorbent in removing heavy metals from AMD, and thereby develop a new AMD treatment method.

The development was based on investigations of humic substance properties (Aleksandrova 1980; Bannikova 1990; Holin 2001; Orlov 1990; Orlov and Osipova 1988; Stevenson 1994; Varshal et al. 1984; etc.) and our preliminary research of sulphide tailings (Bogush and Androsova 2007; Bogush and Lazareva 2008; Bogush et al. 2007a, b). Humic substances are complex mixtures of natural high-molecular phaeochrous organic compounds formed by decomposition of the vegetative and animal residue by microorganisms and abiotic factors (Orlov 1990). Humic substances can be found almost everywhere in the nature, with the highest content (up to 85%) observed in biogenic rock, such as coal, peat, sapropel, and black shales (Perminova 2008). Natural humic substances are a unique and complex mixture of macromolecules with variable and irregular structure, have unique chemical and biological properties, and are environmentally safe. Humic substances are very strong sorbents for heavy metals, and resist biodegradation and thermal destruction. Humic acids in soil are typically 500–5000 years old, and 1500–6500 years old in ground deposits (Gerasimov and Chichagov 1971). The concentration of dissolved humic substances can stay constant for years (Bannikova 1990).

Humic acid is a very important sorbent and complexing compound for elements because it has a high surface area and contains different functional groups (carboxyl, hydroxyl,

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carbonyl, amides, and others). Carboxyl groups in the PHA play an extremely important role for element sorption (Bogush et al. 2007a). Humic acid (Hu-COOH) and sodium humate (Hu-COONa) dissociate to form a humate ion, a hydroxonium ion, and a sodium ion. The humate ion reacts with a metal ion and forms a humate complex:

$$\text{2Hu-COOH} + \text{Me}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Hu-COO-Me-OOC-Hu} + 2\text{H}_3\text{O}^{+}$$

$$\text{2Hu-COONa} + \text{Me}^{2+} \leftrightarrow \text{Hu-COO-Me-OOC-Hu} + 2\text{Na}^{+}.$$

Most metal–humic acid complexes are very stable. Also, humic acids have a high sorption capacity. For example, Holin (2001) found that 1 g of humic acid could sorb 30 mg Cs, 18 mg Sc, 18 mg Cu, 60–150 mg Pb, 80 mg Cr, 300 mg Hg, 300–600 mg Au, and 85–100 mg Pd. Most of the radionuclides in the soil of Chernobyl were bound with humic acid (Varshal et al. 1993). As shown earlier (Bogush and Trofimov 2005; Bogush et al. 2007a), PHA also has a good binding capacity for heavy metals.

Materials and Methods

The laboratory experiments were carried out using a very alkaline (pH = 12) liquid PHA, which was produced by Planet-RA Ltd. by mechanical, chemical, and thermobaric treatment of highly decomposed (50%), high-ash (39.9%) reed swamp peat from the Krugloe deposit (Novosibirsk region, Russia). Much of the world's high quality peats are concentrated in the Siberian region (about 107 billion tons). The content of organic substances in this peat totalled 60.1%, including humic and fulvic acids (43.5 and 26.8% of the total organic content, respectively). However, this includes humate compounds, which are not readily available. Consequently, the yield of humic acids should theoretically be about 1.6% after alkaline hydrolysis of the peat at a ratio of peat: alkaline solution = 1:10. The PHA obtained using the new thermobaric methods is 11.8% dry residue and 4.2% humic acids. Thus, the humic acid content in the liquid PHA is almost three times that of the peat it was derived from, because some of the peat decomposes and new humic acids are formed. On average, 1.7 L of PHA can be produced from 1 kg of this peat.

Drainage waters from the old Gornyak waste pile (Altaypolimetal Ltd., Gornyk, Altay region, Russia) and the Belovo Zinc Plant (Belovo, Kemerovo region, Russia) (Fig. 1) were used for the experiments. The sampled drainages differ in their elemental composition and pH value. The Altaypolimetal AMD is SO_4–Ca–Mg type, with a high concentration of contaminants and low pH (Table 1). The AMD of the Belovo Zinc Plant is SO_4–Cl–Ca–Na type, and the slightly acidic water of the Belovo sludge pond is classified as SO_4–HCO_3–Cl–Ca–Na type, with high contaminant concentrations (Table 1). The dissolved metals in the AMD are present as ions (Me^{2+}) and sulphate ($MeSO_4^0$, $Me(SO_4)_2^{2-}$) complexes. Temperature, pH, and Eh of the water samples were measured at the place of sampling using an 'Ionomer-4151' (Novosibirsk, Russia).

In addition to the PHA and the three drainage waters, haydite (burnt shale) sand (particle size ≈1–3 mm), and activated carbon (GOST (Government Standard) 6217-74) were used in our experiments. Each experiment was conducted in three parallel runs and the results were averaged. The range of variation did not exceed 7% for all of the investigated elements. The laboratory research was carried out at the Analytical Centre of the Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences. Concentrations of SO_4^{2-}, Cl^-, NO_3^-, and F^- in the AMD were analysed by ion chromatography. Concentrations of Al, Fe, Zn, Cd, Cu, Pb, Co, and Ni were determined with an atomic absorption spectrophotometer using electrothermal (Perker-Elmer 3030 Z) and flame (Piy-Unicam SP-9) atomization.

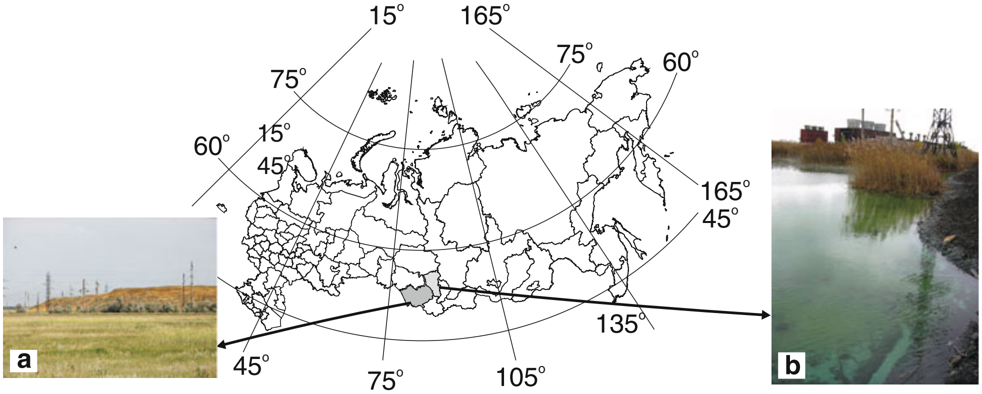

Fig. 1 Location of the mine water sources: the Altaypolimetal Ltd. [Gornyak, Altay region, Russia, photo (**a**)] and the Belovo zinc plant [Belovo, Kemerovo region, Russia, photo (**b**)]

Table 1 The element concentrations in mg/L and pH of the technogenic waters

Sample	pH	Fe	Al	Cu	Zn	Pb	Cd	Ni	Co
AMD of old waste deposit (Gornyak)	2.7	210	350	37	160	0.4	0.86	0.56	0.81
Sludge pond (Gornyak)	2.4	450	620	90	270	0.44	2.3	–	–
AMD of new waste deposit (Gornyak)	3.4	9.3	77	20	94	0.56	0.46	–	–
Belovo AMD	4.1	0.18	21	730	910	–	6.0	5.9	5.1
Belovo sludge pond	4.8	0.22	18	270	120	–	1.2	0.68	0.6
MPC (SanPIN 1996)	–	0.3	0.5	1.0	5.0	0.03	0.001	0.1	0.1

First, element sorption in the PHA was investigated at static conditions. 100 mL of each AMD was placed in a 150 mL glass beaker. The PHA was then added to the AMD, with agitation, in three volumetric ratios: A1) PHA: AMD = 1:1000; A2) 1:500, and; A3) 1:100. The pH of the solution was measured before and after PHA addition. After 1 h, the AMD–PHA mixtures were filtered through ash-free paper filter with 2 µm pores and the solutions were analysed. Then, treatment efficiency was calculated.

Second, a filtration experiment was carried out in order to remove insoluble sediment (sludge) from the treated drainage. Filtration columns (diameter = 2.5 cm, height = 40 cm) were filled with haydite sand (20 g) and activated carbon (20 g) separately. The filtration columns were placed vertically using lab support stands. The graduated jar was placed under the column for filtrate collection. A volume of 1,000 mL of each AMD was placed in 1,200 mL glass beaker. Then 2 mL of the PHA (PHA/AMD ratio = 1:500) were added to AMD with agitation. This ratio was based on the results from the first series of experiment. The mixture of the AMD with the PHA was then filtered through one of the two columns. Finally, the filtration rate, pH, and element concentrations in the filtrate were determined.

Results and Discussion

In the static experiment, a flaky deep-brown sediment was formed by mixing the alkaline PHA (pH = 12) with the AMD. At the A3 ratio (Table 2), the pH of the highly acidic mine drainage of the old Gornyak waste deposit was increased to 3.7 by the PHA. The pH of the Belovo Zinc Plant wastewater reached neutral and even low-alkalinity values (Table 2). Also, the contaminant concentrations in solution decreased. The purification efficiency gradually improved with increased PHA concentrations (Table 2), especially for the Belovo drainage waters. According to Bogush et al. (2007a), potentially toxic elements are sorbed by the PHA. However, in a complex system such as AMD, hydrolysis, physical adsorption of contaminants on aggregate surfaces, and coprecipitation of elements with ferric hydroxide can take place simultaneously. Good results were obtained using the A2 ratio for the Belovo sludge pond water and the A3 ratio for AMD of the Gornyak old waste deposit and the Belovo zinc plant (Table 2).

Table 2 The purification efficiency in % and the pH of treated drainage waters

Sample	pH	Fe	Al	Zn	Cu	Cd	Pb	Ni	Co
A1 (G1)	2.9	21	17	14	8	11	98	17	5
A2 (G1)	3.1	36	26	20	35	43	98	40	21
A3 (G1)	3.7	74	66	58	95	99	98	95	85
A1 (B1)	5.1	95	60	11	11	13	–	3	8
A2 (B1)	5.3	95	99	21	23	23	–	15	18
A3 (B1)	6.2	95	99.9	67	71	80	–	75	76
A1 (B2)	6.4	94	66	60	52	8	–	24	22
A2 (B2)	7.1	94	99.9	96	99	76	–	61	57
A3 (B2)	8.2	94	99.9	99.9	99.9	99.9	–	89	94

A1—PHA-AMD ratio = 1:1000; A2—PHA-AMD ratio = 1:500; A3—PHA-AMD ratio = 1:100; G1—AMD of old waste deposit (Gornyk); B1—Belovo; AMD; B2—Belovo hydraulic-mine dump

The second stage of the AMD treatment method involves separation of the purified solution and the flaky sediment by filtering the mixture through activated carbon and haydite sand. After mixing the Belovo drainage (B2) with the PHA in a ratio of PHA/AMD = 1:500, the flaky deep-brown sediment occupied 5–6% of the volume, and as noted above, the solution had a pH of 7.1. The pH of the first portion of the filtrate increased to 9.3 and then gradually decreased to 7.6 after the treated suspension was filtered with activated carbon. The pH of the solution did not change much when filtered through the column with haydite sand. In both experiments, the filtrates were transparent and all sediments were precipitated onto the filter material of the columns. The filtration rate gradually reduced from 5 to 0.25 L/day in the column with activated carbon and from 36 to 4.8 L/day in the column with haydite sand. This filtering rate reduction occurred because the flaky deep-brown sediment clogged the pore space in the activated carbon and haydite sand. The filtration rate through activated carbon was almost one tenth that through haydite sand, but the contaminant concentrations in the solution filtered through the haydite sand were only slightly changed (Fig. 2), while much lower concentrations resulted from filtering the suspension through the activated carbon (Fig. 2). Activated carbon is a good sorbent and is widely used for water purification, but its permeability is reduced as the activated carbon swells. The total percent of AMD purification after filtration through activated carbon was 99.6% for Zn, 99.2% for Cd, 99.9% for Cu, 95% for Pb, 92.6% for Ni, 91.7% for Co, 98% for Fe, and 80% for Mn.

Conclusion

The PHA is a good sorbent for potentially toxic metals and provides some neutralising capacity. It is most effective for slightly acidic mine drainage and is not very effective for highly acidic drainage. Based on the results of these experiments, the authors suggest that PHA holds promise as a new method of to treat AMD.

The amount of the PHA to be added depends on the AMD composition. A PHA-AMD ratio of 1:500 is effective for slightly acidic drainage, such as from the Belovo sludge pond. Second, the flaky sediment that is formed can be removed by filtration through activated carbon or

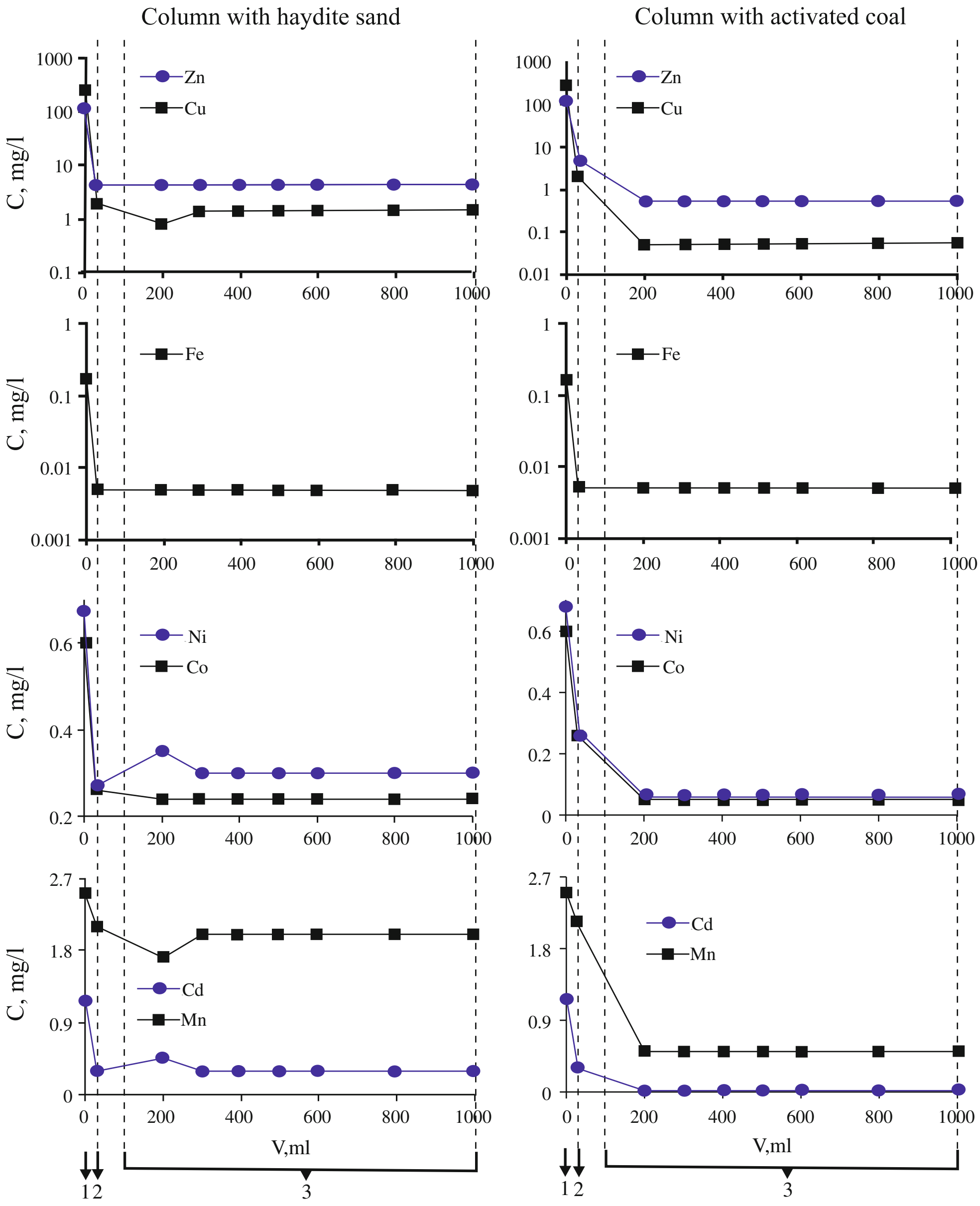

Fig. 2 Changes in contaminant (C) concentration and pH during experimental water treatment: *1*—drainage water of the Belovo zinc plant (on the left side of each graph); *2*—mixture of drainage water with the peat-humic agent, and; *3*—results of filtration through columns with haydite sand and activated carbon. Note that the data on the *x* axis of the top graphs are presented exponentially

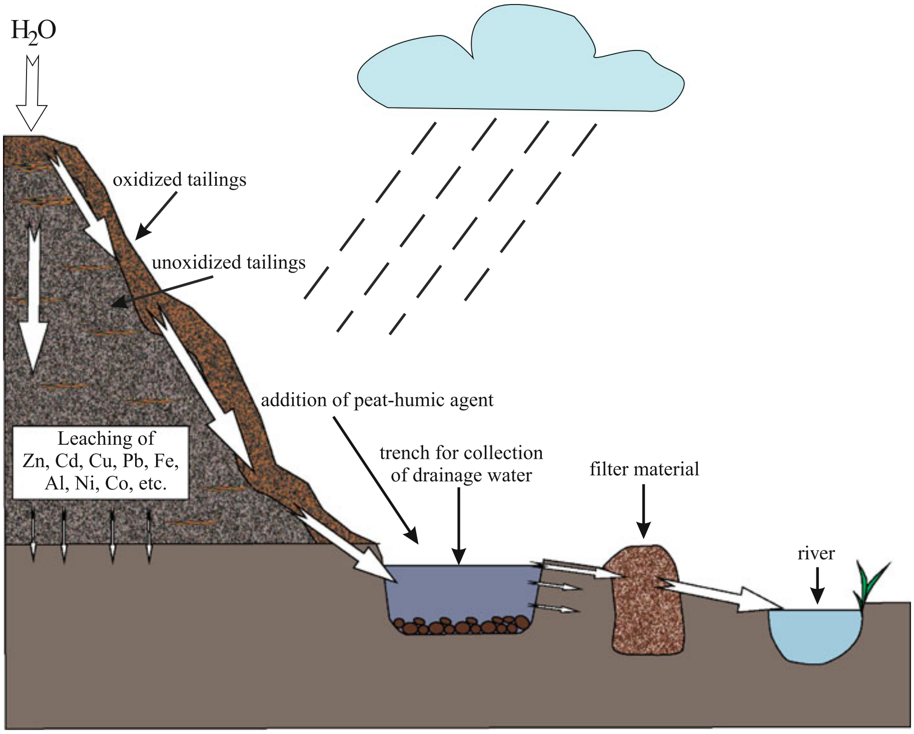

Fig. 3 Schematic of potential acid mine drainage treatment using the peat-humic agent

haydite sand. Activated carbon is best to use after treatment of highly contaminated solutions. However, it is cheaper to use haydite sand, especially for slightly acidic drainage.

It is possible to treat the AMD from old sulphide tailings, which often spreads into the environment and pollutes rivers, reservoirs, soils, and other environmental components (Fig. 3). A trench can be dug around the sulphide tailings to collect the AMD. Then PHA can be added to the trench at a concentration that would depend on the AMD composition. Haydite sand would be placed downstream for filtration, in a permeable reactive barrier, possibly in permeable bags that would make it easy to replace the sand. This approach would reduce the hazardous effect of mine waste on the environment.

The economics of this approach have been considered. The production and transportation cost of 1 m^3 of peat in Russia is about $ 10 (US). On average, 1.7 L of PHA can be produced from 1 kg of peat, and up to 1,000 L/h can be produced in a single reactor. At this rate, the production cost of 1 L of PHA is about $ 0.5, and so the sale price would be about $1. Two litres of PHA would be needed to treat 1,000 L of slightly acidic mine drainage such as Belovo drainage.

The authors intend to continue their laboratory investigations in order to improve and optimize this method, to confirm the stability of the precipitated solids, and to determine if this method can possibly be used to economically recover metals from AMD. We also intend to test it in the field in the near future.

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