Journal of Young Scientist, Volume I, 2013
ISSN 2344 - 1283; ISSN CD-ROM 2344 - 1291; ISSN Online 2344 - 1305; ISSN-L 2344 – 1283

PRELIMINARY INVESTIGATIONS ON THE USE OF DIFFERENT NATURAL SORBENTS FOR REMOVAL OF HEAVY METAL FROM ACID MINE DRAINAGE (CASE STUDY: "Larga de Sus" MINE*)*

Gianina DAMIAN, Simona VARVARA, Roxana BOSTAN

University "1 Decembrie 1918" of Alba Iulia, N. Iorga Street, no. 11-13, Alba Iulia (510009),
Romania, Tel:+40-0258-806130,+40-0258-806273, Fax:+40-0258-812630,
Email: gianina_ln@yahoo.com; svarvara@uab.ro; a_roxananadina@yahoo.com

Corresponding author email: gianina_ln@yahoo.com

Abstract

Acid mine drainage (AMD) is a widespread environmental problem associated with both working and abandoned mining operations, because it generates acidic solutions containing toxic heavy metal ions, such as Fe^{2+}, Zn^{2+}, Mn^{2+}, $Cu^{2+,}$ $Pb^{2+,}$ *which are not biodegradable and tends to accumulate in living organisms causing various diseases.*
The present study aimed at evaluating the possibility of using two low-cost sorbents, i.e. zeolite volcanic tuff from Rupea (Brasov County, Romania) and peat from "Poiana Stampei" (Suceava County, Romania) in the removal process of the heavy metals (Fe, Zn and Mn) from AMD generated at the abandoned mining perimeter of "Larga de Sus" from Zlatna (Alba County, Romania). The composition of the acid mine drainage from "Larga de Sus" Mine before and after the treatment with natural sorbents was determined by X-ray fluorescence spectroscopy. The removal efficiency of Fe, Zn and Mn from AMD was determined at different doses and grain sizes of the natural zeolite and peat. The preliminary results showed that both sorbents can be used as a low cost alternative in the treatment of AMD.

Key words: *Acid mine drainage, heavy metals, natural zeolite, peat moss.*

INTRODUCTION

Acid mine drainage (AMD) is a major cause of environmental pollution associated with the poor management of working and abandoned mining operations. AMD polluted waters typically show low pH values (Macías et al., 2012) and contain important concentrations of iron, sulphate and heavy metals (*i.e.* Zn Mn, Cu, Pb, Cr, Cd) which are toxic for the aquatic fauna and flora, (Yang et al., 2009), damage the ecosystem of soil and receiving rivers or lakes and corrodes the infrastructure (Ruihua et al., 2011).

When a mine is abandoned, the pumping ceases and water floods the underground site (Natarajan, 2008). AMD results from the leaking of acidic water from abandoned mines and mineral wastes and occurs naturally within the environments containing an abundance of sulphide minerals, usually pyrite (FeS_2) which oxidizes and dissolves when in contact with water and air (Pérez-López et al., 2010), according to the following equations (Suteerapataranon et al., 2006):

$$FeS_2(s)+7/2O_2(g)+H_2O \rightarrow Fe^{2+}(aq)+2H^+(aq)+2SO_4^{2-}(aq)$$

$$2Fe^{2+}(aq)+1/2O_2(g)+5H_2O(l) \rightarrow 2Fe(OH)_3(s)+4H^+(aq)$$

Taking into account the predictions on the future loading of dissolved metals from abandoned mines which notify that the sulphide oxidation and release of dissolved metals could carry on for decades to centuries, proper AMD treatments for heavy metals removal are required (Rios et al., 2008).

The conventional methods used for AMD treatment can be divided into either passive or active processes.

Passive treatment technologies rely on naturally occurring chemical and biological processes to buffer the AMD acidity and to remove the sulphate and heavy metals, using one or more of the following treatment methods (Clyde, 2008): anoxic limestone drains, biosorption, anaerobic bioreactors and aerobic wetlands, settling ponds. Active treatment involves the addition of a chemical neutralizing agent ($CaCO_3$, $Ca(OH)_2$, CaO, Na_2CO_3, NaOH etc.) to the source of AMD or directly to the stream that has been polluted. The AMD treatment with limestone does not only neutralize the AMD, but it also serves to precipitate Fe and other metal hydroxides, since the solution pH may increase to 6.0-7.5 and thus allowing the metals to be removed (Rios et al., 2008).

Although the active treatment of AMD could be very successful, it has the disadvantage of requiring continuous operation and maintenance. Apart from chemical precipitation, several treatment procedures for metal contaminated AMDs, including adsorption, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis and solvent extraction have been also investigated.

The choice of a method for AMD remediation is equally based on (Motsi et al., 2011) the concentration of heavy metals in the wastewater, the cost of the treatment procedure and possibility to implement it in remote areas (Wanjing et al., 2010).

The AMD treatment by adsorbents is one of the most efficient and economical technique used for heavy metal removal, especially when natural materials that has potential as low-cost effective sorbents are available and could be easily regenerated.

These include fly ash (Rios et al., 2008; Ahmaruzzaman, 2011), peanut shell (Zhu et al., 2009; Witek-Krowiak et al., 2011) peat moss (Brown et al., 2000; Ringqvist et al.,2002; Qin et al., 2006; Kalmykova et al., 2008; Bulgariu et al., 2008; Caramalău et al., 2009; Gupta et al., 2009; Koivula et al., 2009; Lourie and Gjengedal 2011) lignite (Mohan and Chander, 2006) kaolinite (Sen et al., 2002; Arias et al., 2002; Yavuz et al., 2003; Trevino and Coles, 2003; Kamel et al., 2004; Omar and Al-Itawi, 2007) Neem leaves (Oboh et al., 2009) orange waste (Perez-Marin et al., 2007) pine bark (Kalmykova, 2004) sawdust (Bulut and Tez, 2007) mollusk shells (Chenxi, 2008) sand (Awan et al., 2003) and natural zeolites (Hossein and Hassan, 2006; Burca et al., 2008; Bedelean et al., 2010; Motsi, 2010; Jamil et al., 2010; Wang, 2010; Taffarel,2010; Tetisan, 2010; Popa, 2011; Motsi et al., 2011; Shavandi et al., 2012).

Natural zeolites (clinoptilolite and chabazite) are environmentally friendly, naturally occurring low-cost minerals which posses a structural net negative charge due to isomorphic substitution of cations in the mineral lattice. They have a strong affinity for cations of transition metals, but only little affinity for anions and nonpolar organic molecules.

Due to its significant ion exchange ability and high surface areas, natural clinoptilolite offer a potential for a variety of industrial uses, including molecular sieves, ion-exchangers, adsorbers, catalysts, removal of cations from AMD and industrial wastewater.

Despite numerous studies (Peric, 2004; Hossein, 2006; Buasri, 2008; Taffarel, 2009; Tetisan, 2010; Taffarel, 2010; Bedelean, 2010; Motsi, 2011; Muzenda, 2011) attesting the effectiveness of natural zeolite (clinoptilolite) for the removal of single metal ion from synthetic aqueous solution under different experimental conditions, only limited research (Ouki and Kavannagh, 1997**;** Rıos, 2008; Motsi, 2010) have been carried out on its ability to remove various concentrations of heavy metals from real AMD solutions.

Apart from natural zeolite, peat moss is another low-cost sorbent that has been widely used to remove a variety of materials including organic compounds and heavy metals (i.e. Cu, Cd, Pb, Ni, Cr etc.) from waste waters (Ho, 1995; Ho, 1996; Brown et al., 2000; Arunachalam, 2002; Ringqvist et al.,2002; Qin et al., 2006; Bulgariu et al., 2008; Kalmykova et al., 2008; Caramalău et al., 2009; Koivula et al., 2009; Gupta et al., 2009; Lourie, 2011).

Various functional groups in lignin allow such compounds to bind on active sites of peat. Peat is a heterogeneous mixture of decomposed plant materials accumulated in poorly oxygenated wetlands. The major constituents of peat, namely lignin, cellulose and humic substances, contain structural moieties groups, such as –OH, –COOH, =C=O, –C–O–C–, capable of taking part in protolytic, ion exchange and complexation reactions with adsorbed pollutant species (Balan et al., 2009).

Since, the composition of peat from various sources may vary considerably depending on age, the nature of its original vegetation, the regional climate, the acidity of the water and the degree of metamorphosis (Fernandes et al. 2007), detailed studies to evaluate the adsorption potential of this material in relation to the characteristics of the waste waters, including real AMD solutions are necessary.

The present work focused on evaluating at laboratory-scale the use of two naturally occurring low-cost sorbents, i.e. zeolite volcanic tuff (RNZ) from Rupea (Brasov County, Romania) and peat moss (PM) from “Poiana Stampei” (Suceava County, Romania) in the removal of the heavy metals from real AMD generated at the abandoned mining perimeter of “Larga de Sus” from Zlatna (Alba County, Romania). The composition of the AMD from “Larga de Sus” mine before and after the treatment with natural sorbents was determined by X-ray fluorescence spectroscopy.

MATERIALS AND METHODS

Sampling site

The Zlatna mining perimeter is located in South Apuseni Mountains (Romania) and comprises two main exploitations, “Larga de Sus” and “Hanes” mines, where the extraction of gold-silver ores and the mining of polymetallic ores took place for more than 40 years.

Although the “Larga de Sus” gallery was closed in 2006 (Figure 1a), currently the mine waters are flowing unimpeded in the “Bloria” Creek from nearby and then in the lake formed at the bottom of the tailings (Figure 1d) (Keri et al., 2010).

The mine water drainage channel is arranged inadequately (Figure 1b), as it is a simple 20–50 cm deep trench dug in the topsoil blankets from the abandoned platform (Keri et al., 2010).

On 02 November 2012, four AMD samples were collected from the mine water drainage channel and sealed in polyethylene bottles. The pH and electrical conductivity of the raw water were measured on-site using a pH meter (Hanna instruments) and a Cond 315i conductivity meter (Hanna instruments), respectively.

Figure1. The studied site: a) “Larga de Sus” Gallery b) water drainage channel c) dump d) lake

Chemical composition of the AMD samples was determined in laboratory by X-Ray Fluorescence spectrometry (XRF), using a Quant'X ARL X-ray fluorescence spectrometer (Thermo cientific, USA).

Another problem that has been already identified by A.A. Keri et al. in the area of "Larga de Sus" mine was related to the storage of the gangue material extracted from the gallery (Figure 1c).

There are two dumps situated about 80 m from the pit mouth, encompassing 50 tons of gangue materials in an area of 3.2 ha (Keri et al., 2010). After the final closing of the mine, wastes and materials resulted either from the extraction activity or from the closing of the pit mouths have been dumped in the surrounding environment (Keri et al., 2010)

Adsorbents

In this study, natural zeolite-rich tuff (RNZ) and peat moss (PM) samples were used as sorbents for AMD treatment.

The zeolite-rich tuff samples originating from Rupea (Romania) were provided S.C. Eleolit S.A Company. RNZ samples were used in their natural state ("as received") without any chemical modifications. The particle size of the natural zeolite used in this study was 1-3 mm.

The chemical composition of the natural zeolite was determined by XRF and the results are summarized in Table 1. The values of other physiochemical properties were obtained from the provider of the natural zeolite and included in Table 1.

Prior the experiments, the zeolite samples were washed with distilled water and dried in an oven at 100^0 C for 8 hours.

The mineralogical analysis of RNZ was carried out by the provider using X-ray diffraction (XRD) and the result showed that the sample mainly consisted of clinoptilolite (71-83.3 %), volcanic glass (4.1%-9.7%), plagioclase (6.67 %), SiO_2 (2.25%-2.6%) and traces of other minerals.

The peat moss (PM) samples are originated from Poiana Stampei (Romania). A complete characterization of the peat moss is presented in Angelica-Liliana Kicsi's PhD Thesis: Studies on the use of natural indigenous sorbents for decontamination of wastewater containing heavy metals. The peat material was dried for 24 hours in an oven at 100^0 C, grounded using a vegetables mill (Grindomix GM 200) and sieved using a 1 mm sieve.

Table1. Chemical composition and physico-chemical parameters of the zeolite-rich tuff samples originating from Rupea (Romania)

Chemical composition (%)		Physico-chemical parameters
SiO_2	70.94	Cation exchange capacity
Al_2O_3	16.21	1,51mqv / 100g
CaO	4.72	Specific surface area (BET)
K_2O	3.69	23,4 m² / g
Fe_2O_3	2.82	Specific gravity: 1,65 – 1,75
MgO	0.46	gf / cm³
Na_2O	0.45	Total porosity: 33,08 %
TiO_2	0.25	Water absorption: 16,21 %
BaO	0.10	Density: 2,15 – 2,25 g / cm³
MnO	0.05	Bulk Density: 0,88 kg / dm³
LOI	0.21	

Batch sorption experiment

The efficiency of the two sorbents, RNZ and PM in the removal of the heavy metals from real AMD was investigated at the laboratory scale, using a batch reactor (250 ml) at 22 ± 0.5°C, with continuous stirring at 300 rpm.

3 g of sorbents were left in contact with 100 ml of real AMD solution having an initial pH value of 2.8. Aliquots of supernatant (1 ml) were withdrawn at different time intervals (from 5 min to 72 hours), but the total sampling volume did not exceed 10% of the total solution volume.

The final concentration of the heavy metal ions in the aqueous phase was immediately determined by XRF. When using PST, before XRF analysis, the supernatants were filtered by a 150 mm diameter filter paper.

All sorption experiments were in duplicates in order to observe the reproducibility of the results, and the mean value was used.

The removal efficiency, R.E. (%) of metallic ions by the adsorbent was calculated using the following equation:

$$\mathrm{R.E.}(\%) = \frac{C_i - C_f}{C_i} * 100$$

where, c_i and c_f are the concentrations of the metal ions in the initial and final solutions, respectively.

RESULTS AND DISCUSION

Characterization of AMD samples collected from "Larga de Sus" mine

Table 2 shows the average chemical composition and the physicochemical parameter of the AMD samples collected from "Larga de Sus" mine.

Table2. Average chemical composition and physicochemical parameters of AMD collected from "Larga de Sus" mine

Parameter	AMD	Maximum consent limits (NTPA02) *Romanian Standard NTPA 02 Waste water directly into sewage
pH	2.8	6.5-8.5
Fe, mgL^{-1}	112	5
Mn, mgL^{-1}	20	1
Zn, mgL^{-1}	9.6	0.5
Ca, mgL^{-1}	182.5	
Total solids (TSS), mgL^{-1}	2524	2000
Conductivity, μScm^{-1}	2161	

As it can be seen in Table 2, the water drainage from "Larga de Sus" mine is acidic (pH = 2.8), present a high conductivity and contains various heavy metal ions (Fe, Mn, Zn).

The concentrations of the zinc, iron and manganese in the acidic drainage water from "Larga de Sus" mine exceed more than 19 to 22 times the maximum consent limits established by Romanian Standard NTPA02. The specific orange color of AMD is due to the high concentrations of ferric iron in the solution. It is clear that this water drainage introduces sulphuric acid and toxic heavy metals (Fe, Mn and Zn) into the environment, which pose a serious threat to organisms and natural ecosystem, because AMD is disposed without any remediation treatment.

For instance, on-site it was observed that the AMD infiltrates the soil profile, which retains heavy metals causing constant pollution (Keri et al., 2010).Additionally, severe degradation of the land is caused by the gangue material deposition at the pit mouth (Keri et al., 2010).

AMD treatment using RNZ and PM

The removal of heavy metals from the acidic water drainage collected from "Larga de Sus" mine onto RNZ and PM samples was investigated at different contact times and sorbent:AMD ratios.

Figure 2 illustrates the variation of iron, manganese and zinc concentrations during the contact time, for a sorbent:AMD mixture of 3g:100 ml.

As it can be seen in Figure 2a, both investigated sorbents produced similar trends of the iron removal with an abrupt decrease of its concentration level within the first 5 min, followed by a progressive decrease up to 12 h in the case of PM and 24 h for RNZ, respectively.

At longer contact times, plateau values with very low residual concentrations (< 1 mgL^{-1}) were reached and both sorbents allowed an almost complete removal of iron from AMD. However, at the same contact time and sorbent concentration, the iron removal efficiency of the peat moss sample seems to be higher than the value obtained using natural zeolite.

As shown in Figure 2b, Mn concentration decreases during the first 60 min, when using RNZ and PM. After that a sudden increase of manganese concentration occurred between 1 and 2 hours, followed by a new decrease of its concentration at 6 h in the case of using PM and 24h for RNZ, slightly decreasing further for the rest of the contact time intervals.

It is interesting to note that in the first 2 hours of contact, the percentage of manganese removal is higher when PM was added to AMD as compared to RNZ, while at longer contact times it decreases.

The addition of RNZ produces a steep decrease in Zn concentration within the first 5 min immediately followed by a slight increase at 15 min of contact, after which the metal concentration in AMD constantly decreases for the rest of the time intervals (Figure 2c).

The presence of PM in contact with AMD lead to a steep decrease of the Zn concentration within the first 30 min, followed by a progressive increase up to 60 min; then, an abrupt decrease was observed at 2 hours, followed by a new increase at 12 h, decreasing again for the rest of the contact time intervals (Figure 2c).

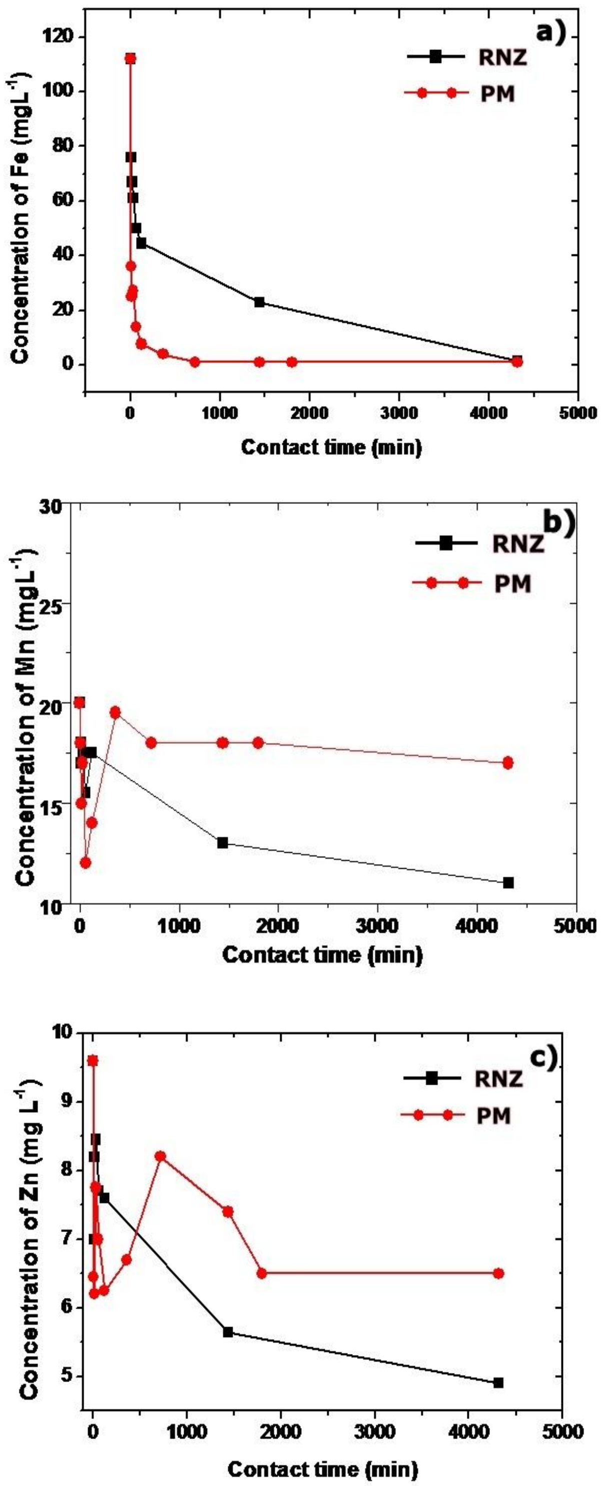

Figure 2 Variation of Fe (a), Mn (b) and Zn (c) concentration as a function of the contact time during the sorption batch experiments (sorbent: AMD mixture of 3 g/100 ml)

The values of the removal efficiency of the two investigated sorbents at different contact times, as a function of the adsorbent dose (3 g) are presented in Table 4.

It is known that the removal of heavy metal ions from aqueous solutions using sorbents is rather a complex process, consisting of ion-exchange and adsorption, but is likely to be accompanied by precipitation of metal hydroxide complexes on the active sites of sorbents surface (Rios, 2008).

The solubility of metals is strongly dependent on the solution pH. Thus, the Fe^{3+} removal from aqueous solution requires low pH value (pH~4.3), Zn^{2+} is precipitated at pH 5.5-7.0 and most of the Mn^{2+} s removed when the solution pH is close to 9.

In our study, the initial pH of acidic water drainage (pH = 2.8) slightly increases during the contact time with the highest investigated quantity of natural zeolite (5 g) to values of 3.0 and 3.3 after 24 and 48 hours, respectively.

The addition the peat moss to AMD leads to a decreases of the solution pH at 2.45 after 72 hours of contact.

Table 4. Treatment of AMD collected from "Larga de Sus" mine using 3 g of natural zeolite (RNZ) and peat moss (PM) at various contact times

Adsorbent	Heavy metal	Time (min)	R.E. (%)	Adsorbent	Heavy metal	R.E. (%)
RNZ	Fe	5	32.1	PM	Fe	67.8
		15	40.1			77.6
		30	45.5			75.8
		60	55.3			87.5
		120	60.2			93.1
		1440	79.4			99.1
		4320	98.7			99.1
	Mn	5	15		Mn	10
		15	10			25
		30	12.5			15
		60	22.5			40
		120	12.5			30
		1440	35			10
		4320	45			15
	Zn	5	25		Zn	32.8
		15	16.6			35.4
		30	17.7			19.2
		60	19.7			27.08
		120	23.9			34.8
		1440	41.1			22.9
		4320	48.9			32.29

As it can be seen in Table 4, in the investigated experimental conditions, both natural sorbents (RNZ and PM) were able to remove significant amounts of heavy metals from AMD collected at “Larga de Sus” mine, especially iron, from solution.

At sorbent doses of 3g/100ml the percent of iron removal was 98.7% after 72 hours, in case of using RNZ, while 91% of iron was removed after 24 hours when using PM.

When comparing removal efficiency of the two investigated sorbents at different contact times, PM gave best removal efficiencies, which are 40% (1 hour) and almost 36% (15 minutes) manganese and zinc respectively, while the percent of manganese and zinc removal was only 45% and 49% after 72 hours, in case of using RNZ.

At sorbent doses of 5 g/100 ml AMD, the percent of iron removal was almost 100% and the final concentrations of iron were reduced to levels less than the maximum consent limit for waste water discharges after 48 hours and 2 hours, when using RNZ and PM, respectively.

Similar results we obtained by Motsi et al. (2010) when treating the AMD from Wheal Jane mine with natural zeolite.

Although Motsi (2010) attributed the high removal rate of iron from the solution to ion-exchange and adsorption processes, but also to precipitation, in our research the probability of iron precipitating out of AMD solution is rather small in the investigated experimental conditions, since the equilibrium pH was lower than the minimum pH value (close to 4.3) needed for the iron precipitation.

On the other hand, the lower removal percent of manganese and zinc obtained using both natural sorbents should be related to the solution pH.

Thus, it might be possible that at low pH values, Mn^{2+} and Zn^{2+} ions removal to be inhibited possibly as a result of a competition between H^+ and heavy metals ions on surface exchangeable sites with an apparent preponderance of H^+ ions (Taffarel et al., 2010).

Although the concentration of zinc and manganese in AMD after treating with natural zeolite and peat moss were higher than the respective consent limits, it is possible to further reduce their final concentrations if higher quantities of sorbents having lower grain-sizes are used or if the AMD solution is contacted with modified sorbents, such as zeolite in Na-form for improving the removal of Zn (Bedelean et al., 2010), manganese oxide coated zeolite (Taffarel et al., 2010) for a better removal of manganese or by treating the peat moss with HNO_3 and NaOH (Bulgariu et al., 2009).

CONCLUSIONS

In the present study two low-cost natural materials, namely zeolite-rich tuff from Rupea (Brasov County) and peat moss from Poiana Stampei (Suceava County) were investigated in batch experiments as potential sorbents for the treatment of acid mine drainage collected from “Larga de Sus” mine (Romania).

The preliminary results indicated that the natural zeolite volcanic tuff and the peat moss samples were able to remove significant amounts of heavy metals, especially iron from AMD.

The removal effectiveness of the heavy metals by the two low-cost sorbents is strongly dependent on their applied dosage and contact time with AMD solution.

In the investigated experimental conditions, PM was proved to be more effective in removing the heavy metals from AMD compared to RNZ sample.

Thus, it was found that RNZ produced a complete removal of iron after 48 h of contact time when a dosage of 5 g was used, while PM was effective in reducing Fe concentration within the first 2 hours of contact leading to a percent of iron removal of almost 100%.

In the same investigated experimental conditions, the removal of manganese and zinc by the two natural sorbents was not very efficient, probably due to the low pH of the solution.

The reaction between RNZ and AMD after 48 hours of contact produced decreases in the manganese and zinc concentration of 50% and 73%, respectively. The maximum efficiency of peat moss in the removal of the two above-mentioned metallic ions after 2 hours of contact was of 30% for Mn and 27% for Zn.

Our preliminary results showed that the two investigated natural sorbents have the potential for use in treating actual acid mine drainage.

However, further researches, including column studies are needed in order to find the best conditions for using natural sorbents to clean-up AMD at industrial scale economically.

The possibility of regenerating the sorbents used for AMD treatment is another issue to be further investigated.

ACKNOWLEDGEMENTS

The authors thank Eng. Gelu Chiorean from S.C. Eleolit S.A Company (Rupea, România) and to Mrs. Carmen Fodor (Poiana Stampei, România) for supplying us the zeolite-rich tuff and the peat moss samples, respectively.

REFERENCES

Ahmaruzzaman M.,2011, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, Advances in Colloid and Interface Science, 166, 1–2, 36–59

Arias M., Barral M.T., Mejuto J.C., 2002, Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids, Chemosphere, 48, 1081–1088

Arunachalam A. M., 2002, Adsorption/Absorption features of Peat Moss for water pollution control - Feasibility Studies for St. John's Harbour Water Pollution, Annual Conference of the Canadian Society for Civil Engineering, Montréal, Québec, Canada, June 5-8

Awan A., Qazi I. A., Khalid I., 2003, Removal of heavy metals through adsorption using sand, Jolunal of Environmental Sciences, 15, 3, 413-416

Balan C., Bilba D., Macoveanu M., 2009, Sphagnum Moss Peat as a potential sorbent and reductant for Chromium (VI) removal from aqueous solutions, Cellulose Chem. Technol., 43(1-3), 99-104

Bedelean H., Maicaneanu A., Burca S., Stanca M., 2010, Investigations on some zeolitic volcanic tuffs from Cluj County (Romania), used for zinc ions removal from aqueous solution, Studia Universitatis Babeş-Bolyai, Geologia, 55 (1), 9 – 15

Brown P. A.,Gill S. A., Allen S. J., 2000, Metal removal from wastewater using peat, Wat. Res., 34, 16, 3907-3916

Buasri A., Chaiyut N., Phattarasirichot K., Yongbut P., Nammueng L., 2008, Use of Natural Clinoptilolite for the Removal of Lead (II) from Wastewater in Batch Experiment, Chiang Mai J. Sci., 35(3), 447-456

Bulgariu L., Răţoi M., Bulgariu D., Macoveanu M., 2008, Equilibrium study of Pb(II) and Hg(II) sorption from aqueous solutions by moss peat, Environmental Engineering and Management Journal, 7, 5, 511-516

Bulgariu L., Robu B., Macoveanu M., 2009, The Pb(II) Sorption from Aqueous Solutions by Sphagnum Moss Peat, Rev. Chim. 60, 2, 171-175

Bulut Y., Tez Z., 2007, Removal of heavy metals from aqueous solution by sawdust adsorption, Journal of Environmental Sciences, 19, 160–166

Burca S., Vermesan G., Bulea C., Stanca M.,, Bedelean H., Maicaneanu A., 2008, Removal of iron and zinc ions from electroplating wastewaters by ionic exchange, Journal of Environmental Protection and Ecology, 9, 4, 868–882

Caramalău C., Bulgariu L., Macoveanu M., 2009, Cobalt (II) Removal from Aqueous Solutions by Adsorption on Modified Peat Moss, Chem. Bull. "POLITEHNICA" Univ. (Timisoara), 54(68), 1, 13-17

Chenxi Li, 2008, Batch and Bench-Scale Fixed-Bed Column evaluations of heavy Metal removals from aqueous solutions and synthetic landfill leachate using low-cost natural adsorbents, Thesis submitted to the Department of Civil Engineering, Queen’s University Kingston, Ontario, Canada

Clyde E.J., 2008, The applicability of passive treatment systems for the mitigatiun of acid mine drainage at the Williams Brothers Mine, Mariposa Country, California: Bench-and Pilot-Scale Studies, A thesis submitted to the Department of Geological Sciences and Geological Engineering, Queen’s University Kingston, Ontario, Canada

Fernandes A.N., Almeida C.A.P., Menezes C.T.B., Debacher N.A., Sierra M.M.D., 2007, Removal of methylene blue from aqueous solution by peat, Journal of Hazardous Materials, 144, 412–419

Gupta B.S., Curran M., Hasan S., Ghosh T.K., 2009, Adsorption characteristics of Cu and Ni on Irish peat moss, Journal of Environmental Management, 90, 954–960

Ho Y.S., Wase D.A.J., Forester C.F., 1995, Batch Nickel Removal from aqueous solution by Sphagnum moss peat, Wat. Res., 29, 5, 1327-1332

Ho Y.S., Wase D.A.J., Forester C.F., 1996, Kiinetic Studies of competitive heavy metal adsorbtion by Sphagnum moss peat, Environmental Technology, 17, 71-77

Hossein K., Hassan M.M., 2006, Elimination of Cd^{2+} and Mn^{2+} from Wastewaters Using Natural Clinoptilolite and Synthetic Zeolite P, Iran. J. Chem. Chem. Eng., 25, 4, 91-94

Jamil T.S., Ibrahim H.S., El-Maksoud I.H., El-Wakeel S.T., 2010, Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions, Desalination, 258, 34–40

Jorge C. Trevino M., Coles C.A., 2003, Kaolinite properties, structure and influence of metal retention on pH, Applied Clay Science, 23, 133– 139

Kalmykova Y., 2004, Leachate treatment of heavy metals by natural and residual product materials , Master’s Thesis, Chalmers University of Technology, Goteborg

Kalmykova Y., Stromvall A., Steenari B., 2008, Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations, Journal of Hazardous Materials, 152, 885–891

Kamel M.M., Ibrahm M.A., Ismael A.M., El-Motaleeb M.A., 2004, Adsorption of some heavy metal ions from aqueuus solutions by using kaolinite clay, Ass. Univ. Bull. Environ. Res., 7, 1, 101-110

Keri A.A., Avram S., Rusu T., 2010, Characteristics Regarding the Geomorphological Change of Land at the Larga de Sus Mine, the Zlatna Mining Perimeter, the County of Alba, ProEnvironment, 3, 318 – 321

Kicsi A., 2010, Studies on the use of natural indigenous sorbents for decontamination of wastewater containing heavy metals, Iasi

Koivulaa M.P., Kujala K., Rönkkömäkib H.,, Mäkeläb M., 2009, Sorption of Pb(II), Cr(III), Cu(II), As(III) to peat, and utilization of the sorption properties in industrial waste landfill hydraulic barrier layers, Journal of Hazardous Materials, 164, 345–352

Lourie E., Gjengedal E., 2011, Metal sorption by peat and algae treated peat: Kinetics and factors affecting the process, Chemosphere, 85, 759–764

Macías F., Caraballo M. A., Rötting T. S., Pérez-López R., Nieto J. M. , Ayora C., 2012, From highly polluted Zn-rich acid mine drainage to non-metallic waters: Implementation of a multi-step alkaline passive treatment system to remediate metal pollution, Science of the Total Environment, 433, 323–330

Mohana D., Chander S., 2006, Removal and recovery of metal ions from acid mine drainage using lignite-A low cost sorbent, J Hazard Mater., 137(3), 1545-53

Motsi T., 2010, Remediation of acid mine drainage using natural zeolite, A thesis submitted to The University of Birmingham, School of Chemical Engineering, The University of Birmingham, United Kingdom

Motsi T., Rowson N.A., Simmons M.J.H., 2011, Kinetic studies of the removal of heavy metals from acid mine drainage by natural zeolite, International Journal of Mineral Processing, 101, 42–49

Muzenda E., Kabuba J., Mollagee M., Mulaba – Bafubiandi A.F., 2011, Cu (II) Removal from Synthetic Waste Water by Ion Exchange Process, Proceedings of the World Congress on Engineering and Computer Science, II WCECS, San Francisco, USA

Natarajan K.A., 2008, Microbial aspects of acid mine drainage and its bioremediation, Transactions of Nonferrous Metals Society of China, 18, 6, 1352–1360

Oboh I., Aluyor E., Audu T., 2009, Biosorption of Heavy Metal Ions from Aqueous Solutions Using a Biomaterial, Leonardo Journal of Sciences, 14, 58-65

Omar W., Al-Itawi H., 2007, Removal of Pb+2 Ions from Aqueous Solutions by Adsorption on Kaolinite Clay, American Journal of Applied Sciences, 4 (7), 502-507

Ouki S.K., Kavannagh M., 1997, Performance of Natural Zeolites for the Treatment of Mixed Metal-Contaminated Effluents, Manag, Res., 15, 4, 383-394

Pérez-López R. Castillo J., Quispe D., Nieto J.M., 2010, Neutralization of acid mine drainage using the final product from CO_2 emissions capture with alkaline paper mill waste, Journal of Hazardous Materials, 177, 1–3, 762–772

Perez-Marın A.B., Zapata V. M., Ortuno J.F., Aguilar M., Saez J., Llorens M., 2007, Removal of cadmium from aqueous solutions by adsorption onto orange waste, orange waste, Journal of Hazardous Materials, 139, 1, 122–131Peric J., Trgo M., Medvidovic N.V., 2004, Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms, Water Research, 38, 1893–1899

Popa G.M., 2011, Unconventional ecological methods, for cleaning wastewaters, University of Agricultural Sciences and Veterinary Medicine of Cluj-Napoca, Cluj Napoca

Qin F., Wen B., Shan X., Xie Y., Liu T., Zhang S., Khan S.U., 2006, Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat, Environmental Pollution, 144, 669-680

Ringqvista L., Holmgrenb A., Bornc I.O., 2002, Poorly humified peat as an adsorbent for metals in wastewater, Water Research, 36, 2394–2404

Rios C.A., Williams C.D., Roberts C.L., 2008, Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites, Journal of Hazardous Materials, 156, 23–35

Ruihua L., Lin Z., Tao T., Bo L., 2011, Phosphorus removal performance of acid mine drainage from wastewater, Journal of Hazardous Materials, 190, 669–676

Sen T.K., Mahajan S.P., Khilar K.C., 2002, Adsorption of Cu^{2+} and Ni^{2+} on iron oxide and kaolin and its importance on Ni^{2+} transport in porous media, Colloids and Surfaces A: Physicochem. Eng. Aspects, 211, 91-102

Shavandi M.A., Haddadian Z., Ismail M.H.S., Abdullah N., Abidin Z.Z., 2012, Removal of Fe(III), Mn(II) and Zn(II) from palm oil mill effluent (POME) by natural zeolite, Journal of the Taiwan Institute of Chemical Engineers, 43, 750–759

Suteerapataranon S., Bouby M., Geckeis H., Fanghanel T., Grudpan K., 2006, Interaction of trace elements in acid mine drainage solution with humic acid, Water Research, 40, 2044 – 2054

Taffarel S.R., Rubio J., 2009, On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites, Minerals Engineering, 22, 336–343

Taffarel S.R., Rubio J., 2010, Removal of Mn^{2+} from aqueous solution by manganese oxide coated zeolite, Minerals Engineering, 23, 1131–1138

Tetisan A., 2010. Research and development on the use of zeolite tuff from Barsana area for cleaning wastewaters, Babes-Bolyai University, Cluj-Napoca

Wang S., Peng Y., 2010, Natural zeolites as effective adsorbents in water and wastewater treatment, Chemical Engineering Journal, 156, 11–24

Wanjing X., Loretta Y. Li, John R.G.,2010, Zinc removal from acid rock drainage by clinoptilolite in a slurry bubble column, Applied Clay Science, 50, 158–163

Witek-Krowiak A., Szafran R.G., Modelski S.,2011, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination, 265, 126–134

Yanga J., Leea J.Y., Baekb K., Kwonc T., Choia J., 2009, Extraction behavior of As, Pb, and Zn from mine

Yavuza O., Altunkaynakb Y., Guzelc F., 2003, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Research, 37, 948–952

Zhua C., Wanga L., Chena W., 2009, Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull, Journal of Hazardous Materials, 168, 739–746