Pol. J. Environ. Stud. Vol. 24, No. 6 (2015), 2773-2777
DOI: *10.15244/pjoes/59307*

Short Communication

Application of a Manganese Ore Constructed Wetland for Radium Removal from Lead-Zinc Mine Water

Chunhui Zhang*, Xiangyu Gao, Liangliang Wang, Zheng Li, Haoran Li, Zhihe Zhang, Minying Jin

School of Chemical and Environmental Engineering,
China University of Mining and Technology (Beijing),
Room 607, Yifu Science and Research Building, No. Ding 11, Xueyuan Road, Beijing 100083, China

Received: July 25, 2015
Accepted: September 5, 2015

Abstract

To remedy the radium (Ra) in lead-zinc mine water, a laboratory-scale horizontal subsurface flow constructed wetland was designed. In lab-scale wetlands, a manganese ore constructed wetland was proven to be a feasible treatment technology for Ra removal. The results showed that with the influent flow loading rate of 0.096 m/d, after the treatment of manganese ore constructed wetlands (CWs), the ^{226}Ra and ^{a}Ra removal efficiencies were 89.5-94.7% and 84.1-92.3%. And the removal efficiencies of SO_4^{2-}, Zn, Pb, Cu, Cd, As, Fe, and Mn were 65.4%, 93.7%, 88.5%, 86.2%, 82.4%, 76.3%, 98.3%, and 97.8%, respectively.

Keywords: radium, radioactivity, manganese ore, lead-zinc mine, constructed wetland

Introduction

In Hunan province, China, a lead-zinc mine ore is associated with radium (Ra). After all mining activities have ended, Ra will be dissolved in lead-zinc mine water and discharged into surface water, groundwater, and soil. Ra is a source of an additional and unexpected contaminant of the natural environment: radioactivity. Absorbed into the human body, Ra will accumulate and endanger human health. Internal radiation sources from the long-lived nuclides will radiate for a lifetime and cause long-term damage to human tissue. Irradiated human tissue cells by Ra may damage genetic DNA material and cause carcinogenic, mutagenic, and other malignant diseases [1, 2]. The literature includes few studies that relate to Ra treatment, remediation, and elimination. For instance, Ipek et al. studied the removal of some artificial radionuclides in secondary treatment and radioactivity behavior in biological treatment [3]. However, the current methods for treatment of Ra are under continuous improvements. A lot of experiments are performed to test new and sometimes rather expensive techniques, like titanate nanofibers [4]. Due to the high cost of the above treatment methods, a search for substitutes is underway. Such adsorbents should be readily available, economically feasible, and should be regenerated with ease.

Recently, Ra elimination has been investigated by adsorption with a variety of economically priced sorbents. Materials like zeolite apatite, bone char, calcined phosphate, and oxy/hydroxides are examples of low-price adsorbents. Chalupnik et al. applied the possibility of zeolite as adsorption media for removal of radium from mine water [5]. However, the main problems in using these materials are their low adsorption capacities and the difficulty in removing the adsorbed pollutants from the adsorbents [6]. Co-precipitation is another cheap approach for Ra elimina-

*e-mail: truemanjung@163.com

tion. Chen et al. applied natural Mn ore to treat Ra. The results showed that Ra in wastewater can be remediated from 2-7 kBq/m^3 to 0.3 kBq/m^3 [7]. In this process, Mn ions react with OH^- to form $Mn(OH)_2$ firstly. After that, $Mn(OH)_2$ reacts with dissolved oxygen. Then, $MnO(OH)_2$ are formed. Finally, Ra can be absorbed by $MnO(OH)_2$. The reaction processes can be interpreted by the following equations.

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \quad (1)$$

$$Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO(OH)_2 \quad (2)$$

The constructed wetlands (CWs) have received increasing attention in water and wastewater treatment over the last several decades, especially for wastewater advanced treatment. The main advantages of CW are their low operating costs, the fact that it does not require an external energy source, and its integration with the landscape. Generally, CW can be classified as surface-flow (SFCW) or vertical-flow wetlands (VFCW) [8]. Some previous studies have shown the overall effectiveness of SFCW or VFCW in treating municipal or industrial wastewater [9, 10]. In general, temperature, hydraulic residence time (HRT), vegetation type, media material, and CW type plays an important role in treating wastewater [11]. Assuredly, CW can be an option for sufficient removal of radioactive pollutants. In this study, a kind of horizontal subsurface flow constructed wetland with manganese ore as padding medium was designed to remove Ra in lead-zinc mine water. This approach can be combined with the advantages of CWs and co-precipitation with Mn ore medium.

Materials and Methods

Configuration of Lab-Scale Constructed Wetlands

Fig. 1 shows a schematic of the experimental layout of a lab-scale manganese ore constructed wetland. The horizontal subsurface flow constructed wetland was confined inside a PVC tank that is 2 m long, 0.5 m wide and 0.6 m high. The substratum layer is 50 cm deep, composed of 6-8 mm manganese ore without any soil on the surface. The manganese ore (MnO_2: 38.6% and density 3.56 g/cm^3; mass fraction of elements: O 33.95%, Mn 40.15%, Fe 12.67%, K 0.62%, Ca and Mg 6.23%, Al, 2.11%, Si 4.27%) was purchased from Henan Filter Co. Ltd, China. Reed planting density was set at 16-20 plants per square meter, spacing of plants was 20-25 cm. Gravels were arranged at influent and effluent areas to guarantee the even distribution of water. The lead-zinc mine water was manipulated by a constant flow peristaltic pump. The feed of lead-zinc mine water continued for 24 h. The experiment started in April 2015 at a hydraulic retention time (HRT) of five days. After continuous operation for two weeks, fresh reed roots (30 cm long) were transplanted to the CWs at a depth of 5-10 cm. When sprouts appeared in May and grew healthily, the monitoring of influent and effluent started. In order to facilitate sampling and analysis, the passing tubes were installed at starting and ending edges, and at 1/4, 2/4, and 3/4 of the middle in CWs.

Characteristics of Lead-Zinc Mine Water

The water samples, which were pretreated by clarification, coagulation, and filtration, were collected from a lead-zinc mine ore in Hunan province, China. The characteristics of the lead-zinc mine water were summarized in Table 1.

Analytical Reagents and Methods

All reagents used in analysis were obtained from Beijing Chemical Reagent Company (Beijing, China) and conformed to the purity requirements of analytic grade. The water quality parameters such as Ra, pH, SO_4^{2-}, Zn, and Pb, etc., were analyzed according to standard methods of China [12]. The pH value was determined by a Shanghai Leici PHS-3D brand pH meter. The temperature and ORP were determined by a temperature sensor (PHB-2, Shanghai Leici, China). Fe and Mn were measured using spectropho-

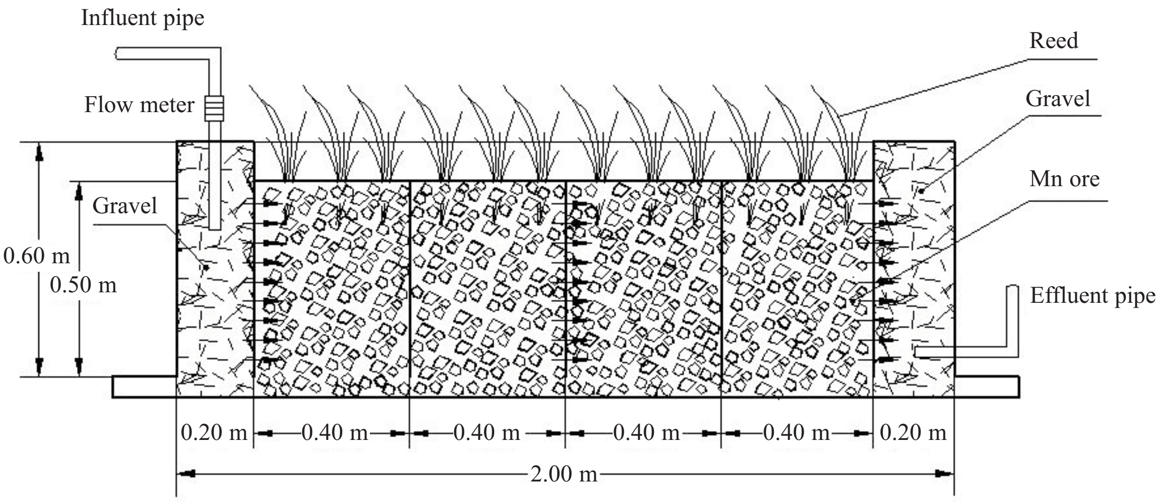

Fig. 1. Experimental set-up of lab-scale constructed wetland.

Table 1. Characteristics of lead-zinc mine water samples.

Parameter	^{226}Ra	^{a}Ra	pH	SO_4^{2-}	Zn	Pb	Cu	Cd	As	Fe	Mn
	(kBq/m^3)			(mg/L)							
Concentration	2.3-4.8	9.7-15.6	5.5-8.5	139-658	12.85	0.92	0.082	0.221	0.01	12.26	13.50

tometry. For the measurements of radium in the liquid sample, the radiochemical method was applied based on co-precipitation of radium isotopes with a barium carrier. The resulting precipitate is mixed with the gelling scintillating cocktail LumaGel™. Determination of ^{226}radium was implemented according to GB11214-89 and determination of aradium was implemented according to GB11218-89 [13, 14].

Results and Discussion

Removal of Radium

The experiment results show that the CW system has superior performance and strong capability of resisting hydraulic loading impact when the hydraulic loading rate is set at 0.096 m/d. With the influent flow loading rate of 0.096 m/d and the fluctuation of water temperature from 16.3ºC to 27.8ºC, ^{226}Ra and ^{a}Ra variations and removal efficiencies of the CW were assessed (Figs. 2, 3).

As seen in Figs. 2 and 3, manganese ore wetland showed good and stable removal efficiencies of ^{226}Ra and ^{a}Ra. The ^{226}Ra and ^{a}Ra removal efficiencies were 89.5-94.7% and 84.1-92.3%, respectively.

Removal of Other Pollutants

Under the same experimental conditions described above, the removal efficiencies of other pollutants in lead-zinc mine water by CW were described in Table 2.

It can be seen from Table 2 that the removal efficiencies of SO_4^{2-}, Zn, Pb, Cu, Cd, As, Fe, and Mn were 65.4%, 93.7%, 88.5%, 86.2%, 82.4%, 76.3%, 98.3%, and 97.8%, respectively. In 63 days of operation of CW, not only the removal efficiencies for Ra, but the removal efficiencies for other pollutants are very stable.

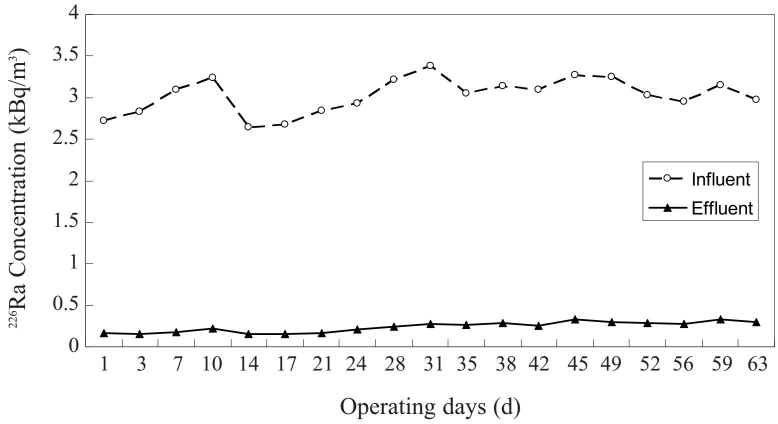

Fig. 2. ^{226}Ra concentration variation in manganese ore constructed wetlands.

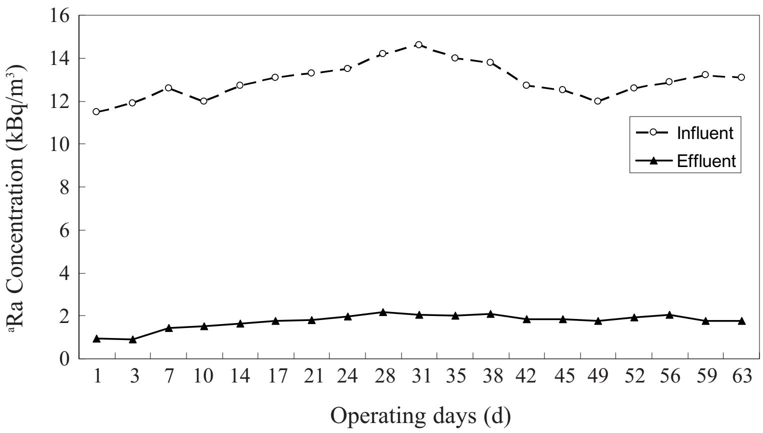

Fig. 3. ^{a}Ra concentration variation in manganese ore constructed wetlands.

Table 2. Removal efficiencies of other pollutants in lead-zinc mine water*.

Parameter	Influent (mg/L)	Effluent (mg/L)	Removal (%)
SO_4^{2-}	453.2±23.6	156.8±8.1	65.4
Zn	10.13±3.3	0.63±0.15	93.7
Pb	0.90±0.58	0.10±0.03	88.5
Cu	0.088±0.006	0.012±0.006	86.2
Cd	0.230±0.008	0.040±0.002	82.4
As	0.01±0.005	0.002±0.0005	76.3
Fe	12.42±0.22	0.21±0.06	98.3
Mn	12.95±2.84	0.28±0.08	97.8

*Sample numbers: 4;
all values were reported as mean±standard deviation.

Discussion

In previous studies, co-precipitation absorption by $MnO(OH)_2$ was proposed as one of the major reasons to remove pollutants in wastewaters by CWs. When oxygen is available, the formed Mn oxide deposit facilitates the adsorption of pollutants in wastewaters [15]. Rather, plant uptake and decay, plus retention of pollutants by inorganic and organic soil components, are auxiliary probable mechanisms of accumulation of pollutants near the soil surface [16]. Redox potential can be used to reflect the amount of dissolved oxygen (DO) and the redox state in the water environment. In the CWs, it is difficult to detect the DO. So, in this experiment, the redox potential of mine water in CWs was measured by ORP meter. The ORP probes were placed in the deep of 30 cm and 5 cm from the subsurface of CWs. The detection values were -205 mV and 306 mV, respectively. In the deep of 30 cm in CWs, the DO is consumed by the oxidation process of Mn. So the removal of Ra and other non-ferrous metals mainly depends on the adsorption of $MnO(OH)_2$. By comparison, the removal of pollutants near the subsurface of CWs mainly depends on plant uptake.

Chalupnik et al. applied an underground treatment installation to remove radium from mine water. For ^{226}Ra and ^{228}Ra removal, the efficiency of treatment averaged 90% [17]. Some scholars have utilized ion exchange resins by adsorption of reverse osmosis or polymeric columns to remove Ra in water [18, 19]. For treatment of Ra in water using CW, there was no previous experience to fall back on concerning construction, application, and management.

Since CW is a cheap and effective treatment method, in recent years it has been widely used in water and wastewater treatments. Base on our research, a possible solution for a passive technology might be the application of CW with manganese ore medium for removal of not only Ra but also some other pollutants from lead-zinc mine water. The application of CW is expected to be significantly cheaper than the methods used so far. However, a detailed financial study has to be done in the future.

Conclusions

The main goal of these experiments was to use an inexpensive passive method – like manganese ore CW – for the treatment of a lead-zinc mine water to remove radium isotopes. It can be clearly seen that the results of treatment by manganese ore CW for Ra were very good. The ^{226}Ra and ^{a}Ra removal efficiencies were 89.5-94.7% and 84.1-92.3%. And the removal efficiencies of SO_4^{2-}, Zn, Pb, Cu, Cd, As, Fe, and Mn were 65.4%, 93.7%, 88.5%, 86.2%, 82.4%, 76.3%, 98.3%, and 97.8%, respectively.

References

1. AUVINEN A., KURTTIO P., PEKKANEN J., PUKKALA E., ILUS T., SALONEN L. Uranium and other natural radionuclides in drinking water and risk of leukemia: a case–cohort study in Finland. Cancer Cause. Control. **13**, 825, **2002**.
2. KURTTIO P., SALONEN L., ILUS T., PEKKANEN J., PUKKALA E., AUVINEN A. Well water radioactivity and risk of cancers of the urinary organs. Environ. Res. **102**, 333, **2006**.
3. IPEK U., ARSLAN E. I., ASLAN S., DROGU M., BAYKARA O. Radioactivity in municipal wastewater and its behaviour in biological treatment. B. Environ. Contam. Tox. **7**, 319, **2004**.
4. YANG D. J., ZHENG Z. F., ZHU H. Y., LIU H. W., GAO X. P. Titanate nanofibers as intelligent adsorbents for the removal of radioactive ions from water. Adv. Mater. **20**, 2777, **2008**.
5. CHALUPNIK S., FRANUS W., WYSOCKA M., GZYL G. Application of zeolites for radium removal from mine water. Environ. Sci. Pollut. Res. Int. **20**, 7900, **2013**.
6. LADEIRA A. C. Q., GONCALVES C. R. Influence of anionic species on uranium separation from acid mine water using strong base resins. J. Hazard. Mater. **148**, 499, **2007**.
7. CHEN S. A., LIU J., YU K. Treatment of waste water in tailings dam of an uranium mill by lime precipitation – air aeration. Uranium Mining and Metallurgy. **2**, 52, **1983**.
8. ZHANG C. H., NING K., ZHANG W. W., GUO Y. J., CHEN J., LIANG C. Determination and removal of antibiotics in secondary effluent using a horizontal subsurface flow constructed wetland. Environ. Sci. Proc. Impacts. **15**, 709, **2013**.
9. VYMAZAL J. Removal of nutrients in various types of constructed wetlands. Sci. Total Environ. **380**, 48, **2007**.
10. ZHANG H. G., CUI B. S., HONG J. M., ZHANG K. J. Synergism of natural and constructed wetlands in Beijing, China. Ecol. Eng. **37**, 128, **2011**.
11. VYMAZAL J. The use constructed wetlands with horizontal sub-surface flow for various types of wastewater. Ecol. Eng. **35**, 1, **2009**.
12. XI D. L., SUN Y. S., LIU X. Y. Environmental monitoring, Higher Education Press. Beijing, **2004**.
13. China Ministry of Environmental Protection (MEP). Analytical determination of radium-226 in water. GB11214-89, Beijing: MEP, **1989**.
14. China Ministry of Environmental Protection (MEP). The determination for alpha-radio nuclide of radium in water. GB11218-89, Beijing: MEP, **1989**.
15. HSU P. Waters treatment theory and principles. China Architecture & Building Press, Beijing, **2000**.

16. DUNBABIN J. S., BOWMER K. H. Potential use of constructed wetlands for treatment of industrial wastewaters containing metals. Sci. Total Environ. **111**, 151, **1992**.
17. CHALUPNIK S., WYSOCKA M. Radium removal from mine waters in underground treatment installations. J. Environ. Radioactiv. **99**, 1548, **2008**.
18. BAEZA S., SALAS A., GUILÉN J. Adaptation of working conditions of an operating drinking water treatment plant to remove naturally occuring radionuclides. Water Air Soil Poll. **223**, 5057, **2012**.
19. MIRO C., BAEZA A., SALAS A., PASTOR-VALLE J. F., PASTOR-VILLEGAS J. Adaptation of ^{241}Am and ^{226}Ra from natural water by wood charcoal. Appl. Radiat. Isotopes **66**, 95, **2008**.