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-
Chen et al. applied natural Mn ore to treat Ra. The results showed that Ra in wastewater can be remedi-ated from 2-7 kBq/m³ to 0.3 kBq/m³ [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.

\[
\begin{align*}
\text{Mn}^{2+} + 2\text{OH}^- & \rightarrow \text{Mn(OH)}_2 \\
\text{Mn(OH)}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{MnO(OH)}_2
\end{align*}
\]

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 (MnO₂: 38.6% and density 3.56 g/cm³; 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, SO₄²⁻, 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-
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 $^{226}$Ra was implemented according to GB11214-89 and determination of $^{238}$Ra 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 16.3°C to 27.8°C, $^{226}$Ra and $^{238}$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 $^{238}$Ra. The $^{226}$Ra and $^{238}$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.

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{226}$Ra ($\text{kBq/m}^3$)</th>
<th>$^{238}$Ra ($\text{kBq/m}^3$)</th>
<th>pH</th>
<th>SO$_4^{2-}$ (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Cd (mg/L)</th>
<th>As (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>2.3-4.8</td>
<td>9.7-15.6</td>
<td>5.5-8.5</td>
<td>139-658</td>
<td>12.85</td>
<td>0.92</td>
<td>0.082</td>
<td>0.221</td>
<td>0.01</td>
<td>12.26</td>
<td>13.50</td>
</tr>
</tbody>
</table>

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

Fig. 3. $^{238}$Ra concentration variation in manganese ore constructed wetlands.
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 $^{228}$Ra removal efficiencies were 89.5-94.7% and 84.1-92.3%. And the removal efficiencies of SO$_4$, 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


