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A novel conversion process for waste residue: Synthesis of zeolite from electrolytic manganese residue and its application to the removal of heavy metals

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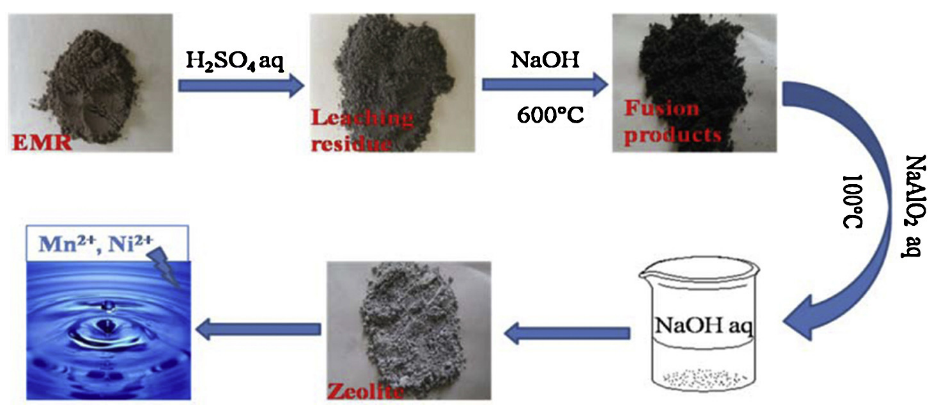
HIGHLIGHTS

- A novel conversion process for the utilization of EMR was first proposed.
- Effect of Si/Al ratio on the EMRZ synthesis was investigated.
- EMRZ showed good adsorption properties for removal of Mn^{2+} and Ni^{2+} ions.
- The adsorption mechanism and kinetics were systematically studied.
- Ion exchange was responsible for metal ions removal.

GRAPHICAL ABSTRACT



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ABSTRACT

The zeolite material was first synthesized from electrolytic manganese residue (EMRZ), by a two-step synthetic procedure using NaOH and $NaAlO_2$ within a short aging period. Based on the detailed analyses using XRD, FT-IR, FE-SEM, XRF, CEC and BET surface area measurement, the product synthesized at Si/Al ratio = 1.5 was mainly composed of Na-A zeolite with a specific surface area of 35.38 $m^2\,g^{-1}$. Then, the removal characteristics of Mn^{2+} and Ni^{2+} ions by EMRZ were investigated under various operating variables like contact time, solution pH and initial metal concentration. The adsorption equilibrium for both Mn^{2+} and Ni^{2+} was best described by the Langmuir model, confirming the applicability of monolayer coverage of metal ions onto EMRZ particles. The maximum sorption capacities for Mn^{2+} and Ni^{2+} shown by EMRZ were 66.93 $mg\,g^{-1}$ and 128.70 $mg\,g^{-1}$, respectively. It was also found that adsorption of Mn^{2+} and Ni^{2+} by EMRZ followed second-order kinetics and rate constants for Mn^{2+} and Ni^{2+} sorption were found to be 0.001091 and 0.005668 $g\,mg^{-1}\,min^{-1}$, respectively at 30 °C. These results indicate that the synthesized EMRZ is a promising and low-cost adsorbent for removing heavy metals from wastewater due to higher adsorption capacity than other adsorbents.

1. Introduction

Rapid industrialization has led to increased disposal of heavy metals into the environment, causing serious soil and water pollution [1]. Meanwhile, heavy metals are not biodegradable and tend

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to accumulate in living organisms causing various diseases and disorders [2,3]. Moreover, heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic or industrial applications. Thus considerable attention has been paid to methods for metal removal from industrial wastewaters as the global interests in this issue increase over the past decades [3–5].

To date, numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [6]. Among them, ion exchange techniques using solid adsorbents has been a promising method for treating wastewater, owing to its advantages such as operational simplicity, low cost, availability in large amount and ability to treat pollutants in a sufficiently large scale operation [6,7]. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals [8]; however, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. Consequently, the use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Electrolytic manganese residue (EMR) is a potentially harmful industrial solid waste that comes from the electrolytic manganese industry and has rarely been recycled in large quantities [9]. In the electrolytic manganese metal (EMM) industry, about 6∼9 tons of EMR is discharged into the environment per ton of produced EMM [10]. The common practice in China is collecting the EMR in open sites near the plants. It is highly questionable if the EMR generated is managed properly. Because EMR contains some heavy metal elements and compounds, the untreated discharge can cause serious pollution of surrounding soil and receiving water bodies [11,12]. Additionally, high volume EMR resulting from large scale industrial activities have long been considered to be a burden, due to the high costs for their associated post-treatment, storage and disposal [10,11]. Owing to its mineral composition, EMR has been mostly recycled as hydraulic cement, concrete aggregate, road base, brickmaking materials in civil engineering work, as well as for the production of chemical fertilizers in agricultural work [13–16]. Yet, problems associated with above disposal, such as the potential environmental impacts and the severe environmental regulations, make the recycling of slag difficult. It is, therefore, essential to continuously develop new and advanced recycling processes of EMR.

Recently, our research group found that zeolite can be synthesized using EMR as Si and Al sources. Zeolites are known as ion-exchange materials where the indigenous charge-balancing cations (typically sodium and calcium) are not rigidly fixed to the hydrated aluminosilicate framework and are readily exchanged with metal cations in solution [6,17]. Meanwhile, the fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from wastewaters [17,18]. Moreover, zeolites can transfer a heavy metal contamination problem of many thousands of liters to a few kilos of easily handled solid. The toxic metals are firmly held in the crystal structure and do not leach, however for ultimate environmental protection the solid zeolite can be cement stabilized or vitrified [2]. Given these advantages, zeolites (including natural, commercial, and chemically synthesized zeolites) have been intensively studied recently for the removal of heavy metals [17–19]. Accordingly, making use of EMRZ to remove heavy metals can not only reduce the cost, but also comply with the requirement of green economy.

The objective of the present study was to propose a novel conversion process of EMR to zeolite in order to make full use of the economic potential of EMR, and to find out its potential use as low-cost adsorbent for the removal of heavy metals from aqueous solution. Mn^{2+} and Ni^{2+} ions were chosen as a target contaminant to characterize the adsorptive properties of the synthesized zeolite. For the present study, the uptake of heavy metals on EMRZ was evaluated as a function of initial metal ions concentration, pH, and contact time. Further, models to fit the adsorption equilibrium and kinetic data were presented to understand the adsorption mechanism.

2. Materials and methods

2.1. Materials

The EMR investigated in this study was mainly generated in leaching process of the manganese ore (with part of residue generated in electrolytic cell process) at an electrolytic manganese company, situated in western of Hunan province, China. The chemical composition of EMR used in this study is listed in Table 1. This chemical composition is fairly common in EMR produced in China's EMM industry.

Stock solutions of Mn^{2+} and Ni^{2+} ions with concentration at 1000 mg L^{-1} were prepared by dissolving given amounts of $MnSO_4{\cdot}H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$, respectively, in distilled water. The solutions of different concentrations used in various experiments were obtained by dilution of the stock solutions.

2.2. Zeolite synthesis

The fabrication process of EMRZ is shown in Fig. 1. Based on our previous related studies [20], a fusion method, involving alkaline fusion followed by hydrothermal treatment, was adopted for the synthesis of zeolite in this research. During the hydrothermal reaction process, various amounts of sodium aluminate ($NaAlO_2$) were added into the reaction system to investigate the effect of the ratio of Si/Al. At the end of the process the solid phase was collected by filtration, washed several times with distilled water, and then dried at 100 °C. The obtained samples were labeled based on their initial Si/Al ratios. Namely, the samples with initial Si/Al ratio of 1.5, 2.0 and 2.5 were labeled as EMRZ15, EMRZ20 and EMRZ25, respectively.

2.3. Adsorption studies

The adsorption of heavy metals was performed by shaking 0.3 g of adsorbents with a 100 mL solution of known solute (Mn^{2+} and Ni^{2+} ions) concentration ranging from 100 to 600 mg L^{-1} at 200 rpm in a constant temperature shaker bath. A portion of the solution was collected at predetermined time intervals for kinetics and at equilibrium time for isotherms. The residual concentration was centrifuged at 5000 rpm for 2 min and then determined in triplicate using Thermo SOLAAR atomic absorption spectrophotometers (Thermo Electron, USA). The equilibrium adsorption capacity q_e (mg g^{-1}) was calculated using the following equation.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e (mg L^{-1}) are the concentration of the test solution at the initial stage and under equilibrium conditions, respectively. V (L) is the volume of the test solution and m (g) is the mass of the adsorbent used.

To determine the effect of experimental parameters such as pH and contact time on adsorption process, this method was also applied by varying the corresponding condition. The pH of solution investigated was changed between 1.0 and 6.0 using 0.5 mol/L HCl solutions.

2.4. Characterization

The crystal phase was identified by XRD (D8 Discover, Bruker, Germany). Chemical analysis of EMR, leaching residue and EMRZ