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Removal of basic dye (methylene blue) from aqueous solution using zeolite synthesized from electrolytic manganese residue

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ABSTRACT

The zeolite synthesized from electrolytic manganese residue (EMRZ) was investigated as adsorbents to remove methylene blue (MB), a cationic dye, from aqueous solutions. The effects of various experimental parameters, such as contact time, initial MB concentration, temperature and pH on the adsorption capacity were investigated. The results showed that the adsorption behavior of EMRZ was greatly affected by pH and temperature. And higher solution pH and temperature resulted in higher adsorption capacity of MB. The experimental data were also analyzed by the Langmuir and Freundlich models of adsorption. The adsorption of MB onto EMRZ agrees well with the Langmuir isotherm and the thermodynamic parameters such ΔH, ΔS and ΔG were determined to be +37.46 kJ mol^{-1}, +201.03 J mol^{-1} K^{-1}, −23.45 to −25.46 kJ mol^{-1}, respectively, showing adsorption to be an endothermic yet spontaneous process. Moreover, pseudo-first-order and pseudo-second-order models were considered to evaluate the rate parameters. The adsorption process could be described well by pseudo-second-order model, with an activation energy of +13.71 kJ mol^{-1}. These results indicate that the synthesized EMRZ is a promising and low-cost adsorbent for removing dyes from wastewater due to the high adsorption capacity.

Introduction

Dyes are widely used in industries such as textiles, pulp mills, leather, dye synthesis, printing, food, and plastics, etc. It is estimated that over 7×10^5 t are produced annually, with 10–15% being discharged into the environment in wastes [1]. From the viewpoint of the aesthetic nature of environment, color is the first contaminant to be recognized in wastewater. Their presence in aquatic systems, even at very small amounts, is highly visible and undesirable. By reducing solar light penetration, dyes also have a derogatory effect on photosynthesis [2]. Meanwhile, many dyes and their degradation products are toxic and even carcinogens, which pose a serious hazard to human being and the aquatic organisms [3]. Accordingly, the removal of dyes is of great concern as the global interests in this issue increase over the past decades.

Since dyes have a synthetic origin and complex aromatic molecular structures, biological procedures, although widely utilized in the removal of color, are very inefficient due to their physicochemical, thermal, and optical stability [4]. To date, beside biological procedures, many purification methods have been developed such as chemical coagulation, chemical oxidation, membrane separation, electrochemical process, and adsorption techniques [5]. Among them, physical adsorption 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]. Adsorption processes using activated carbons has been found to be effective for removal of dyes from aqueous solution. However, commercially available activated carbon is expensive. Widespread use of commercially available activated carbon is restricted due to high cost. Hence, in the last years, special emphasis on the dye removal utilizing wastes and products synthesized from wastes has been given due to low cost and resource recycling [2,7–10].

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 [11]. Since 2000, China has become the world's largest producer, consumer, and exporter of electrolytic manganese metal (EMM). In the EMM

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industry, about 6–9 t of the solid waste is discharged into the environment per ton of produced EMM [12]. The common practice in China is to collect the EMR in open sites near the plants. These collection sites are often not well managed to prevent releases to the soils and surrounding areas. Because EMR contains some heavy metal elements and compounds, the untreated discharge can cause serious pollution of surrounding soil and receiving water bodies [13,14]. In addition, these collection sites occupy massive land resources [14,15]. 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. It is, therefore, essential to continuously develop new and advanced recycling processes of EMR.

As there is rather high M_n content in EMR, more or less 4% in w/w in general, sometimes even as high as 15% [12], the untreated discharge results in a huge loss of precious manganese element. Hence, various investigations have been implemented by some researchers focused on extraction of value manganese metals. As reported in literatures, it is well known that manganese could be easily recovered from EMR by a simple acid leaching [16]. However, as for the bulk leaching residue obtained from leaching process, there is scanty information in the literature on the utilization of leaching residue. Recently, our research group found that zeolite can be synthesized using leaching residue as Si and Al sources. And the efficient utilization of EMR as ingredients of other materials may be advantageous in reduction of not only waste generation but also manufacturing costs. Moreover, zeolites (including natural, commercial, and chemically synthesized zeolites) have been investigated for the removal of methylene blue (MB), a cationic dye [2]. Accordingly, making use of EMR-made zeolite (EMRZ) to remove dyes can not only reduce the cost, but also comply with the requirement of green economy.

The purpose of this work was to prepare zeolite from EMR 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 dyestuff from aqueous solution. Methylene blue (MB), a water-soluble cationic dye, was used as a target contaminant to characterize the adsorptive properties of the synthesized zeolite. For the present study, the uptake of MB on EMRZ was evaluated as a function of initial MB concentration, pH, temperature, and contact time. Further, models to fit the adsorption equilibrium and kinetic data were presented to understand the adsorption mechanism.

Materials and methods

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. The raw slag mainly consists of Al_2O_3, SiO_2, CaO, MnO and Fe_2O_3. This chemical composition is fairly common in EMR produced in China's EMM industry. Meanwhile, the phase composition of EMR is shown in Fig. 1 and the phase is very complex in the EMR as shown by XRD.

Table 1
Major chemical composition in EMR.

Constituent	Na_2O	SiO_2	Al_2O_3	MgO	K_2O	CaO	MnO	Fe_2O_3	TiO_2
Mass (wt%)	2.7	24.6	12.2	1.7	2.4	8.6	4.6	7.9	0.4

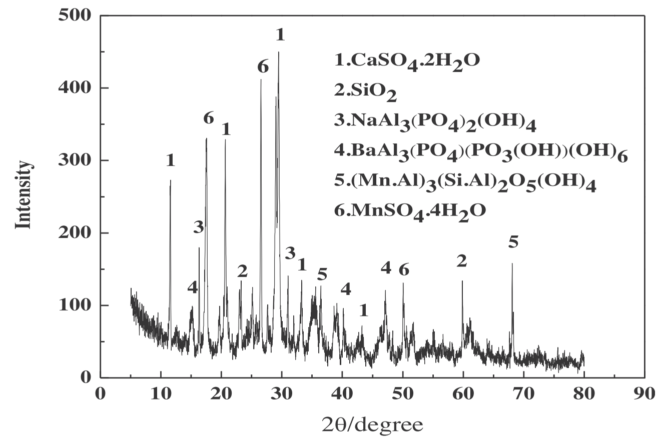

Fig. 1. XRD pattern of EMR.

Methylene blue (Tianjing chemical reagent research institute, China) was used without any further purification. And the chemical structure of MB was shown in Fig. 2. A stock solution with concentration at 1000 mg L^{-1} was prepared and the solutions for adsorption tests were prepared from the stock solution to the desired concentrations.

Synthesis of EMRZ from EMR

Prior to synthesis of EMRZ, the raw slag was ball-milled and screened using a 50 mesh sieve to facilitate dissolution. First, 10.0 g of the ball-milled slag was dissolved in 100 mL of 1.5 mol L^{-1} H_2SO_4 aqueous solution, and subsequently the temperature was elevated to 80 °C and stirred for 2 h to achieve a complete dissolution of EMR. The obtained suspension was separated into leaching residue and leachate mainly containing plenty of manganese elements by filtration. As for the thus obtained leaching solution, the valuable metal, namely Mn, can be recovered from the metal cations extracted from EMR using convenient chemical reagents [16].

The synthesis of zeolite was performed using leaching residue, with the aim of making full use of the chemical components of EMR. The chemical composition of the leaching residue was listed in Table 2. Based on the previous related studies [17,18], a fusion method, involving alkaline fusion followed by hydrothermal treatment, was adopted for the synthesis of zeolite in this research. First, three grams of leaching residue were mixed with NaOH powder (analytical reagent grade) to obtain a homogeneous mixture and the ratio of leaching residue to NaOH was kept at 1:1.3 (w/w). The mixture was then heated in a ceramic crucible in air at 600 °C for 90 min. Then, the resultant solid mass was crushed. A 3.0 g fusion products powder was dissolved in 25 mL of 0.5 mol L^{-1} NaOH aqueous solution until homogenized and then another 50 mL of aqueous solution containing 2.0 g of sodium aluminate was next added dropwise. The obtained slurry was vigorously stirred for 1 h at 100 °C, subsequently aged at the same

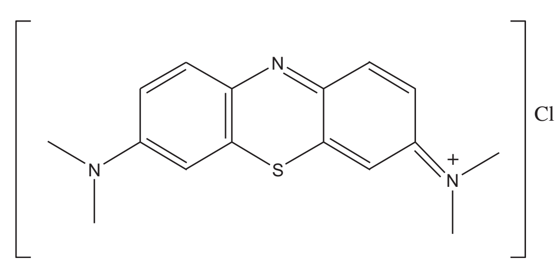

Fig. 2. Molecular structure of MB.