Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Adsorption of methylene blue on modified electrolytic manganese residue: Kinetics, isotherm, thermodynamics and mechanism analysis

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ARTICLE INFO

Article history:
Received 10 August 2017
Revised 8 October 2017
Accepted 15 November 2017
Available online xxx

Keyword:
Electrolytic manganese residue
Adsorption
Methylene blue
Low cost adsorbent

ABSTRACT

Electrolytic manganese residue (EMR) is a solid waste found in filters after sulphuric acid leaching of manganese carbonate ore. In this work, modified electrolytic manganese residue (MEMR) as a high-efficiency adsorbent for the removal of methylene blue (MB) was synthesized via hydrothermal method. The characterizations of MEMR were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, N_2 adsorption/desorption isotherms, and scanning electron microscope. The results showed that with the BET specific surface area of 500.8 m^2/g the MEMR reached the maximum adsorption capacity (548.15 m^2/g) within 50 min when the pH of initial solution was 6.05 and the initial concentration of MB was 1600 mg/L. The adsorption kinetics and equilibrium isotherms were accurately described by the pseudo-second-order model and Langmuir isotherm, respectively. The FTIR spectra indicated that electrostatic attraction and stacking interaction were the main adsorption mechanisms. Thermodynamic analyses showed that the adsorption of MB on MEMR was a spontaneous and exothermic physisorption process. This study revealed that MEMR can be used as a low cost and eco-friendly potential adsorbent for removing MB from wastewater.

1. Introduction

In recent years, water pollution caused by dye industries has seriously affected human health. Dye industrial wastewater treatments were necessary before discharge. Biological methods and physical-chemical methods have often been used to remove dyes from wastewater [1,2]. Biological methods, such as membrane separation technology, anaerobic process, and aerobic process, are often used for dye wastewater treatment. These methods are inefficient due to the physicochemical thermal optical stability of dyes. Physical-chemical methods, such as advanced oxidation, sonolysis, photo-catalysis and electrochemical oxidation, need highly efficient oxidative catalysts and the addition of oxidative agents [3].

Adsorption technique has been a promising method for treating dye wastewater, owing to its operational simplicity and availability in treating a bulk of pollutants [4]. Various adsorbents [5], such as ZnAPSO-34 nanoporous [6], SBA-15 [7], MIL-100(Fe) [8], polydopamine microspheres, magnetic polyacrylamide microspheres, hierarchical porous sulfonatedpoly [9] and silver nanoparticles decorated carbon microspheres [10], have been newly developed to adsorb dyes from wastewater, but have not been extensively applied into practice for its high cost, long processing route and the immaturity technology. However, zeolites [11,12] and silicates with high absorptive property have been widely used as traditional adsorbents [13]. Magnesium silicate is used as an ideal absorbent in many fields for its unique structure, ion exchange and adsorption characteristics [14]. With the features of cation-exchange and negatively charged magnesium silicate could be applied for the separation and recovery of dyes and toxic heavy metal ions from wastewater [15]. Magnesium silicate can be obtained by hydrothermal synthetic method in which the electrolytic manganese residue (EMR) could be used.

EMR found in filters after sulphuric acid leaching of manganese carbonate ore has seriously damaged the ecological environment because it mainly contains manganese and ammonia nitrogen [16,17], and it is extremely difficult to be disposed of due to its diversity, humidity and fineness. In China, the accumulated amount of EMR during the past decades is huge amounting to more than 120 million tons, and the situation has worsened as the

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https://doi.org/10.1016/j.jtice.2017.11.020
1876-1070/

grade of manganese ores decline with the depletion of mineral resources. Hence, deposited EMR has seriously hindered the development of the world's manganese industry, and developing a new advanced process to resource utilization EMR is crucial to EMM industry [18,19]. The EMR consists of SiO_2, $CaSO_4{\cdot}2H_2O$, Al_2O_3, CaO, MnO and Fe_2O_3 [20]. Hydrothermal treatment on EMR may create new adsorption sites which could enhance its adsorption property.

To explore the potential value of EMR as an adsorbent for adsorbing MB from wastewater, modified electrolytic manganese residue (MEMR) are synthesized via hydrothermal method in this study. The morphology, structure and composition of the obtained adsorbents are investigated by scanning electronic microscope (SEM), X-ray diffraction (XRD), N_2 adsorption/desorption isotherms, Fourier transform infrared spectra (FTIR) and BET. In addition, the MB adsorption on MEMR is evaluated at different pH, initial MB concentration, temperature, and contact time. Kinetics, isotherm and the related thermodynamic parameters are also carried out.

2. Experimental

2.1. Materials

The EMR used in this study was supplied by Jiayuan Mining Co. Ltd. (Chongqing, China). Wet EMR was dried to a constant weight at 80 °C, and artificially broken until it passed through a 80-mesh sieve. Methylene blue (MB), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) and sodium metasilicate nonahydrate ($NaSiO_3{\cdot}9H_2O$) were purchased from Chongqing Boyi Chemical Reagent Co., Ltd., China. All reagents are analytical grade and all solution was prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10).

2.2. Preparation of adsorbent

EMR (3.0 g) was dissolved in 50 mL of $Na_2SiO_3{\cdot}9H_2O$ (12.0 g) aqueous solution, and 30 mL of aqueous $MgCl_2{\cdot}6H_2O$ solution was dropwise added into the mixed solution under stirring. Then the suspension was transferred into a Teflon Tank, and the substances in suspension reacted at different hydrothermal temperature and time, which were discussed in the Supporting materials. All the modified electrolytic manganese residue (MEMR) samples were collected via a 0.45 mm membrane filter and washed three times with deionized water, and then dried at 383 K for 24 h and stored in desiccators. In this paper, the optimal reaction parameters (reaction temperature at 393 K, reaction time 24 h, and Si/Mg dosage ratio of 1:1) were mainly studied.

2.3. Absorption experiments

The MB stock solution (100, 200, 600, 800, 1200, 1400, and 1600 mg/L) for the adsorption tests was prepared by dissolving a certain amount of MB in distilled water. Batch adsorption experiments were conducted by adding the MEMR and MB solution into a 150 mL beaker at a shaking speed of 120 rpm and 293 K in triplicate. Adsorption kinetic and equilibrium data were obtained by batch technique in each MB-MEMR system. Various operating parameters on MB removal, such as initial MB concentration, initial pH of the solution, adsorbent dosage, and contact time and adsorption temperature, were investigated. The initial pH was adjusted to the range of 1.8–12.0 by adding 0.05 mol/L NaOH or 0.05 mol/L HCl. The solution was rapidly separated from the adsorbent by a 0.25 μm filter after reaction.

The retained concentration in the adsorbent phase (q_e, mg/g) at equilibrium and at different time 't' were calculated using Eqs. (1) and (2), respectively; and the removal efficiency of MB was calculated using Eq. (3).

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

$$q_t = \frac{(C_0 - C_t \times V)}{m} \tag{2}$$

$$\%R = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{3}$$

Where C_0, C_e and C_t are the initial, equilibrium concentration (mg/L) of MB and the concentration of MB at different time 't', respectively. V is the volume of the MB solution (L), and m is the mass of the MEMR (g).

2.4. Kinetics, isotherm and thermodynamics models

In this study, pseudo-first-order and pseudo-second-order kinetic models were analyzed to test the experimental data. These two models can be expressed in a linear form as Eqs. (4) and (5), respectively [21].

$$ln(q_e - q_t) = ln(q_e) - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where q_e (mg/g) and q_t are the amount of MB adsorbed at equilibrium and different time (min), respectively. And k_1 (/min) and k_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order model rate constant, respectively.

Equilibrium adsorption isotherm is important to the design of adsorption systems, which could provide information about the surface property of adsorbent and the adsorption behavior [22]. Langmuir models and Freundlich's isotherm model are expressed in a linear form as Eq. (6) and Eqs. (7), respectively. [23].

$$\text{Langmuir models}: \frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \tag{6}$$

where K_L is the adsorption equilibrium constant (L/ mg), q_0 is the maximum monolayer adsorption capacity, and q_e is the amount adsorbed on a unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L).

$$\text{Freundlich's isotherm model}: \ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{7}$$

where K_F ((mg/g) (L/g)^n) and $1/n$ are Freundlich constants related to sorption capacity and sorption intensity of adsorbents.

Thermodynamic parameters, such as enthalpy change ($\triangle H^0$), Gibbs free energy change ($\triangle G^0$) and entropy change ($\triangle S^0$), can be determined by Langmuir isotherm as the following Eqs. (8) and (9) [24,25].

$$\Delta G^0 = -RT\ln(K_L) \tag{8}$$

$$\ln(K_L) - \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{9}$$

Where K_L is the Langmuir equilibrium constant (L/mol); R and T represent the universal gas constant (8.314 J/K/mol) and the system temperature (K), respectively. $\triangle G^0$ can be easily obtained using Eq. (8). and $\triangle S^0$ and $\triangle H^0$ are determined from the intercept and slope of the Van't Hoff plots of $\ln(K_L)$ versus $1/T$.

Please cite this article as: J. Shu et al., Adsorption of methylene blue on modified electrolytic manganese residue: Kinetics, isotherm, thermodynamics and mechanism analysis, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.11.020