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Adsorption characteristics of Congo red on carbonized leonardite

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A B S T R A C T

In this study, a low-rank coal (leonardite) was used as adsorbent for the removal of Congo red (CR) aqueous solution, a model compound representing an anionic azo dye. The effects of oxygen-containing groups, particularly carboxylic, lactonic, and phenolic groups, on the adsorption of CR on leonardite after carbonization at various temperatures were studied. It was determined that the surface chemistry change of carbonized leonardite greatly influenced its adsorption characteristics. Solution pH affects not only the surface charge of the adsorbents but also the ionization of the CR dyes. Based on the experimental data, a mechanism of interaction between CR anionic dye and carbonized leonardite was proposed. A comparison of kinetic and isothermal models demonstrated that the CR adsorption process was best described by a pseudo-second-order kinetic model and Redlich–Peterson model. Further thermodynamic investigations indicated that the adsorption was an endothermic and spontaneous process.

1. Introduction

Wastewater-containing dyes from the textile industry are highly difficult to treat using conventional wastewater treatment methods because dyes are very stable organic compounds refractory to chemical or biological degradation. It is estimated that 10%–15% of the overall dye produced is released into the environment via wastewater (Ghodbane and Hamdaoui, 2009). The presence of very small amounts of dyes in aquatic systems is aesthetically displeasing, reduces light penetration, and affects gas solubility. Physical contact with dissolved dyes may cause eye and skin irritation in humans. In this context, adsorption is considered to be an attractive technology for the treatment of wastewaters owing to its simplicity of design and ease of operation (Cengiz et al., 2012).

Low-rank coal represents a potential low-cost sorbent for a number of diverse applications including the remediation of wastewater (Butler et al., 2008), air purification (Zelenka and Taraba, 2014; Izquierdo et al., 2001), and metal ion recovery (Janõs et al., 2007a; Arpa et al., 2000). Such low-rank coal contains large amounts of organic substances and various inorganic minerals. The sorption ability of low-rank coal is given primarily by oxygen functional groups and natural polyelectrolytes immobilized *in situ* in coal matrix (Kurková et al., 2004). Among the types of low-rank coal, leonardite shows great potential for usage as an adsorbent because it either is derived from lignite that has undergone oxidation during surface exposure or represents sediments enriched in a humic substance (Kalaitzidis et al., 2003). Humic substances include both hydrophobic and hydrophilic components as well as many chemical functional groups such as carboxylic, lactonic, and phenolic groups connected with the aliphatic or aromatic carbons in the structure. The existence of surface oxygen groups causes humic substances to be positively-negatively charged in aqueous solutions; hence, an adsorbate that possesses the opposite charge can bind to the adsorbent. The adsorption ability of leonardite is influenced by electrostatic interaction between the charge of surface oxygen groups and the degree of ionization of the adsorbate. However, the charge of the humic substance contained in leonardite changes with pH owing to the dissociation of functional groups (*e.g.,* carboxylic group undergoes dissociation at pH greater than 4) (Lorenc-Grabowska and Gryglewicz, 2005). Thus, the adsorption of leonardite is influenced by the solution pH. The sorbate–sorbent interactions, which can be either attractive or repulsive, strongly depend on the charge densities for both the surface oxygen and the adsorptive molecule (or ion). Accordingly, it would be interesting to study the enhanced adsorption ability of leonardite that can be used in a wide pH range.

In general, natural leonardite has a wide range of organic compositions (20–70%). During the carbonization process, the organic substance can be converted to activated carbon. It is expected that such activated carbon can be used as adsorbent for the

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removal of pollutants from aqueous solution with a wide range of pH levels. Practically, coal-based sorbents are capable of retaining various types of pollutants, ranging from inorganic ionic species (heavy metal cations) to low-polarity organic compounds, including ionic organic compounds (Janõs et al., 2007b). Many researchers have studied leonardite or activated leonardite as low-cost adsorbents for the removal of heavy metal cations (Lao et al., 2005; Chammui et al., 2014a; Hanzlík et al., 2004; Chammui et al., 2014b; Lao-Luque et al., 2014; Katanyoo et al., 2012; Zeledoń-Toruño et al., 2005; Hanzlik et al., 2004) and polycyclic aromatic hydrocarbons (PAHs) (Zeledoń-Toruño et al., 2007; Wang et al., 2012) from aqueous solutions. However, no such efforts for the adsorption of dyes have been reported.

In this research, dye adsorption using natural leonardite adsorbent obtained from lignite mines in Lampang province, which is in the northern region of Thailand, has been studied. Congo red (CR) [1-naphthalene sulfonic acid, 3,3′-(4,4′-biphenylenebis (azo)) bis(4-amino-) disodium salt] was chosen as the model dye in this test. The effects of initial pH, adsorption time, concentration of CR, and adsorption temperature were extensively studied in this work. The kinetics and isotherms were explored to describe the experimental data. Moreover, the adsorption ability of leonardite has been developed by a thermal treatment process. It was indeed expected that the properties and sorption ability of the carbonized leonardite can be used for a wide pH range. The adsorbent was characterized by X-ray fluorescence spectroscopy (XRF), thermogravimetric analysis/derivative thermogravimetric analysis (TGA/DTG), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), number and type of surface oxygen groups, Brunauer–Emmett–Teller (BET) surface area, and pore volume. Recently, a completely green preparation without any chemical pretreatment of carbonized leonardite adsorbent exhibited the advantages of being cost effective and environmentally friendly (Ausavasukhi et al., 2013).

2. Materials and methods

2.1. Adsorbent preparation and characterization

The leonardite sample was obtained from the Mae Moh lignite mine in Lampang province, Thailand (Fig. 1). After being well mixed, the sample was dried at room temperature, crushed, sieved (80 mesh), and kept for use in CR adsorption experiments and characterization. The leonardite samples were carbonized at 300, 500, 700, and 900 °C for 5 h under an N_2 stream. Hereafter, the carbonized leonardite will be designated as Leo(300), Leo(500), Leo(700), and Leo(900) according to their thermal treatment.

The cost of adsorbent is an important factor when it is to be used for industrial applications. The cost of the leonardite samples collected from dumped waste at the Lampang lignite coal mine is approximately US$ 10–15 per ton (Chammui et al., 2014a). From the economic feasibility calculations, the activated carbon from leonardite by thermal activation is cheaper (approximately US$ 150–200 per ton) owing to the lower cost of labor and utilities in Thailand compared to USA.

XRF (Bruker AXS SRS 3400) was carried out to determine the chemical composition of the leonardite samples. XRD (Bruker AXS D8 Advance) was employed to determine the phase formation and crystallographic state (Cu*Kα* radiation (λ = 0.154 nm)). For TGA (Perkin Elmer STA 6000), the sample (10–15 mg) was heated from 50 to 900 °C under a flow of N_2 (or O_2) with a heating rate of 10 °C/min based on the information on weight loss upon thermal treatment. FTIR (Perkin Elmer Spectrum 100) data were recorded in the transmission mode at room temperature over the wavenumber range of 4000–650 cm^{-1}. The BET surface area and pore volume

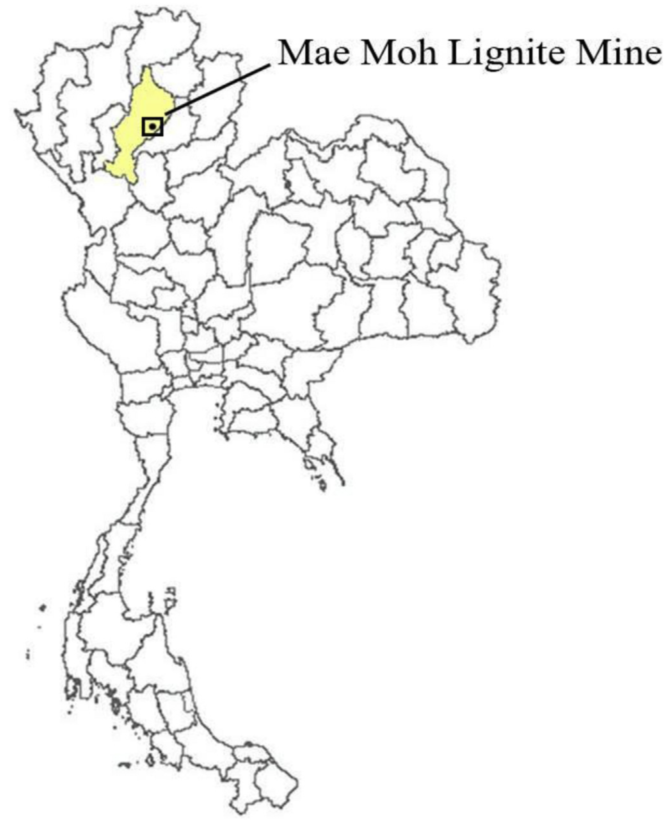

Fig. 1. Location map of the Mae Moh lignite mine in Lampang province, Thailand.

were determined by gas adsorption analysis (Quantachrome Autosorb-1), after drying at 150 °C for 15 h. The number and type of surface oxygen groups of the parent and carbonized leonardite was analyzed by Boehm titration (Boehm, 2002). The determination of the point of zero charge (pH_{pzc}) of the samples was carried out as described in Rivera-Utrilla's report (Rivera-Utrilla et al., 2001).

2.2. Adsorption activity for CR removal

The adsorption activity of the adsorbent to decolorize the CR was tested in a batch reactor. The adsorption conditions were as follows: pH solution, 5.0–9.0; adsorption time, 15–240 m; adsorption temperature, 25–50 °C; CR concentration, 25–500 mg/L; adsorbent content, 0.25 g; solution volume, 200 mL. The color removal of CR dye solutions was analyzed by measuring the absorbance with a UV–Vis spectrophotometer (Shimadzu UV-2450) at λ_{max} = 496 nm.

3. Results and discussion

3.1. Characterization of adsorbents

Table 1 shows the approximate chemical composition of the parent leonardite determined by XRF and the volatile matter and moisture determined by TGA.

The formation of leonardite is a result of the oxidation of lignite. Therefore, depending on the content of humic substances and the conditions of the processes, leonardite with various organic matter, mineralogical and elemental compositions is formed. Leonardite is a highly dispersive aluminosilicate with macrocomponents SiO_2 and Al_2O_3 containing impurities such as Fe, Ca, K, Mg, Na, Ti and S. In previous studies on low-rank coal used as an adsorbent, the