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Original Research Article

Adsorption of Methylene Blue dye and Cu(II) ions on EDTA-modified bentonite: Isotherm, kinetic and thermodynamic studies

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ABSTRACT

Dyes and metals are hazardous pollutants commonly found in industrial wastewaters requiring complex and expensive removal technologies. This study investigated the potential of ethylenediaminetetraacetic acid-modified Philippine bentonite (EMB) as a low-cost adsorbent material for the removal of Methylene Blue dye (MB) and copper ions (Cu(II)) from aqueous solutions. Batch adsorption experiments showed that EMB has superior adsorption capacity compared to the unmodified bentonite, with an enhancement of up to 40% for MB and more than 100% for Cu(II). The adsorption capacity of EMB improved with increasing solution pH and contact time and decreased with higher solution temperature and higher salt concentration in solution. The Langmuir isotherm model was found to best describe MB and Cu(II) adsorption on EMB with maximum capacity of 160 and 27 mg g^{-1}, respectively. The pseudo-second order kinetic model best fit the experimental data with $R^2 > 0.99$. Lastly, the thermodynamic study confirmed that the adsorption process was spontaneous, exothermic and reversible.

1. Introduction

The textile industry is one of the most water-consuming industries in the world and an average-sized textile mill uses about 1.6 million liters of water for a daily output of around 8000 kg of fabric [1]. As a result, the industry produces large volumes of wastewaters which contain hazardous compounds such as dyes, heavy metals like Cu(II), and surfactants. These chemical species can have an important ecological impact on ecosystems due to their strong toxicity, environmental persistence, and tendency to bioaccumulate and thus have to be removed from industrial effluents prior to discharge to recipient waters [2].

Various wastewater treatment technologies such as ion-exchange, adsorption, chemical precipitation, membrane filtration, flocculation, coagulation, flotation and electrochemical methods have been employed to treat dye and heavy metal contaminated effluents. Of these, adsorption has been widely used with bentonite as one of the most extensively studied adsorbent material because it is naturally available, inexpensive and has good adsorption capacity mainly due to its physical and chemical stability, high superficial area and good cation exchange capacity [2,3]. The surface characteristics of bentonite are critical to its ability to attract various chemical species. However, bentonite from different parts of the world varies in mineralogy as this is affected by the geochemical conditions during its formation. Bentonite also has a swelling capacity potential that allows modifying agents to enter its interlayer regions thereby improving the adsorption performance of the material [4].

Ethylenediaminetetraacetic acid or EDTA is a synthetic chelating agent that has been used to improve the surface properties of conventional adsorbent materials such as bagasse fly ash [5], maize

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cobs [6], chitosan [7], mesoporous silica [8], chitosan–silica hybrid materials [9], and zinc oxide nanoparticles [10]. Recently, EDTA was used to modify the surface of chitosan/SiO_2/Fe_3O_4 adsorbent with water-soluble carbodiimide as cross-linker for the adsorption of heavy metals [11].

In this study, EDTA-modified bentonite was synthesized and used as an adsorbent material for the removal of Methylene Blue (MB) dye and copper ions from aqueous solutions. The effects of initial concentration, adsorbent dosage, salt concentration and solution pH on the adsorption process were investigated. The raw and modified bentonite were characterized through particle size distribution, scanning electron microscopy, X-ray diffraction (XRD) spectroscopy, energy dispersive X-ray fluorescence and Fourier transform infrared analyses. Isotherm, kinetics and thermodynamic studies were conducted to evaluate the controlling mechanisms of MB and copper adsorption onto EDTA-modified bentonite.

2. Experimental

2.1. Materials

Bentonite was collected from a processing company in Northern Luzon, Philippines. All reagents used were analytical grade and were not subjected to additional purification. MB dye ($C_{16}H_{18}ClN_3S$), copper sulfate ($CuSO_4$) and EDTA disodium salt ($C_{10}H_{14}N_2Na_2O_8$) were all purchased from Ajax Finechem Pty. Salts, namely sodium chloride (NaCl), potassium chloride (KCl) and sodium nitrate ($NaNO_3$) were all obtained from J.T. Baker. Distilled water was used to prepare all aqueous solutions in the study.

2.2. Synthesis of EDTA-modified bentonite

The EDTA-modified bentonite (EMB) was prepared similar to the methods described in previous studies [5,12]. A mixture of 20 g bentonite and 2 g EDTA were added to 1.0 M NaOH and stirred in a water bath shaker (LSB-030S, Daihan LabTech) for 1 h at 30 °C. It was then kept soaked in the solution for 24 h. The EMB was then filtered from the mixture, washed with distilled water and, dried at 55 °C for 24 h.

2.3. Batch Cu(II) and MB adsorption

Batch adsorption experiments were done by adding known amounts of EMB to 50-mL solutions of MB dye (10–100 mg L^{-1}) and Cu(II) (1–12 mg L^{-1}). The solution pH was adjusted accordingly using NaOH and HNO_3 solutions. Different salts (NaCl, KCl and $NaNO_3$) were also added at varying concentrations (0.1–0.4 M) to study the effect of ionic strength. Then, the mixture was placed in a water bath shaker set at 120 rpm at the desired temperature (30–50 °C) and duration (1–120 min). After the reaction, the spent EMB was filtered and dried at 55 °C for 4 h, while the filtrate was collected for residual MB or Cu(II) concentration analysis.

The concentration of MB was measured at a maximum wavelength of 665 nm using a UV–Vis spectrophotometer (UVmini-1240, Shimadzu), while Cu(II) concentration was determined with copper Vacu-vials® instrumental kit and a multi-analyte photometer (V-2000, CHEMetrics). Respective calibration curves were established to calculate the concentration of each compound. The adsorption capacity (q), or the amount adsorbed per gram of EMB (mg g^{-1}), was obtained using Eq. (1), where C_i and C_f (mg L^{-1}) are the initial and final concentrations, respectively, V (L) is the solution volume, and M (g) is the amount of EMB used.

$$q = \frac{V\left(C_i - C_f\right)}{M} \quad (1)$$

2.4. Adsorbent characterization

The adsorbent particle size was analyzed through dynamic light scattering (Quadix Scatterscope I) by preparing a 1% bentonite solution in water. The elemental composition of the samples was determined through energy dispersive X-ray fluorescence (EDXRF-720, Shimadzu). Information on the crystalline structures was obtained through XRD analysis (XRD-600, Shimadzu). The surface morphology of the adsorbents was examined using a scanning electron microscope (S-3400N, Hitachi), set at an accelerating voltage of 5.0 kV and 1000× magnification. The surface functional groups were investigated using Fourier transform infrared spectroscopy (FTIR) analysis (Nicolet 6700).

The point of zero charge (PZC), or the pH at which the adsorbent material has a net zero surface charge, was obtained using pH drift method [13]. Solutions of 0.01 N NaCl were prepared with pH levels varying from 2 to 8. The adsorbent, weighing 0.15 g, was added to the NaCl solutions, and the mixtures were placed in a water bath shaker for 48 h. The initial pH of the NaCl solutions was plotted against the final pH to determine the pH_{PZC} ($pH_{initial} = pH_{final}$).

3. Results and discussion

3.1. Characterization of unmodified and EDTA-modified Philippine bentonite

The scanning electron micrographs in Fig. 1a and b show raw bentonite as aggregated crystal-like flakes and EMB as larger aggregates compared to raw bentonite. This is supported by the results from the particle size distribution analysis (Fig. 1c) where the average particle size for raw bentonite and EMB were found to be 201 and 256 nm, respectively. During EDTA modification of bentonite, the swelling of bentonite — mainly separation of clay particles sometimes coupled with intra-aggregate and inter-aggregate adsorption, and diffuse double layer formation [14] — exposed the positively-charged metal ions in its interlayer region and at the same time, allowed the entry of EDTA molecules in its layers. This facilitated the attraction between the interlayer cations and the negatively-charged carboxyl groups of EDTA. The swelling also allowed the exposure of sites with a negative charge, which is favorable to the adsorption of cationic MB and Cu(II).

The XRD patterns of the raw bentonite and EMB samples are shown in Fig. 1d. The diffraction peaks at around 6.5 and 20° confirmed the presence of montmorillonite [$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$] which is the usual main component of bentonite that gives it its swelling properties. Other minerals, such as quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$) and calcite ($CaCO_3$), were also detected. The characteristic diffraction peaks were found to be the same for both raw bentonite and EMB although the spectra for EMB had sharper and more intense peaks.

The FTIR spectra of raw bentonite and EMB are shown in Fig. 1e and f. Characteristic peaks of raw bentonite were found at 3000–3750, 1635, 900–1200, and 517 cm^{-1}. The broad absorption bands observed at 3000–3750 cm^{-1} correspond to O–H stretching and H–O–H bending. Bending vibrations of H–O–H is signified by the peak found at 1635 cm^{-1}. The strong band between 900 and 1200 cm^{-1}, centered at 995 cm^{-1}, represents the stretching vibrations of the Si–O groups, while the small peaks at around 517 cm^{-1} are due to the Al–O–Si and Si–O–Si bending vibrations [15,16]. Similar characteristic peaks were found for EMB with new peaks at

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