Chemical Engineering Journal 187 (2012) 79–88

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye

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ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form 19 January 2012
Accepted 19 January 2012

Keywords:
Bentonite
Adsorption isotherms and kinetics
Diffusion
Dye removal
Congo red

ABSTRACT

Low adsorption capacity of natural clay minerals is a key technical and economical issue which limits their industrial application as low cost absorbents for removal of hazardous contaminants from wastewater. Herein, natural bentonite was modified by thermal activation (TA), acid activation (AA) and combined acid and thermal activation (ATA). In this study, we studied how the key operational parameters: contact time, dye concentration, bentonite dosage, pH and temperature could affect the adsorption performance for the removal of Congo red (CR). The thermodynamic parameters revealed that adsorption reaction using the modified clays is spontaneous and exothermic. The experimental data were analyzed by Langmuir and Freundlich isotherm, Pseudo-kinetic and particle diffusion models. The results revealed that Freundlich isotherm provided a better fit to the experimental data. The adsorption kinetics followed both the pseudo first and second-order rate equations, while the second order giving a better fit. The adsorption process also showed a intra-particle diffusion mechanism. The ATA bentonite demonstrated the highest adsorption capacity by removing over 95% of CR and its adsorption fitted best to all models.

1. Introduction

The effluent discharged by textile industries contains large amounts of dyes which can be very toxic even at a very low concentration. The synthetic dyes are generally non-biodegradable and difficult to be removed by conventional biological treatment process, such as activated sludge process. These toxic dyes have significant impact on the human health and the aquatic life [1]. Various physical and chemical methods have been employed for the treatment of dyes, including coagulation, flocculation, precipitation [2], ozonation [3], oxidation [4], photocatalysis [5], and ultrasound irradiation [6]. All these methods have some economic and environmental drawbacks, such as high capital and operating cost, sludge production and complexity of the treatment processes [2,3].

Adsorption is a widely used technique for the removal of dyes due to economical and environmentally friendly reasons [7]. The process cost for dye removal by adsorption lies mainly on the cost of the adsorbent and the regeneration of adsorbent. Activated carbon is currently the most widely used adsorbent due to its large surface area and high adsorption capacity. However, the use of activated carbon is becoming restricted by its high cost and regeneration difficulties. Many low-cost adsorbents are being developed worldwide to replace activated carbon. Clays are one of the most widely used low-cost alternatives due to its abundant availability. Generally these low-cost adsorbents have a low adsorption capacity. Among these clay minerals, bentonite is one of the most extensively used adsorbents [8]. Our recent studies have demonstrated that the adsorption capability can be enhanced by modification of these adsorbents via physical and chemical processes.

Modification of bentonite is vital for the adsorption of anionic dyes, as the net negative charge on the dye and clay surface brings charge repulsion and thus, resulting in lowering surface interaction and adsorption [8,9]. We recently have conducted laboratory studies on how to enhance the adsorption capacity of the natural bentonite by thermal activation, acid activation and combined acid and thermal activation. The thermal activation and acid activation have been recognised as cost-effective methods which are commonly used for modifying adsorbents. Our work may be one of a few studies to identify technically and economically feasible modification methods to enhance adsorption capacity of natural bentonite. So far, no studies on using combined acidification and thermal activation for adsorbent modification is found in the literature. Our results revealed that the modified clay performed a promising adsorption capability and performance as an adsorbent for the removal of anionic dyes. Herein, in this study, we will identify and determine key operating parameters: initial dye concentration, adsorbent dosage, contact time and temperature, so as to maximize the adsorption capacity and efficiency of the modified bentonites for the removal of Congo red. The experimental data will be evaluated by Langmuir and Freundlich adsorption isotherms. The pseudo-first order and pseudo-second order kinetics models

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doi:10.1016/j.cej.2012.01.089

will be studied to understand the kinetics of adsorption. The mechanism of adsorption is analyzed by intra particle diffusion model. This study is for the first time to determine and compare adsorption isotherm, kinetics and diffusion of modified natural bentonite using three activation methods.

2. Material and methods

2.1. Materials

2.1.1. Bentonite

Australian sodium bentonite obtained from Unimin Australia Limited in Sydney has high montmorillonite and low grift content. This bentonite was used as received for modification without any further purification. The natural bentonite contains 56% SiO_2, 16% Al_2O_3, 4.6 Fe_2O_3 3.3% MgO, 2.9% Na_2O and 10% H_2O. Average particle size is 75 μm. The cation exchange capacity is 95 mequiv. $(100\,g)^{-1}$.

2.1.2. Congo red

Congo red (CR), a diazo dye, was used as a surrogate indicator to simulate industrial wastewater in order to evaluate the adsorption capacity of bentonite in the study. The Congo red obtained from Labchem Ajax Finechem, Australia was used as received without any purification. The chemical formula of CR is $C_{33}H_{22}N_6Na_2O_6S_2$ with Color Index 22120. The molecular weight of CR is 696.7 $g\,mol^{-1}$. The IUPAC name of CR is [1-napthalene sulfonic acid, 3,3′-(4,4′-biphenylenebis (azo)) bis (4-amino-) disodium salt]. Congo red contains $-NH_2$ and $-SO_3$ functional groups. The CR sodium salt is responsible for dying cotton full red and is the first synthetic dye capable of directly dying cotton [10]. The color of CR changes from red to blue in the presence of inorganic acids. The change of color is due to the resonance between charged canonical structures [11]. The red color is stable in the pH range of 5–10 [9]. The stock solution of CR was prepared by dissolving known quantity of CR powder in double-ionized water obtained from Barnstead nanopure Diamond Water ion exchange system with 18.2 MΩ. The successive dilutions were made to obtain the working solution at desired concentrations.

2.2. Modification and activation of raw bentonite

Modification of raw bentonite has been investigated in our group recently and was reported in detail in other case [8]. Herein, we only provide the brief information for the modification methods and their optimal conditions used.

2.2.1. Thermal activation

The thermal activation (TA) was performed by heating the samples at 100 °C in a muffle furnace [8]. The temperature was allowed to rise steadily to the desired temperature for 5 min. The samples were heated at 100 °C for 30 min, and thereafter were cooled and stored in air-tight plastic bottles in a desiccator for further use.

2.2.2. Acid activation

The acid activation (AA) of bentonite was carried out in a rotary shaker (Ratek OM 15 orbital) with temperature and agitation control. Raw bentonite was treated with 0.5 M HCl at 30 °C. The clay to acid ratio was fixed at 1:10 (g/mL). After 1 h the reaction was terminated with addition of large amount of double-ionized water. The acidified bentonite was then washed several times with double-ionized water till Cl^- ion was undetectable in the supernatant using silver acetate solution. The final sample was centrifuged with Allegra X-12, and dried at 55 °C for 12 h and then stored in air-tight plastic bottles in desiccator for further use.

2.2.3. Acid and thermal activation

The acid and thermal activation (ATA) of bentonite followed a two-step procedure. In the first step bentonite was activated using 0.1 M HCl at 30 °C. The acidified bentonite was further subjected to TA in the second step. Then the reaction was terminated after 1 h with addition of large amount of double-ionized water. The samples were exhaustively washed until Cl^- ions were undetectable while pH 5 was maintained. The acidified bentonite was then subjected to thermal activated by calcination at 100 °C for 20 min in a muffle furnace. The samples were then cooled in a desiccator and stored in air-tight plastic bottles for further use.

2.3. Characterization of bentonite

The specific surface area and average pore size of the bentonite samples were analyzed using, respectively, the BET and BJH methods. The determinations of the surface area and pore size were based on isotherms of adsorption and desorption of nitrogen at 77 ± 0.5 K using a Gemini V2.00 surface analyser (Micromeritics, USA) [8]. The sample tubes were loaded with 0.3 g of modified bentonite samples. The samples were then degassed under vacuum at 378 ± 1 K for 12 h in Vacuum Prep 061 sample degas system prior to surface area measurements. The morphological features and surface characteristics of samples were obtained from scanning electron microscopy (SEM) using Philips XL20 scanning electron microscope at an accelerating voltage of 10 kV, as detailed in our previous report [8]. The samples were coated with gold by electrodeposition under vacuum prior to analysis.

2.4. Experimental set up

Adsorption of CR on bentonite was carried out in a batch system. The batch technique was selected due to its simplicity and reliability. 50 mL CR solution ($100\,mg\,L^{-1}$) in the flasks were agitated in a rotary shaker (Ratek OM 15 orbital) at 150 rpm and 30 °C. The agitation was carried out for 24 h to ensure that the equilibrium is reached. The samples were then centrifuged in Eppendorf Centrifuge 5415R (Germany) at 3200 rpm for 20 min to separate the dye solution from the adsorbent.

All adsorption trials and sample tests were carried out in triplicates.

2.5. Analysis and calculation

CR concentration was determined by UV–visible spectrophotometer (model γ, Helios, UK) at 496.5 nm [12]. The absorbance concentration profile was obtained by plotting the calibration curve between absorbance and dye concentration. The absorbance for each sample was converted using calibration factor obtained from the calibration curve to calculate the final dye concentration. The amount of dye adsorbed on the surface of adsorbent at time t can be estimated from the mass balance equation:

$$251, 658, 240q_e = (C_i - C_e)\frac{V}{m} \qquad (1)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent ($mg\,g^{-1}$), C_i is the initial dye concentration ($mg\,L^{-1}$), C_e is the equilibrium dye concentration ($mg\,L^{-1}$), V is the volume of dye solution (mL) and m is the mass of bentonite (g). Standard derivations were calculated based on the results obtained from triplicate samples and tests.

Chi-square (χ^2) error function was calculated to assess any errors in results obtained from the linearisation of models. The Chi-square is the sum of squares of differences between the experimental data and data predicted by the kinetic models, with each squared difference divided by the corresponding data obtained by