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Removal of methylene blue from aqueous solution by adsorption on pyrophyllite

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ABSTRACT

The effectiveness of adsorption for dye removal from solutions has made it an ideal alternative to other expensive treatment methods. The ability of raw and pickling–grinding modified pyrophyllite powders to adsorb methylene blue has been investigated in this study by looking at the dependence of absorption on pH values, adsorbent mass and the initial methylene blue concentration. The measured D_{50} of raw particles was 21.42 μm, which was decreased to 7.18 μm after grinding treatment, and to 5.55 μm after pickling–grinding. We showed that the raw and modified pyrophyllite powders have a high adsorptive capacity for dyes. The absorption ability of raw and modified pyrophyllite powders decreased with the increase of the initial methylene blue concentration in solution, while increased with the pH value. Increase in the adsorption with adsorbent mass was attributed to increase adsorbent surface area and availability of more adsorption sites. The adsorption capacity of raw powders reached 3.71 mg/g, and the numbers of pickling, grinding and pickling–grinding powders increased to 3.83 mg/g, 3.94 mg/g and 4.24 mg/g, respectively.

1. Introduction

Due to rapid industrial development, pollution of water bodies by industries is an issue of major concern. Many industrial processes in China use different synthetic chemical dyes to color their final product. Most of the used solutions containing dyes are discarded as effluents. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which produce micro-toxicity to fish and other organisms [1,2]. Among the various available water treatment techniques adsorption is the most reliable and efficient technique for decoloration, in which the recovery and recycling of the adsorbent materials can be achieved along with the distinct advantages of nonproduction of any toxic sludge and cost effectiveness [3–14]. This has encouraged the development of adsorbents that are abundantly available and economical. The use of clean, cost-efficient, and biodegradable adsorbents could be a good tool to minimize the environmental impact caused by manufacturing and textile byproducts [14–16]. Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decoloration process. Commercially activated carbon is a remarkably highly adsorbent material with a large number of applications in the remediation of contaminated groundwater and industrial wastes such as colored effluents. Since activated carbon is an expensive adsorbent due to its high costs of manufacturing and regeneration, much attention has been focused on various naturally occurring adsorbents such as chitosan, zeolites, fly ash, coal, papermill sludge, and various clay minerals [17]. Among these new adsorbents, clays have been shown to be the most promising alternatives due to their local availability, technical feasibility, easy engineering applications, highly specific surface area, and cost effectiveness [15,16,18–24].

Nowadays numerous low cost adsorbents are available including products of agricultural origin such as wood dust, sugarcane, fruit peel, wheat straw, and apple pomance [3]. Recently, the application of pyrophyllite on waste water treatment has become of great interest in China because of its abundance in local reserves as well as its inexpensiveness. The characteristics of pyrophyllite are related to its powerful adsorbent properties and its ability to adsorb organic or inorganic ions from aqueous solution. A considerable amount of work has also been reported in the literature regarding the potential use of pyrophyllite in the removal of heavy metals and dye molecules [25–27]; however, the adsorption properties of pyrophyllite on methylene blue (MB) are still scarcely known. The purpose of this study is to focus attention on the adsorption of MB on pyrophyllite from aqueous solutions. The dynamical behaviors of adsorption were measured on the effect of reaction time, MB concentration, pH value and temperature. Furthermore, raw pyrophyllite particles were modified by a pickling–grinding treatment and a comparative study of the removal of MB from aqueous solutions by raw and pickling–grinding particles was carried out as well.

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2. Materials and methods

The pyrophyllite mineral used in this study originated from the Zhejiang province, located in the south-eastern region of China. The pyrophyllite powder composed of (wt.%): 66.08 SiO_2, 19.92 Al_2O_3, 0.70 Fe_2O_3, 0.64 K_2O, 0.21 Na_2O, 0.12 CaO, 0.27 Ti_2O and 12.33 of weight loss, was used in this study. Particle sizes were analyzed by the LS-POP laser particle size analyzer. Pickling–grinding particles were prepared by pickling raw particles in 0.55 mol/L HCl solution at a temperature of 80 °C for 6 h. The remaining HCl was removed by washing until the pH of the suspension was close to 7. Pickling particles were then milled in water in a Planet Style Ball Mill for 3 h. Finally, the pickling–grinding particles were obtained by filtration and dried at 110 °C for 2 h. Thermogravimetric analysis and differential thermal analysis (TG–DTA) were carried out simultaneously in static air with an automatic thermal analyzer system (Pyris Diamond). To get the TG–DTA curves, powder samples of about 40 mg were packed loosely into a platinum holder and were thermally treated under flow of air at a heating rate of 10 °C/min (range: 20–1000 °C). Calcinated α-alumina was taken as the reference.

Methylene blue with a labeled purity of more than 98% was used as model dye without further purification. Deionized water was used to make the dye solutions of desired concentration. The MB solution shows an intense absorption peak in the visible region at 665 nm. In an adsorption process, a change in the intensity of this peak can be used to characterize the removal of dye from the solution. The adsorption of MB on pyrophyllite was calculated by monitoring the changes in absorption value of the solution on a spectrophotometer (Shimadzu UV-2550) at ambient room temperature, using a 1 cm quartz cell. Adsorption tests of MB on prepared pyrophyllite particles were studied using a batch process by mixing 0.1–1.0 g of adsorbent mass in plugged conical flasks with 100 mL of MB solutions of concentration ranging from 10 to 60 mg/L. The contents of the dye solution were then shaken for a given amount of reaction time using a magnetic stirrer operated at a constant speed. A constant temperature bath was used to keep the temperature constant at 20 ± 1 °C. The effect of pH was studied over a pH range of 7–11. The pH value was adjusted by the addition of dilute aqueous solutions of NaOH (0.10 M). Samples were withdrawn at appropriate time intervals and the contents were then centrifuged and the supernatant solution was pipetted out and monitored instantaneously on the spectrophotometer for absorption values. The absorbance values obtained in solutions before and after adsorption were then used to calculate the removal of the MB on pyrophyllite powders. Each experimental point was an average of three independent adsorption tests.

3. Results and discussion

3.1. Characteristics of pyrophyllite

The pyrophyllite has an $Al_2[Si_4O_{10}](OH)_2$ unit-cell formula and a hydrous aluminium phyllosilicate with the dioctahedral structure. Since the tetrahedral–octahedral–tetrahedral unit is electrically balanced as neutral on the basal plane, the successive 2:1 layers are held together by Van der Waals forces [28]. Thus, breaks occur easily along the plane between layers and crystal imperfections widely occur in pyrophyllite, for example, Al^{3+} instead of Si^{4+} and Fe^{2+} instead of Al^{3+}. The existence of impurity (K, Fe, Ti, Na) was found, together with the theoretical composition of pure pyrophyllite. A complicated chemical composition plays an important role in ion exchange and adsorption. For instance, since some Al^{3+} were substituted by Fe^{2+} or Ti^{2+}, surface particles would form negative charge sites. Consequently, positive ions must be adsorbed to keep a balanced charge. This is considered to be one of the major factors causing the MB dye molecules to be adsorbed by pyrophyllite particles. Additionally, the chemical analysis of pickling particles showed an obvious decrease of Al^{3+}, Fe^{2+} and Ti^{2+}. Pickling showed that adsorption could be improved by dissolving Al^{3+}, Fe^{2+} and Ti^{2+} from the octahedral layer into acid solution and forming more hydrophilic –OH groups on the vacant sites. Adsorption is further influenced by particle sizes [3]. The measured D_{50} of raw particles was 21.42 μm, while the D_{50} of pickling particles was decreased to 7.18 μm after grinding treatment, and to 5.55 μm after pickling–grinding. Pickling particles were milled to decrease the particle size, thus caused the destruction of Van der Waals forces [28].

The TG–DTA curves of raw pyrophyllite are shown in Fig. 1. According to directions of the various peaks, the DTA curve can be divided into three regions. In the first region, up to 100 °C, endothermic dehydration of pyrophyllite is the major thermal reaction. The second region is between 380 and 700 °C, and the mass loss for pyrophyllite in this region is 2.7%. The exothermic DTA peaks at 417.9 and 447.6 °C may be expected from the release of structural OH for an ideal pyrophyllite. The third region occurs at temperatures above 700 °C, and the broad endothermic peak centered at 919.1 °C may be due to the dehydroxylation reaction of pyrophyllite and the crystallization of mullite [21,29].

3.2. Methylene blue adsorption on raw and modified pyrophyllite

Experiments were conducted with raw and modified pyrophyllite at constant adsorbent dosage (0.2 g/100 mL), pH (neutral), and temperature (20 °C) for 24 h by varying MB concentrations (10–60 mg/L). It is evident from Fig. 2 that pickling–grinding powder has more adsorption efficiency in comparison to other powders at all initial MB concentrations studied. Decolorization of solution was 70.1%, 71.2%, 75.5% and 79.7% by raw, picking, grinding, and pickling–grinding powders, respectively, at 20 mg/L dye concentration. The absorption ability of four powders decreased with the increase of the initial MB concentration in solution. Four materials had almost similar adsorption efficiency and intendancy if initial MB concentration in solution was up to 60 mg/L. The difference observed here may arise from the morphology and size of the particles and the total surface area of the materials used [21].

3.3. Effect of solution pH

pH is one of the most influencing factors for dye adsorption as it directly affects the dissociative and adsorptive ability of the dye on the adsorbent surface [3]. To study the effect of pH on MB adsorption on raw and modified pyrophyllite, the experiments were carried out at 10 mg/L initial MB concentration with 0.2 g/100 mL adsorbent mass at 20 °C for 24 h equilibrium time. Fig. 3 shows the effect of solution pH on MB adsorptions. All samples showed a similar adsorption efficiency at high pH solution above 11. The adsorption reaction was affected by

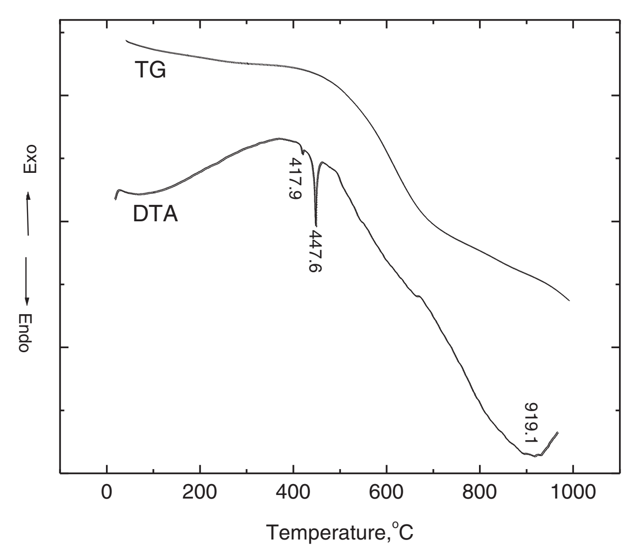

Fig. 1. Thermal analysis of raw pyrophyllite.