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Acid modified local clay beads as effective low-cost adsorbent for dynamic adsorption of methylene blue

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ABSTRACT

Locally sourced clay was harnessed to study its adsorptive potential of methylene blue (MB) in wastewater streams. The clay was modified with sulfuric acid and aluminum hydroxide. The raw and modified freeze dried clay bead RHC and MHC were subjected to batch and batch/fixed-bed adsorption studies, respectively. Elemental analysis, morphological structures were determined, and surface area of 19.3 (RHC) and 101.2 (MHC) m^2/g were obtained. Langmuir, Freundlich and Redlich–Peterson isotherms models were analyzed and the modification increased adsorption capacity from 58.02 to 223.19 mg/g at 30 °C. The MB adsorption on RHC/MHC was spontaneous, exothermic and obeyed pseudo-second-order model.

1. Introduction

The existence of clay is synonymous to the age of the planet earth but yet its applicability has not been exhausted. Clays either in natural form or processed has found applications in many facets of life, these includes: construction, farming, catalyst support, in detergent industries, adsorption, chemical industry, beverage, photochemical, ceramics, paper filling and coating, sensors and biosensors [1]. Raw and modified clays have been used extensively for adsorption purposes but the fact that new challenges of pollution problems keeps emanating, it calls for a continuous research towards finding a cheaper, effective and efficient solution to the problems [2,3]. One form of the commonest problems of pollution is indiscriminate discharge of untreated dyes to the environment which affects the entire ecosystem due to their low-degradability, mutagenic and carcinogenic effect on man and constituting as impediment to free penetration of light in water hence affecting photosynthesis ability of aquatic plants [4–6]. Amongst methods of beneficiation of clay for adsorption processes, calcinations, acid treatment, pillaring, cation and anion exchange have yielded good results in producing clay adsorbents [7,8]. Clays are very good substitute for expensive commercial activated carbon used in adsorption processes [9,10]. They have many advantages over other low cost adsorbents such as availability, affordability, ion exchange capability, high adsorption capacity and surface area, mechanical and chemical stability, and different structural and surface characteristics [11].

Nano-meter scale nature of clay which enhances its surface area as well as favorability in adsorption processes is still a major challenge because of difficulties in the dispersing or separation procedures they pose after usage [12,13]. Many adsorption processes using clay adsorbents employ services of other separation techniques such as decantation, filtration and centrifugation for the purpose of separating the adsorbent from the supernatant thereby increasing labor and cost of the adsorption activity; and moreover, the use of these additional techniques in adsorption process are yet to be standardized [14].

Application of adsorption technique for large waste-water treatment usually employs continuous adsorption process while selective sorption and performance of the adsorbent in the process are determined in batch adsorption studies. The advantages of continuous adsorption process over batch process are that large volume of polluted water can be treated at shorter time, high possibility of scale up from laboratory level and the process is much easier to operate [15].

This study is aimed at investigating the potential of abundant local clay from Ipoh in Perak state of Malaysia as substitute to commercial activated carbon adsorbent for adsorption of methylene blue from aqueous solution in a fixed-bed column. The acid treated, cationized and calcined local clay was transformed into beads to reduce labor and time wastage often incurred whenever powdered clay adsorbents are used for adsorption. Desorption test of the modified local clay was investigated.

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2. Materials and methods

2.1. Materials

A synthetic textile dye, methylene blue (MB), sulphuric acid (H_2SO_4) and aluminum hydroxide ($Al(OH)_3$) of analytical grade were purchased from Sigma–Aldrich chemicals, Merck chemical company and R & M marketing Essex, U.K., respectively; and used without further purification. The clay adsorbent used was gotten from Ipoh in Perak state of Malaysia; it was crushed, ground, sieved to particle sizes of 20–45 μm and dried at 100 °C in an oven for 8 h.

2.2. Preparation of clay adsorbent

The dried local clay (HC) was activated with 2 M H_2SO_4, ratio 0.2 g clay/mL (clay/acid) in a 500 mL beaker placed on hotplate magnetic stirrer; the temperature of the mixture was set at 90 °C and stirred vigorously for 3 h. Then the clay was washed with distilled water to reduce excess moieties and to ensure that the supernatant attain neutrality (pH 6.8–7), thereafter the clay was dried in an oven at 100 °C for 6 h. The dried acid activated HC was refluxed for 2 h at 90 °C after adding about 100 mL of 0.5 M $Al(OH)_3$; the refluxed solution was allowed overnight before washing. The acid activated refluxed clay solution was dried in an oven at 110 °C and then calcined for 3 h at 500 °C. The calcined HC was transformed into beads using sodium alginate binder before freeze drying. Raw dried HC was also molded into beads with the aid of sodium alginate binder and freeze dried. The raw freeze dried HC beads (RHC) and the freeze dried modified HC beads (MHC) both of particle sizes between 1 and 2 mm were kept in air tight container for further use. The RHC and MHC structures are presented in Fig. 1.

2.3. Characterization of the clay adsorbents

The RHC and MHC adsorbents were characterized for elemental analysis, surface morphology and surface area using scanning electron microscope (SEM/EDX analyzer) and Brunauer Emmett Teller (BET) analysis, respectively.

Energy-dispersive X-ray spectroscopy (EDX) for elemental analysis and morphological structure of the adsorbents were performed using scanning electron microscope (Model EMJEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system.

The Brunauer Emmett Teller (BET) analysis was carried out by nitrogen adsorption–desorption method using nitrogen temperature (−196 °C) with an autosorb BET apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer. The analysis procedure was automated and operated with static volumetric techniques. The sample was first degassed at 200 °C for 2 h before each measurement was recorded.

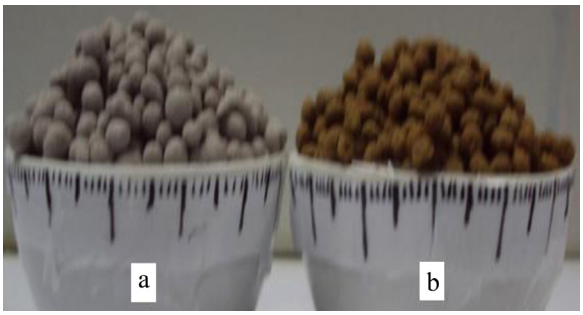

Fig. 1. Structural view of the adsorbents (a) MHC and (b) RHC.

2.4. Batch equilibrium adsorption studies

The batch equilibrium adsorption studies were undertaken using a set of Erlenmeyer flasks (250 mL) containing 200 mL of MB solutions at various initial concentration (30–300 mg/L). The RHC adsorbent 0.2 g (1–2 mm) was added and placed in water bath isothermal shaker at 30 °C for 12 h, at 140 rpm shaker speed to attain equilibrium. The final concentrations of MB solution in the flasks after equilibrium were determined using UV–vis spectrophotometer (Shimadzu UV/Vis 1601 spectrophotometer, Japan) at maximum wavelength of 668 for MB. Afterwards, temperature of water bath shaker was adjusted to 40 °C and 50 °C, and the procedure was repeated with another set of flasks containing similar different initial MB concentration. The adsorbent was changed to MHC and similar procedure was administered. The amount of the MB adsorbed at time t, at equilibrium Q_e (mg/g) was evaluated by the following equation:

$$Q_e = \frac{C_o - C_e}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentration of the MB at initial and at equilibrium, respectively; $V(L)$ is the volume of the solution; and $W(g)$ is the mass of the dried adsorbent (RHC or MHC).

2.5. Effect of solution pH on MB adsorption by both RHC and MHC

The effect of initial pH on MB adsorption on both RHC and MHC was carried out using either 0.1 M NaOH or 0.1 M HCl for adjustment of pH of the solutions in the range 3–12. Adjustment of the pH was valued using pH meter (Model Delta 320, Mettler Toledo, China). The study was administered in a set of 250 mL Erlenmeyer flasks charged with 200 mg/L and 0.20 g of the MB concentration and adsorbent beads, respectively at a temperature of 30 °C for 12 h.

2.6. Batch kinetic studies

A limiting step upon which adsorption process design is based is the transfer rate of solute to the adsorbent from the bulk solution. This was done by determining the MB solution concentration at pre-set intervals of time. The measure of the dye at time t adsorbed, Q_t (mg/g) was calculated using equation:

$$Q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_o and C_t (mg/L) are the liquid-phase concentration of the MB at the initial and any time t, respectively; $V(L)$ is the volume of the solution; and $W(g)$ is the mass of the either RHC or MHC adsorbent used.

2.7. Desorption studies

An amiable quality of an adsorbent is its predisposition for reuse. This was investigated through desorption and regeneration studies which are valuable attributes in adsorption processes. The recovered pre-adsorbed 0.2 g of MHC from 100 mg/L dye solution was slightly washed using distilled water to eliminate the un-adsorbed MB on the sorbent surface, air dried and then placed in 100 mL of distilled water of pH 4 in a water-bath shaker at 30 °C, shaker speed of 140 rpm for the predetermined equilibrium time of the adsorption process. Desorption efficiency of MB was determined as:

$$\text{Desorption efficiency}\,(\%) = \frac{M_d V_d}{W \times Q_e 100} \times 100 \quad (3)$$