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# Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue

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## HIGHLIGHTS

- Modified Ball clay was coalesced with chitosan to form composite adsorbent (MBC–CH).
- MBC–CH gave high adsorption of methylene blue in batch and fixed-bed systems.
- MBC–CH activity can be sustained on the event of adsorption system failure.
- MBC–CH can be regenerated and reused in many cycles of adsorption with resilience.

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## ABSTRACT

Modified Ball clay (MBC) and chitosan composite (MBC–CH) was prepared and its application for methylene blue (MB) adsorption from aqueous solution in an industrial prototype fixed-bed column adsorption was investigated. Morphological structure and functional groups of the MBC–CH were determined by scanning electron spectroscopy and Fourier transform infrared spectroscopy analysis, respectively. Batch adsorption studies revealed that MB adsorption on MBC–CH increased with increase in initial concentration and solution pH 4–12. Study on effect of some inorganic salts on MB adsorption revealed that sodium sulphate anions ($SO_4^{2-}$) had greater inhibition effect than those of sodium chloride and sodium bicarbonate on both MBC and MBC–CH. The effects of initial concentration (30–300 mg/L), adsorbent bed height (2.5–4.5 cm) and influent flow rate (5–10 mL/min) on fixed-bed column adsorption breakthrough curves were evaluated. Column sorption capacities were 70 mg/g for MBC and 142 mg/g for MBC–CH. Dynamic modeling analysis revealed that Bohart–Adams model can best be used to predict the effluent breakthrough curves for successful design of MB adsorption than Yoon–Nelson model. Adsorption system failure studies showed that the adsorbents were resilient with some improvement observed at time of exhaustion and increased volume of effluent treated. The MBC–CH had above 50% adsorption uptake capacity after five regeneration cycles, this was higher than MBC. Adsorption of MB on MBC–CH was spontaneous, endothermic and had great affinity between the adsorbate and adsorbent. The findings of this study revealed that MBC–CH is a potential adsorbent for cationic dye pollution remediation.



## 1. Introduction

Conventional batch adsorption is widely used in laboratory experiments to assess adsorption capacity of adsorbents and to generate design data for large scale systems; however, it can only be used to treat small volume of wastewater and as such is not popular in industrial applications [1–3]. Fixed-bed adsorption system is commonly used for gas and liquid pollution control. It is designed in such a way that the flowing polluted fluid comes in contact with a fixed amount of adsorbent thereby creating room for treatment of large volume of effluent fluid with less monitoring requirement [4]. The system is simple to operate, low cost and can easily be scaled up [5].

Several alternative low cost adsorbents have been developed from minerals, agricultural and industrial waste materials amongst others. These adsorbents applicability for treatment of dye and heavy metals wastewaters, gas and pharmaceutical wastes pollution and oil spillage control have been investigated. Clay minerals application in pollution control has received gross attention over

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the past decades. Modification of clay through acid treatment, calcinations, functionalization and pillaring are among several ways that effort has been made by researchers to enhance its usability beyond its application in natural form [6]. Chitosan is a biopolymer derived from N-deacetylatilation of chitin which is found in abundance naturally. The high content of hydroxyl and amino functional groups of chitosan are potentials that has been harnessed in the field of adsorption of substances [7]. However, chitosan has some mechanical and chemical deficiency challenges which when improved upon, increases its adsorption capability [8,9].

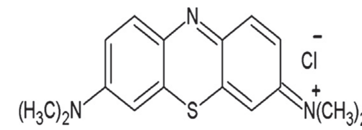
Integration of an adsorbent with other materials through methods such as grafting, impregnation, chelation and crosslinking has better adsorption properties than the individual components effects [10]. The synergy of adsorbent materials as composites have been tailored for gas, metals, pharmaceutical wastes, dyes and pesticide remediation. Composite adsorbents can be prepared with the sole aim of enhancing their selectivity, regeneration, surface area, mechanical strength and surface chemistry amongst others [11,12].

Among classes of dyes, the cationic dyes are commonly used for different purposes due to their ease of applicability, durability, and good fastness to materials; however, their demerit effects are immense. Cationic dyes are known to have carcinogenic, mutagenic and high coloring effects on the entire ecosystem when discharged as waste in the environment [13]. Methylene blue (MB) a cationic dye has very wide applications which make it one of the common pollutants or constituent of color effluents. Several attempts have been made by previous researchers to address MB health effect as a pollutant in wastewater through the development and application of different adsorbents for its uptake [14–17].

In continuation with the exploration of effective MB pollution mitigating measure which has been the bane of researchers towards ensuring sustainability of serene environment, potentials of local clay in Malaysia for industrial application as adsorbent was investigated in this research. The modified Ball clay (MBC) previously reported [18] was composited with chitosan for adsorption of MB in a fixed-bed column. Behavior of breakthrough curves was studied through variation of the MB influent initial concentration, bed height and solution flow rate. The fixed-bed column adsorption was modeled with Bohart–Adams and Yoon–Nelson models. The use of some various salts in the textile industries to improve color fastness was investigated through studying effect of some inorganic salts on adsorption, and the adsorbent reusability test was conducted through desorption studies.

## 2. Materials and methods

Chitosan flakes ((molecular weight, MW = 400,000 Da, degree of deacetylation, DD = 90%) was obtained from Hunza Pharmaceutical Sdn Bhd., Nibong Tebal, Malaysia. Aluminum hydroxide ($Al(OH)_3$), sodium hydroxide (NaOH), sulfuric acid ($H_2SO_4$) and acetic acid ($CH_3COOH$) were purchase from Merck chemical company, while methylene blue (MB) was obtained from Sigma–Aldrich Chemicals, Malaysia. Ball clay was locally sourced in Malaysia. Schematic structure of methylene blue and its properties are shown in Scheme 1.

| | |
|---|---|
| Name of dye | Methylene blue |
| Molecular formula | $C_{16}H_{18}N_3SCl$ |
| Molecular weight (g/mol) | 319.85 |
| Methylene blue purity (%) | ≥85 |
| Maximum wavelength λ (nm) | 668 |
| Chemical structure |  |



**Scheme 1.**

### 2.1. Preparation of MBC–CH adsorbent

The procedure for preparation of modified Ball clay (MBC) is as reported in our previous work [18]. Chitosan (1 g) was dissolved in 52 mL of 0.7 M acetic acid, and then 1 g of MBC (powder MBC prior to mixing with sodium alginate to form beads) was added and stirred for 24 h. The mixture was drop-wisely transferred to 0.67 M NaOH solution to form beads and was freeze dried. The freeze dried beads MBC–CH) were crushed into particle sizes of 0.5–2.0 mm and were tagged MBC–CH.

### 2.2. MBC–CH adsorbent characterization

Scanning electron microscope (EMJEOL-JSM6301-F) model and an Oxford INCA/ENERGY-350 microanalysis system was used for determination of MBC–CH morphological structure before and after adsorption of MB.

Perkin Elmer Spectrum GX Infrared Spectrometer with resolution of 4 $cm^{-1}$ in the range of 2000–400 $cm^{-1}$ was used for the FTIR analysis of MBC–CH. The MBC–CH adsorbent and potassium bromide (KBr) were dried in an oven and then ground together in a ratio of 20:1 (KBr:MBC–CH) for FTIR measurement using disc sample method.

### 2.3. Kinetic and equilibrium adsorption studies

Initial concentrations (30–300 mg/L) of 100 mL MB was put in a set of Erlenmeyer flasks where 0.1 g of MBC–CH was added. The flasks were place in water-bath shaker set at 140 rpm and 30 °C until equilibrium concentration between the adsorbent and solution was attained. Prior to equilibrium, kinetics of the adsorption process was studied by sampling the residual MB concentration in solution using UV–Vis spectrophotometer (Shimadzu UV/Vis 1601 spectrophotometer, Japan) at a maximum wavelength of 668 nm.

The adsorbent adsorbate uptake, $q_t$ (mg/g) was evaluated as:

$$q_t = \frac{(c_o - c_t)_v}{w} \qquad (1)$$

where $C_o$ and $C_t$ (mg/L) are the initial MB liquid-phase concentration and at any time $t$, respectively; $V$ (L) is the volume of the solution; and $W$ (g) is the mass of the MBC–CH. The entire process was repeated by varying water-bath shaker temperature to 40 and 50 °C.

In a similar manner as the equilibrium adsorption studies, about 0.5 and 1.0 M salts of NaCl, $NaHCO_3$ and $Na_2SO_4$ were added to the initial MB solution to study their effect on the adsorption process. The effect of solution pH 4–12 effect on MB adsorption was studied in the batch operation experiment by adding either 0.1 M of NaOH or HCl to adjust the initial pH.

### 2.4. Regeneration of adsorbent

Adsorbent recovered after batch equilibrium studies were rinsed mildly with distilled to remove residual dye particles and then dried. The dried adsorbent was placed in a stripping solution contained in 250 mL Erlenmeyer flask. The solution was 100 mL