

Desorption Studies for Methylene Blue Dye Removal by Kaolinite

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Received: 30 June 2021

Accepted: 21 August 2021

Online first: 31 August 2021

ABSTRACT

In wastewater treatment, the reusability of an adsorbent strongly relies on the feasibility of contaminant desorption from the spent adsorbent. This research aims to investigate the Methylene Blue (MB) release from the spent kaolinite clay mineral against a variety of desorbing eluent in an aqueous solution. Malaysia's kaolinite was characterised using Scanning Electron Microscopy (SEM), surface area analysis, and Fourier Transform Infrared (FTIR) Spectroscopy. The MB desorption was performed using eluents of distilled water, solutions of HCl, NaOH, and NaCl (0.01 M and 0.1 M), and ethanol: water mixtures (30:70, 50:50, and 70:30 v/v ratios). It was found that the MB desorption only occurs in 0.1 M NaOH (pH 12.7). A 4.2% MB desorption was recorded in 1 hour and was increased to 19.5% within 24 hours desorption time. The pH change measurement also reveals the favorability for highly alkaline conditions for MB desorption. The overall finding indicates that the MB retention towards kaolinite is strong, and its adsorption occurs via electrostatic and hydrophobic interaction, as suggested by the FTIR analysis. Kaolinite is a good scavenger for removing the MB dye from contaminated water but requires a strong eluent in the desorption process for its future reusability process.

Keywords: desorption, methylene blue, spent kaolinite, retention, interaction



INTRODUCTION

In recent years, the removal of synthetic dyes from polluted water has become an important effort to protect the environmental sustainability of water resources [1]. Most dyes are poorly biodegradable and resistant to environmental conditions, creating major wastewater treatment problems [2]. For example, Methylene Blue (MB) is an azo dye used in the textile industries for its intense color. However, its excessive exposure is hazardous to human health and aquatic life [3]. Dyes removal from water resources is often carried out using chemical oxidation, coagulation, photocatalytic, ion exchange, and adsorption. The latter approach is considered the most cost-effective and simplest method [4]. Clay minerals, a natural aluminosilicate, are commonly used as the adsorbent for this process due to their natural abundance, low toxicity, and high capabilities in adsorbing ionic contaminants like dyes. For example, kaolinite clay mineral ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) has been previously used in water treatment of dyes with excellent performance [5, 6].

To minimise the build-up of environmental waste, recycling of spent adsorbent is an alternative and more sustainable approach as compared to disposal or incineration method. In this context, the loaded contaminant retrieved after the treatment should be fully desorbed from the spent adsorbent to allow its reusability on the next treatment cycle [7]. The desorption process needs to dissociate the adsorption forces between adsorbent and adsorbate [8] so that the adsorbent could be regenerated and re-use. Indirectly, the desorption experiment could also be used to deduce the strength of adsorbate (contaminant)-adsorbent (clay) retention to support the postulation of its adsorption mechanism. Desorbing eluents such as acid, base, organic solvent, and chelating agent were commonly used for desorption depending on its desorption capability, cost, and potential toxicity of the by-product [9]. Although highly concentrated acid/base and chelating agents like ethylenediaminetetraacetic acid (EDTA) are strong eluents, their waste treatment is always problematic.

MB-kaolinite retention was typically elucidated using adsorption isotherm theories like the Langmuir and Freundlich model coupled with the kinetics study [5, 10]. However, the postulation of the adsorption mechanism from the perspective of desorption is rarely discussed. Comprehensive

reusability studies involving kaolinite's desorption, regeneration and adsorption cycles are also still lacking in the literature [11]. This study aims to investigate the desorption profile of MB from the MB-loaded raw kaolinite (RK) to find the best desorbing eluent and understand the dye's retention towards kaolinite. For this purpose, Malaysia's natural kaolinite retrieved from a local supplier will be used as the adsorbent. The MB dye will be loaded into kaolinite through a pre-determined adsorption condition and then immersed in various desorbing eluents to undergo the desorption process. The quantity of MB released from the spent kaolinite (SK) is measured and compared. FTIR analysis will be carried out to support the postulation of the MB-kaolinite interaction mechanism derived from the desorption data.

MATERIALS AND METHOD

Chemicals and Reagents

Raw kaolinite (Grade KM40, purchased from Kaolin Malaysia Sdn. Bhd.) was used without further purification. Methylene Blue (MB) (minimum 82% purity) is from R&M Chemicals. Hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH, 96%) were from R&M Chemicals and of analytical grade. Other chemical reagents such as ethanol (98% assay) and sodium chloride (NaCl) were of analytical grade.

Characterisation

The raw kaolinite was characterised via Scanning Electron Microscope (SEM), N₂ adsorption-desorption isotherm, and Fourier Transform Infrared (FTIR) spectroscopy. SEM analysis was performed using a scanning microscope (Quanta 450 FEG) using a high vacuum mode with a 60,000x magnification factor. Meanwhile, the FTIR spectra were collected using the Perkin-Elmer infrared spectrophotometer-ATR mode at a wavenumber of 4000 – 650 cm⁻¹ with a 4 cm⁻¹ resolution and 32 scans. The N₂ adsorption-desorption isotherm was performed via the Sorptometric 1990 series. Before analysis, the sample was degassed first at 90°C for an hour and subsequently to 180°C for four hours.

Preparation of Spent Kaolinite (SK)

To produce the spent kaolinite (SK), the adsorption experiment was first carried out according to our previous work [6] to ensure a 100% MB uptake by the kaolinite. Briefly, 0.5 g of kaolinite was mixed with 10 mL of 50 ppm MB solution. After one hour agitation, the suspension was centrifuged at high speed (2500 rpm) for 20 minutes. The supernatant was collected, and the concentration of MB in the supernatant was analysed using a UV-Vis spectrometer (PGInstrument Ltd, T80+) at the maximum wavelength of 665 nm [4].

Desorption of MB from SK

A series of eluent consisting of distilled water (DW), ethanol: water mixture, and 0.1 *M* and 0.01 *M* of HCl, NaCl, and NaOH, respectively, were prepared. Only mild concentration was used for the eluents to ensure an environmentally benign desorption approach. The MB-loaded-kaolinite known as spent kaolinite (SK) was agitated in a 10 mL aqueous solution of each desorbing eluent for up to 24 hours. The pH changes of the suspensions were recorded using a pH meter before and towards the end of the agitation process. The concentration of MB release into the desorbing eluent was measured using a UV-Vis spectrometer, and the desorption efficiency was calculated according to the formula:

$$\% \text{ desorption} = \frac{\text{concentration of dye desorbed by eluent}}{\text{concentration of dye adsorbed on adsorbent}} \times 100\% \quad (\text{Equation 1})$$

RESULT AND DISCUSSIONS

Morphology and Porosity of Kaolinite

In the SEM image, the morphology of raw kaolinite (RK) appears as stacked pseudo-hexagonal platelets with a flat basal surface and thick edge (Figure 1(a)). Some irregular surfaces in a non-hexagonal feature were also present. Kaolinite is well-known to have a strong hydrogen bonding between its layers [12], explaining the tight stacking of kaolinite's platelet in the SEM image. Alongside, this clay has a relatively low Brunauer-Emmett-Teller

(BET) surface area ($9.1\text{m}^2\text{g}^{-1}$) with an average pore volume of $0.0423\text{cm}^3\text{g}^{-1}$. The Barrett-Joyner-Halenda (BJH) pore volume distribution showed the highest peak at the pore width between 20 to 50 Å (Figure 1(b)).

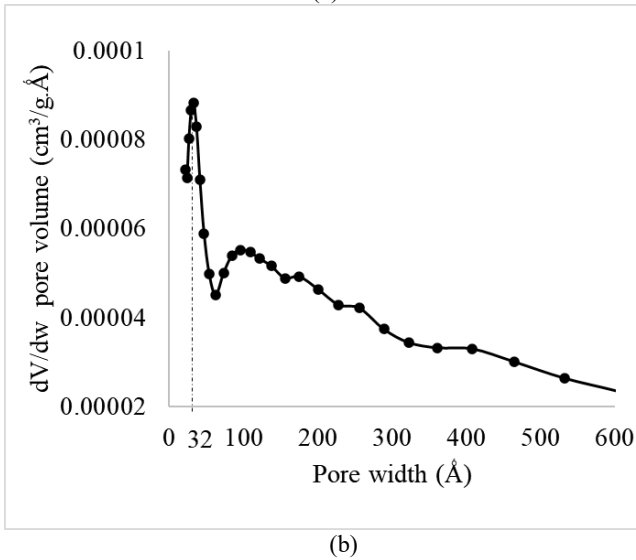
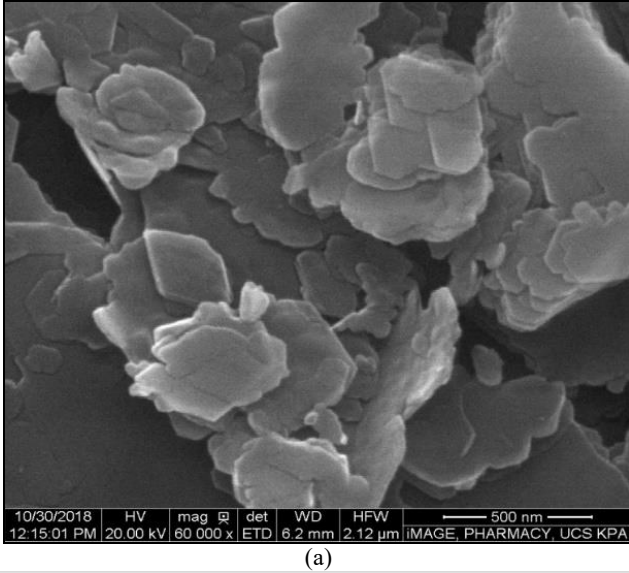


Figure 1: (a) SEM Image of Raw Kaolinite (RK), and (b) BJH Pore Size Distribution of RK (Source by Author)

Desorption of Methylene Blue from Kaolinite

This study reveals that no MB desorption from spent kaolinite was recorded using various eluents with the time (1 to 24 hours) and concentration (0.01 *M* to 0.1 *M*) increment except for 0.1 *M* NaOH. This eluent gives a 4.17% and 19.5% MB desorption at one hour and 24 hours, respectively. Meanwhile, a non-desorption of MB by distilled water and HCl suggested that the dyes' retention towards kaolinite is not merely governed by the physisorption process [13] or cationic exchange mechanism as previously reported [14]. On the other hand, ionic salt-like NaCl could increase the anionic characteristics of kaolinite in suspension [15], giving it a more favourable and stronger electrostatic interaction with the cationic MB. This later prevents the MB desorption from the spent kaolinite. In a previous study, ethanol successfully desorbed the MB ascribed to the solvent's polarity, solubility of MB in ethanol, and the ease of penetration to the pores at a higher temperature [16]. However, a similar finding is not observed in this study probably due to factors like the low porosity of kaolinite (as previously mentioned), ambient temperature use (25 °C), and existence of a stronger hydrophobic interaction between the MB and kaolinite.

Measurement of pH change was performed to deduce the influence of initial pH towards MB desorption. All kaolinite suspensions in desorbing eluent exhibited a minimum pH change except for the NaCl and ethanol/water solution (Table 1). It is clear that a strong basicity (pH 12 and above) as in 0.1 *M* NaOH is needed to permit a good MB desorption from the spent kaolinite (Table 1). This is ascribed to the structural changes of clay at high pH [17-18] that weaken the clay-MB interaction and propagate the MB's dissolution. Likewise, a small pH increment in HCl eluent suggests that the cation exchange mechanism occurring between the H⁺ with the loaded-MB⁺ is minor. Based on the desorption studies, the electrostatic and hydrophobic interaction is deduced to be the important mechanism for MB-kaolinite retention.

Table 1: pH Change for Different Eluent Suspension

Desorbing eluent	pH before desorption	pH after 24 hours desorption
Distilled water	6.33	7.74
0.01 M HCl	1.71	2.35
0.1 M HCl	0.73	1.13
0.01 M NaOH	11.4	11.1
0.1 M NaOH	12.7	12.3
0.01 M NaCl	4.76	8.42
0.1 M NaCl	4.28	7.36
<i>Ethanol : distilled water</i>		
30 : 70	4.65	7.06
50 : 50	4.56	7.00
70 : 30	4.44	6.47

Interpretation of FTIR Spectra

To support the postulation of MB-kaolinite retention mechanism proposed by the desorption study, the FTIR spectra of raw kaolinite (RK), spent kaolinite (SK), and spent kaolinite after desorption with 0.1 M NaOH (SKD) were investigated (Figure 2, Table 2). In the RK spectrum, typical bands associated with kaolinite, such as the Al-O and Si-O stretching were observed [19] (Table 2). Meanwhile, the band at 3681 cm^{-1} associated with the interlayer -OH stretching [20] of kaolinite was shifted to a higher wavenumber (3696 cm^{-1}) in SK. The shifting indicates the weakening of the hydrogen bonding in the kaolinite's interlayer due to its interaction with MB. The -OH stretching (913 cm^{-1}) and Si-O-Si/Al (752 cm^{-1}) bands of the kaolinite in SK were getting weaker and shifted to a higher wavenumber (Figure 2 and Table 2). This observation indicates a strong involvement of these silanol and aluminol groups as the potential active site for the adsorption of MB towards kaolinite; in good agreement with the previously reported work [21]. The blue-shift of these bands also demonstrates the decrease of molecular mass of the functional groups, presumably due to surface complexation [20]. Hence, electrostatic interaction arises between the negative surface charge of kaolinite with the cationic MB is postulated, as similarly suggested by previous studies [19, 21]. Besides, a molecular

simulation study had also predicted the preference of hydrophobic interaction of MB with the siloxane surface in kaolinite [22].

The adsorption of MB towards kaolinite is supported by the new bands in the wavenumber region of 1300 to 1700 cm^{-1} that belonged to the dyes' functional groups. Specifically, the bands at 1600 to 1300 cm^{-1} were assigned to the aromatic ring structure of the heterocycle of this dye. This involved the C=C, C=N ($\sim 1600 \text{ cm}^{-1}$), C-C (1560 cm^{-1}) and C-N vibrations (1540 cm^{-1}) from the amide II group in MB [23]. The bands at 1351 cm^{-1} and 1297 cm^{-1} could also be assigned to the C-N and C = S⁺ stretching vibrations [23]. Whereas the band at 1281 cm^{-1} was for C-H bending vibration. The medium intense peak at 1689 cm^{-1} denotes the C-N stretching vibrations found in the C_{het} = N⁺(CH₃)₂ of the heterocycle [23]. Therefore, the presence of all these bands in the IR spectrum of SK suggests that MB's adherence towards kaolinite was achieved via electrostatic and hydrophobic interaction.

The IR spectrum of spent kaolinite desorbed with 0.1 M NaOH (denoted as SKD) was investigated. The bands associated with the C-N and C-S were diminished (Figure 2). The disappearance of these bands through MB desorption from kaolinite signifies their participation in the MB-kaolinite interaction. It is noteworthy that a broad band around 1527 – 1345 cm^{-1} in SKD could be associated with the partial un-desorbed MB remaining in the kaolinite. The Al-OH stretching band of kaolinite originally at 913 cm^{-1} (as in the IR spectrum of RK) was restored while the Si-O-Si stretching bands (around 752 and 695 cm^{-1}) were broadened almost disappeared. Such changes respectively depict electrostatic interaction occurrence via aluminol site and hydrophobic interaction on the siloxane groups that were affected once the MB was desorbed from the spent kaolinite. Overall, the FTIR analysis regarding the MB-kaolinite interactions was in good agreement with the postulation derived from the desorption studies as described earlier.

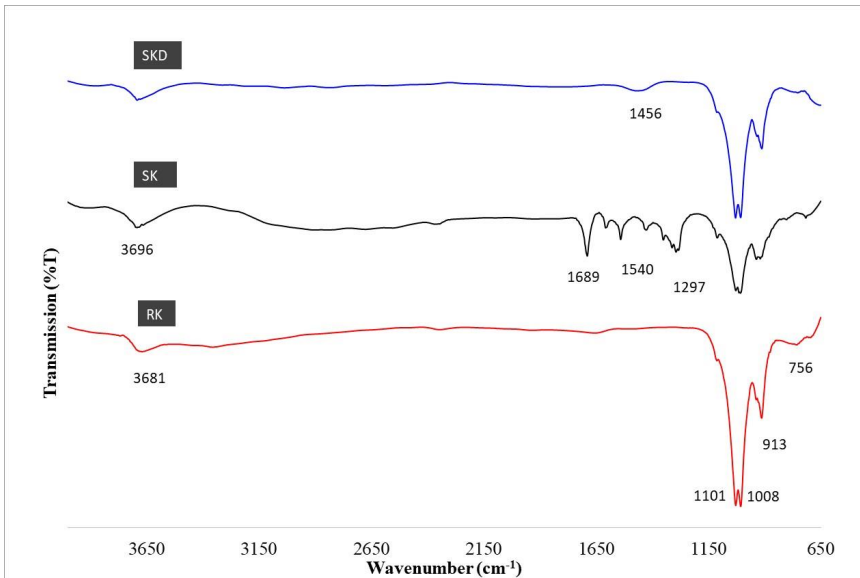


Figure 2: FTIR Spectra of Raw Kaolinite (RK), Spent Kaolinite (SK), and Spent Kaolinite After Desorption with 0.1 M NaOH (SKD) (Source by Author)

Table 2: Functional Groups Present in RK and SK

Functional group / Material	Raw kaolinite (RK)	Spent kaolinite (SK)
-OH stretching (interlayer)	3681	3696
Si-O stretching	1101, 1008	1015, 1007
Al-OH stretching	913	919
Si-O-Si/Al stretching vibration	752, 695	801, 717
C-C and C-N stretching (aromatic ring)	-	1600-1540
C-N stretching ($C_{\text{het}} = N^+(\text{CH}_3)_2$)	-	1689
C=S ⁺ stretching	-	1297
C-H bending	-	1281

CONCLUSION

A 19.5% MB desorption from spent kaolinite was achieved using 0.1 M NaOH as desorbing eluent in 24 hours. From the desorption perspective, the MB-kaolinite retention is considered strong and involves specific interaction, including electrostatic and hydrophobic interaction, as supported by the FTIR analysis. This preliminary work promotes the use of strong base as a suitable desorbing eluent to allow the reusability of spent kaolinite. For a complete MB desorption, a higher concentration of desorbing eluents and a longer desorption time may be necessary. However, the post-treatment for the discharge of highly acidic/basic or complexing suspension eluents in desorption will require careful environmental consideration. Future works shall include the kinetic studies of MB desorption and the use of more sophisticated spectroscopic techniques to deduce the adsorption mechanism at a molecular level.

ACKNOWLEDGEMENT

Partial funding through the *Fundamental Research Grant Scheme* (FRGS/1/2019/STG07/UITM/02/15) sponsored by the Ministry of Higher Education of Malaysia is greatly acknowledged. The authors would like to thank Universiti Teknologi MARA, Negeri Sembilan branch for the technical facilities to carry out this research.

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