

VARIATION OF CATIONIC DYE ABSORPTION CAPACITY WITH THE SINTERING TEMPERATURE OF NATURAL MONTMORILLONITE CLAY

G.D.K.Heshan¹, W.G. Jayasekara², A.Wijayasinghe³
^{1, 2, 3}National Institute of Fundamental Studies, Kandy, Sri Lanka
Heshankamaljith@gmail.com

ABSTRACT: Development of montmorillonite clay as inexpensive natural absorbent to remove organic anionic dyes from waste water was investigated as the main objective of this study. It was a part of a major project concerning development of local minerals and related materials for low-cost and efficient water purification. The work carried out on investigation of the effect of sintering temperature of the montmorillonite clay on methylene blue adsorption is reported in this paper. It was carried out by sintering the selected clay at different temperatures of 100 -900 °C, followed by an dye adsorption study performed using methylene blue dye. The XRD phase analysis confirmed the existence of appropriate montmorillonite phase in the selected clay. The pore size decreases with the increase of sintering temperature as expected. The endothermic peak was observed at 400 °C due to loss of hydroxyl groups resulting reduction of adsorption above 400 °C. That may result in reduction of reactive sites in clay surface also by minimizing adsorption capacity. Hence this suggests 450 °C as the optimum sintering temperature of this clay, with an adsorption capacity of 12.8 mgg⁻¹ at room temperature, to be used for water filtration application

Keywords: Montmorillonite, Dye, Heat Treatment, Methylene Blue, Adsorption.

1. INTRODUCTION

The industrial effluents of cosmetic, textiles, leather, printing, plastics, paper, rubber, dye manufacturing and food processing contains various types of toxic dyes[1]. Worldwide, more than 10,000 different dyes with over 700,000 metric tons are commercially available annually. Out of them, around 5-10 % of the dyestuffs are discharged as industrial effluents[2]. The uptake of dyes from wastewater is an issue of great interest in the field of water pollution [3]. Generally, anionic dyes are less toxic than basic dyes [4]. Among them, methylene blue (MB) is the most common soluble dye in water. MB is mainly used for cotton, dyeing leather, medicinal purposes, printing, and tannin industries [5]. MB dye is not considerably toxic to human being but it can cause eye irritation, skin irritation, and systemic effects including blood changes [6]. There are a number of different effective methods to remove dye effluents from waste water. Among them, reverse osmosis, ion exchange, membrane filtration, conventional coagulation, chemical precipitation and adsorption are the frequently used techniques to remove dyes from wastewater [7-9]. However, most of these techniques are expensive and rather complicated. Because of that the mostly under developed countries suffering from this pollution can't afford these techniques.

In the meantime, the conventional adsorption is a cheap and better technique because of its simplicity in design and the availability. It widely uses some of the most abundant absorbents such as clay minerals. Clay minerals are capable of absorbing wide range of metal ions, organic dyes and organic pesticides. These clays are consisted of two tetrahedral sheets. The dominant atom in the tetrahedron is the Si⁴⁺ cation, while the Al³⁺ cation can also occur at this site. This is important, because the substitution of Al³⁺ for Si⁴⁺ produces a charge deficiency, which should be counteracted somewhere else in the structure, although in a somewhat different sense. Potential clay minerals are available in large quantities in Sri

Lanka. They are much easy to extract and the annual production is approximately 65,200 metric tons. Already, some research work has been carried out on absorption of heavy metal ions by local clays. However, still no systematic study has been performed on the use of montmorillonite as an effective adsorbent for the removal of cationic dye MB. When selecting clay minerals for such analysis, the indirect absorption mechanisms in dye absorbance varies qualitatively and quantitatively with the clay type and sintering temperature. In this study, the main objective was to investigate the feasibility of montmorillonite clay as inexpensive natural adsorbent to remove organic anionic dyes from waste water. For that, the effect of sintering temperature of the montmorillonite clay on methylene blue adsorption was studied.

2. METHODOLOGY

2.1 Materials and Methods

For this study, the montmorillonite clay was collected locally from Murunkan area in the Northern Province of Sri Lanka. The clay was washed thoroughly with deionized water to remove impurity and then dried in an oven at 100°C for 48 hrs. The dried clay was crushed and grounded by using a ball mill. The resultant powders were sieved using Retsch Standard Sieves and particles with size below 53 micron was used for the study. This powder was then put in muffle furnace to sinter them at different temperatures. To examine the surface morphology of raw and sintered samples, the Scanning Electron Microscope (SEM) (TSM 6400 Gemini Zeiss) was used. Fourier Transform Infrared (FTIR) spectroscopy was used to determine functional groups.

The adsorption studies were performed by batch techniques to obtain rate and equilibrium data. Various MB solutions with different initial concentrations, in the range of 10 - 100 mg L⁻¹, were prepared by diluting stock dye solution (1g L⁻¹). Equilibrium experiments were conducted to determine the adsorption capacity of clay, using 50 mL centrifuge tubes where 0.1 g of clay and 25 ml of the above dye solution were added and shaken for 2 h at 27 °C. Absorbance of 10 mg/l was determined at different wavelengths using Shimadzu 2450 UV-visible Spectrometer and obtained plots of absorbance versus wavelength. By conducting batch mode experimental model studies, the efficiency of the adsorbent was evaluated. Specific amount of adsorbent was shaken in 25 ml. The amount of dye adsorbed was calculated by the relationships; Amount adsorbed = (C_i - C_f) m/v, Where, C_i = Initial concentration (mg/l), C_f = Final concentration (mg/l), m = Mass of adsorbent (g) and V is the volume of dye solution (ml). The effect of sintering temperature was studied by sintering the clay samples at 100, 200, 300, 400, 500, 600, 700, 800, 900 °C. These samples were used in conjunction with 25 ml dye (concentration = 85.55 ppm and pH = 6.5, contact time = 120 min, agitation speed = 100 rpm, temperature = 27 °C).

3. RESULTS AND DISCUSSION

The X-ray diffractogram given in Figure 1 shows the existence of both silicate and montmorillonite phases in the clay mineral selected for this study. Further the data obtained in the sintering study is summarized in Table 1. It is observed that the pore size is reduced with the increase of sintering temperature as shown in the table. Figure 2 presents the effect of sintering temperature on the amount of dye adsorbed per unit weight and on dye concentration. As seen with these results, the endothermic peak at 400 °C can be attributed

to the loss of hydroxyl groups from the clay structure. This is the most responsible factor for reduction of adsorption. Above 400 °C, the dehydroxylation happens and that indicates two hydroxyl groups react together to produce one H₂O molecule and an oxygen atom. This also leads to reduce reactive sites in clay surface and minimize the adsorption capacity. After exceeding 550 °C, it can be clearly seen that the adsorption become stable.

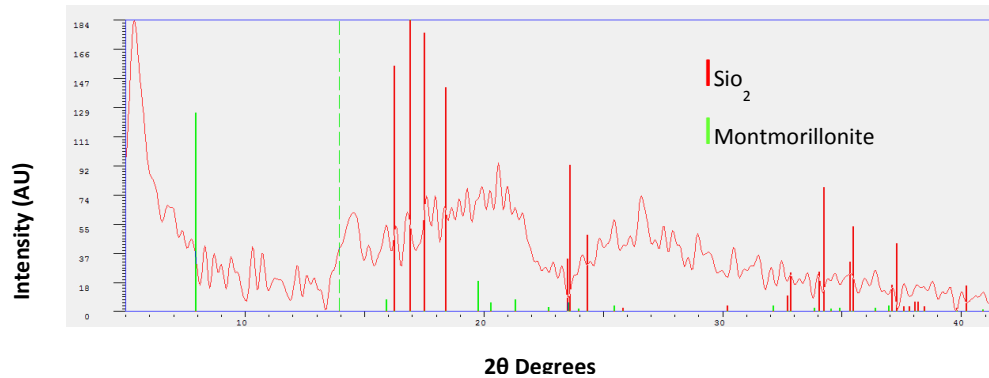


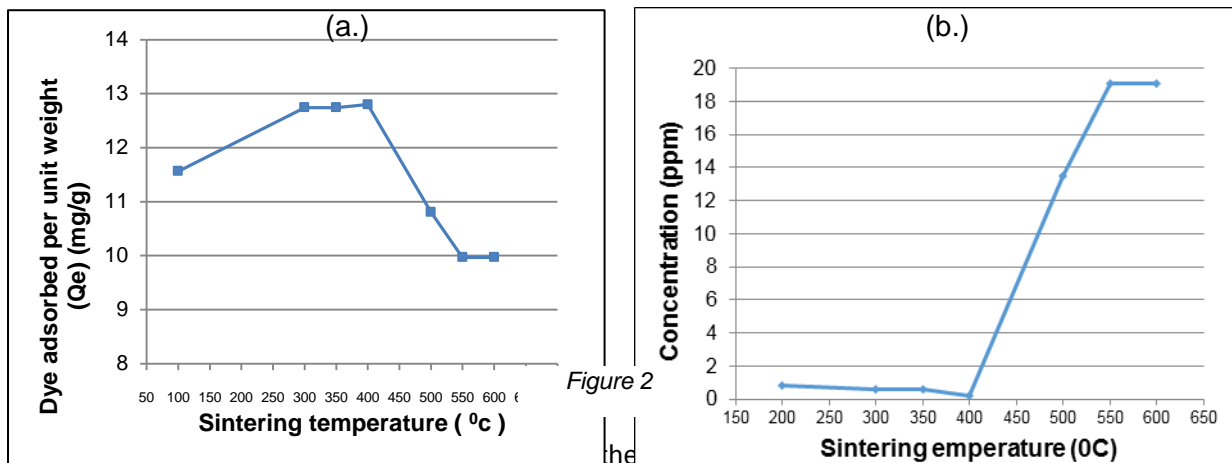
Figure 1

Figure 1 X-ray diffractograms obtained on the selected montmorillonite clay.

Table 1: Data obtained in the sintering study.

Sintering temperature (°C)	Concentration (ppm)	Absorbance (at 660.0 nm wave length)	Remarks
Raw	0.8469	0.1784	85.55 ppm initial solution at 25 °C 6.5 pH initial volume = 15 ml Clay amount = 0.1 g
300	0.596	0.1214	
350	0.5898	0.1200	
400	0.2189	0.0359	
500	13.5192	3.0529	
550	19.097	4.3182	
600	19.097	4.3182	

2.1 Charaterization of sintered clay



Effect of sintering temperature on dye concentration

FTIR spectra shown in figure 3 clearly indicate that O-H stretch and second order H-O-H bend at 3630 cm^{-1} that responsible for water molecules. Aromatic C-H, is responsible for methylene blue aromatic ring hydrogen carbon bond at $900\text{--}670\text{ cm}^{-1}$. Si-O bond, which is at $830\text{--}1110\text{ cm}^{-1}$ can be clearly identified at 1026 cm^{-1} which is revealing the silicate bonds in clay minerals. Aromatic ring stretching vibrations can be seen at $1400\text{--}1600\text{ cm}^{-1}$. Trimethyl or tertbutyl $1395\text{--}1385\text{ cm}^{-1}$ which is significant to MB can be identified at 1393.7 cm^{-1} .

Figure 3. FTIR spectra obtained on raw and dye absorbed clays.

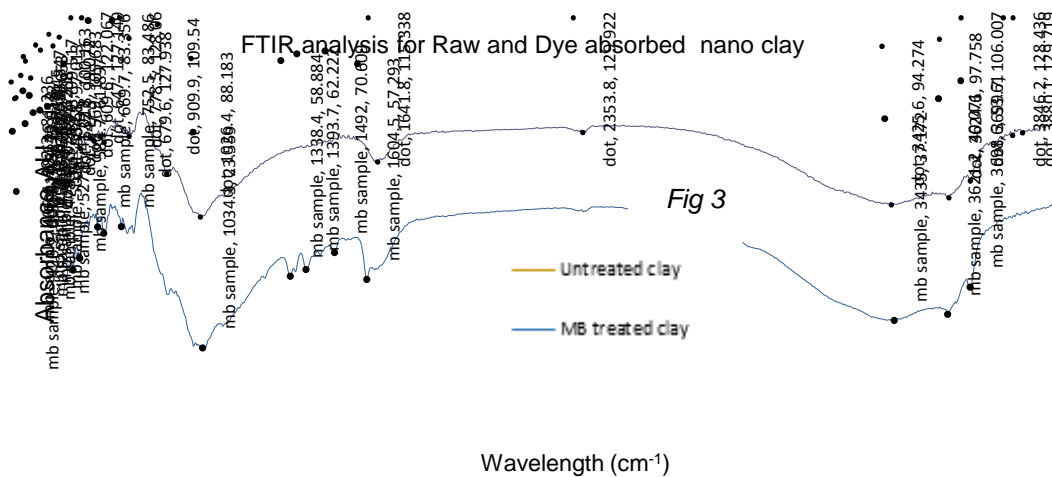


Figure 3

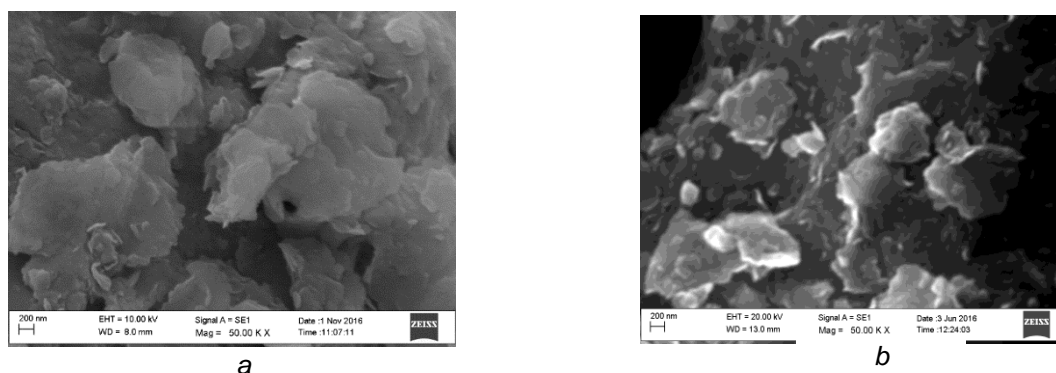


Figure 4. SEM images of clay before (a) and after (b) heat treatment.

The surface morphology of adsorbent was examined by scanning electron microscopy. The surface of natural clay was inspected before and after heat treatment at a higher magnification of 50,000. Figure 4a shows the SEM micrographs obtained on this clay before heat treatment and Figure 4b shows that of after heat treatment. These SEM images of clay before heating show morphology with uneven surfaces and flake-like clay layers. After heat treatment, the surface becomes smooth and can see the reduction of layer structure as in Figure 4b. It clearly indicates that at high temperature there is a tendency of surface area reduction, which may lead to low adsorption capacity.

3. CONCLUSION

The XRD phase analysis confirms the existence of montmorillonite phase in the clay mineral selected for this study. The pore size is reduced with the increase of sintering temperature. The endothermic peak at 400 °C relates to the loss of hydroxyl groups from the clay structure. This can be the responsible factor for reduction of adsorption above 400 °C with the reduction of reactive sites in clay surface and minimizing adsorption capacity. Therefore, this study suggests that the most stable and effective sintering temperature for this clay mineral, for water filtration application, is to be 450 °C. This sintered clay sample showed an adsorption capacity of 12.8 mgg⁻¹ at room temperature.

4. REFERENCES

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