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Study on the Removable of Methylene Blue by Calcined-Kamerotar Clays as an Eco-Friendly Low Cost Adsorbent

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Abstract: *The removable of methylene blue (MB) from aqueous solution by the calcined-Kamerotar bulk clay with & without grinding was studied using Langmuir as well as Freundlich adsorption isotherms at room temperature (301±1 K). The bulk clay sample was collected from the Kamerotar area of Madhyapur Thimi municipality of Bhaktapur, Nepal and was used in the present study composed of vermiculite & muscovite type mica minerals in additions of feldspars and quartz with considerable amounts of iron as well as magnesium oxides. The removable capacity of the MB by the calcined-bulk clay sample at 573 K calcination temperature with and without dry grinding was interpreted using Langmuir and Fruendlich isotherms. The maximum removal efficiency of the MB by the clay sample was observed at pH 7-12. The removable capacity of the calcined-clay sample was increased with dry grinding for 2 hours. The maximum amounts of the MB removed by the modified clay sample using the calcination temperature of 573 K are in the ranges of 15.8-19.5 m mole/g. Present study showed that the dry grinded the calcined-bulk clay has a good potentiality to remove the MB from wastewaters as an eco-friendly low cost adsorbent.*

Keywords: *Adsorption, Methylene blue, Wastewaters, Calcined-clays, Grinding*

1. Introduction

Clay is one of the important materials in the history of human civilization and it becomes the first natural raw materials used for the cultural development of mankind. Clays are fine-grained aluminosilicates layered-structure of mostly monocline or triclinic symmetry which may contain sodium, calcium, potassium, magnesium, iron, titanium and other ions. Two basic structural units are important in the constitution of the clays: tetrahedral structure formed by silicon and oxygen atoms, and octahedral layer formed by aluminium and oxygen atom together with hydroxyl ions. Clays are being used for various purposes from pre-historic times to modern age and they show a large variety of uses and properties that depend on their types, compositions and other factors.

Clay whether common or fine was the main raw materials of ceramic products for more than 16,000 years [1]. Historically, the use of burnt clay, commercial pottery and the existing ceramic industries can be dated back to 14,000 BC, 4000 BC and 1500 BC, respectively [2]. Clays are without doubt the oldest ceramic materials and they exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired at high temperatures in a kiln, permanent physical and chemical reactions occurs which, amongst other changes, causes the clay to be converted into ceramic products. It is because of these properties the clays are mainly used for making pottery items including earthenware, stoneware, porcelains and so on.

In addition, the clay minerals are also used in many industrial processes, such as chemical filtering, paper making and petroleum industries so on. When a small amount of clay is added to water, slurry forms because the clay distributes itself evenly throughout the water. This property of clay mineral is used by the paint industry to disperse pigment (color) evenly throughout paint. Moreover, clay also exhibits medicinal values such as to heal skin infection which is evident since the earliest recorded history. Specific clay minerals proved valuable in the treatment of bacterial diseases, including infections for which there are no effective antibiotics, such as *Buruli ulcer* and multidrug-resistant infections [3]. The most important of these properties are due to the large specific surface areas and the resulting ability to adsorb cations [4]. Therefore, clay minerals are used for large varieties of environmental applications.

Large ratio of internal and external surface areas to volume or fine particles gives clays a set of unique properties for removable of various organic dyes, metals or other environmental pollutants [4]. In addition the ability of these clay particles to adsorb polar and charged chemical species at the external and internal surfaces of clay minerals is a matter of great theoretical and industrial interest. Furthermore, adsorption using inexpensive and easily available adsorbent would make removal of different dyes or metal pollutants from wastewater feasible. The abundance of natural clays of low cost is likely to make them a strong candidate as an adsorbent for the removal of toxic dyes from wastewater and other environments.

Basic dyes, for example methylene blue, are generally more toxic than other classes of dyes [5]. Thus, the removal of basic dyes from the environmental is becoming noteworthy in recent years. Various conventional and non-conventional methods such as physical, chemical, biological and photochemical processes have been tried for the removal of dyes from aquatic environments [6]; [7]; [8]. Adsorption is one of the physical-chemical methods, which is found to be the most simple and economical to remove the dyes from wastewaters. The ability of clays to take up certain organic substances preferentially has been known for a very long time and this is the basis of the wide use of clays for organo-clay interactions studies and the uptake of both basic and the acid dyes on clays has been investigated by various workers for long time [9]; [10]; [11]; [12]; [13]; [14]; [15]; [16].

Despite of many investigations to study adsorption of MB on different types of clays and clay minerals deposited in different parts of the world, clay minerals deposit in Nepal has been studied by a few researchers in the past. Most of the research works were concerned only with physical properties [9]; [10], chemical as well as mineralogical [17]; [18] and geological studies [19]; [20]. Comprehensive studies of ceramic properties of porcelain raw materials deposited in Panchamane (Kathmandu), Daman (Makawanpur) and Deurali (Bhojpur) areas of Nepal were carried out since 1990s [17]; [19]; [20]; [21]; [22]; [23]; [24]; [25];. In recent years, some research groups have studied physical [26]; [27], chemical as well as mineralogical [28] properties of Kamerotar clays deposited in Madhyapur Thimi municipality of Bhaktapur, Nepal. In this context, we aimed to explore the locally available Kamerotar clay minerals for removing dyes from polluted wastewaters. The specific objective of the present research is to study the adsorption behavior of methylene blue, a basic or cationic dyes from aqueous solution onto the modified bulk clay minerals deposited in Kamerotar area of Bhaktapur, Nepal. The modification of Kamerotar clay sample was done by dry grinding for ½ to 2 hours the calcinated-bulk clay sample at 573 K temperature.

2. MATERIALS AND METHODS

2.1 Sampling Site and Sample

The clay sample for the present study was collected from Kamerotar area of Bhaktapur, Nepal. Kamerotar sampling site of Madhyapur Thimi municipality is located within the latitude of 27^{o} 40’ 30”-27^{o} 40’ 50” north and within the longitude of 85^{o} 23’ 40”-85^{o} 24’ 20” east which is shown in Fig. 1. It is accessible either by Araniko highway or Kathmandu-Sanothimi-Bhaktapur road.

The clay sample which is commonly known as ‘*Kamero Maato*’ in Nepali and ‘*Takucha*’ in Newari [28] is being used by local people for various purposes. Mostly, it is used for wall painting to impart white color to soil plastered walls of the traditional local houses. Besides this, it is frequently used for treatment of cuts and wounds in dogs and other pets. It is also believed that it eases the labor pain during the delivery of babies and hence local people have been practicing to feed it to the pregnant women at the time of delivery [28]. These trends seek for the study on medicinal values of ‘*Kamero Mato*’. According to local people it is mixed with kaolinite and other clay minerals for the production of traditional ceramic products

The bulk clay sample was prepared by using US standard sieve, mesh no. 230 (< 63 µm). The organic matter contained in the bulk clay sample was removed by treating with excess amount of 30 % by volume of hydrogen peroxide treatment methods. The bulk clay sample was reported to contain 4.56 % of the organic matter [26]. Kamerotar clay was characterized using chemical, X-ray diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy as well as the thermal analysis. It was reported that the clay is composed mainly the vermiculite and muscovite minerals in addition of feldspars and quartz [26]; [28]. It was also reported that the bulk clay sample of Kamerotar area was contained high amount of silicate and low amount of alumina with considerable amounts of iron, calcium as well as magnesium oxides which is unfavorable composition for the porcelain raw materials [28].

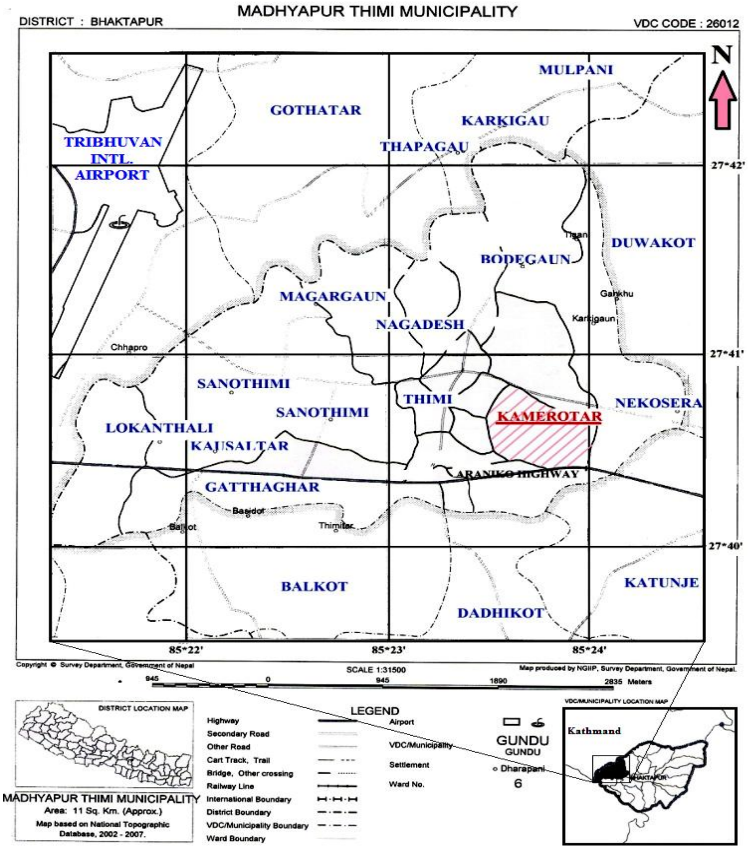

Figure1. *Location map of the clay sampling site*

2.2 Grinding and Calcination of the Bulk Clay

Preparation of the grinded clay specimens was done by dry grinding the bulk clay sample in for different periods of time (i. e., ½ hour, 1 hour and 2 hours) using aluminium mortar and pestle. The grinded clay sample specimens were used to study adsorption of methylene blue. Preparation of the calcined clay sample specimens from the bulk clay sample was done by heating the sample in muffle furnace for 8 hours at different temperatures of 473 K, 573 K, 673 K, 773 K, 873 K and 1073 K. After calcination, the calcined-bulk clay sample at 573K grinded for different grinding times of ½ hour, 1 hour and 2 hours using aluminium mortar and pestle in dry condition. The grinded calcined-clay sample was used to study removable capacity of methylene blue from aqueous solution at room temperature using batch technique.

2.3 Adsorption Study

The concentrations of 25, 30, 35, 40, 45, 50 and 55 m mole/L of methylene blue were prepared in 250 ml volumetric flask using distilled water. The pH of methylene blue solution was adjusted from 2 to 12 by using 0.1 M NaOH and 0.1 M HCl solutions. Buffer solutions of pH 4, pH 7 and pH 9.2 were used to calibrate the pH-meter. For batch adsorption studies, 100 mg of clay sample was mixed with 50 mL of corresponding MB solutions adjusting the initial pH at 7 and equilibrated in a 100 mL polystyrene vessel, as a maximum adsorption of MB was confirmed in these conditions [27]. The vessel was shaken for 2 h using a shaker at room temperature and was left for 20 hours to attain equilibrium. The equilibrium concentration of MB solution was determined using UV-visible spectrophotometer at 665 nm, after centrifuging the clay-MB mixtures. The amount of MB adsorbed onto unit mass of adsorbent (i.e., Kamerotar) was calculated from the mass balance equation given by equation (1). The $C_t = C_e$ and $Q_t = Q_e$ at equilibrium, then the mass balance equation takes the form of equation (2) given below.

$$Q_t = \frac{(C_o - C_t) \times V}{m} \tag{1}$$

$$Q_e = \frac{(C_o - C_e) \times V}{m} \tag{2}$$

where, Q_t is the amount of MB uptake per unit mass of adsorbent (m mole/g) at time 't'. C_o and C_t are the MB concentrations in liquid phase (m mole/L) initially and at time t, respectively. V is the volume of the test solution of MB in liter and m is the mass of the dry adsorbent in gram.

The percentage removal of MB (A %) from the aqueous solution was calculated using following relation (3):

$$A\ \% = \frac{C_o - C_t}{C_o} \times 100 \tag{3}$$

Further experiment was performed at different initial pH values ranging from 2 to 12 at interval of 1 pH unit to study the effect of initial pH on removal of MB. An optimum pH of 7 was selected for further adsorption study. The effect of contact time was studied at optimum pH 7. The sample of clay-MB suspension was shaken for different interval of time from 10 to 140 minutes and the suspension was kept for 20 hours. Then the clay-MB suspension was decanted and separated using centrifugal machine and was analyzed for MB equilibrium concentration. The effect of calcination was studied by heating the bulk clay sample to different temperature starting from 473 K to 1073 K and the calcined-clay sample at 573 K was used to study the adsorption behavior. Langmuir (equations 4 & 5) and Freundlich (equations 6 & 7) adsorption equations were applied to evaluate the maximum methylene blue removable capacity of clay samples in this study.

$$Q_e = \frac{Q_{max} b C_e}{(1 + bC_e)} \tag{4}$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}.b} \tag{5}$$

$$Q_e = K_F C_e^{1/n} \tag{6}$$

$$\log Q_e = \log K_F + 1/n \log C_e \tag{7}$$

Where, Q_e (m mole/g) is the amount of adsorption of methylene blue per gram; C_e (m mole/L) is the equilibrium concentration of MB after adsorption, Q_{max} (m mole/g) is the maximum adsorption capacity, b (L/m mole) is the adsorption energy, K_F and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

3. Results and Discussion

3.1 Effects of pH, Grinding Time and Calcination Temperature

In order to evaluate the effect of initial pH on removal of methylene blue from aqueous solution by the calcined-bulk clay sample, several experiments were performed at different initial pH values from 2 to 12 at room temperature (i.e., 301 K). Figure 2 shows that the MB removal efficiency by the Kamerotar bulk clay. It is increased with increasing initial pH and reaches maximum value at about pH 7 and it remained steady up to 12 pH. Hence the optimal pH for MB removal by clay sample was selected at 7 in all other experiments in this study.

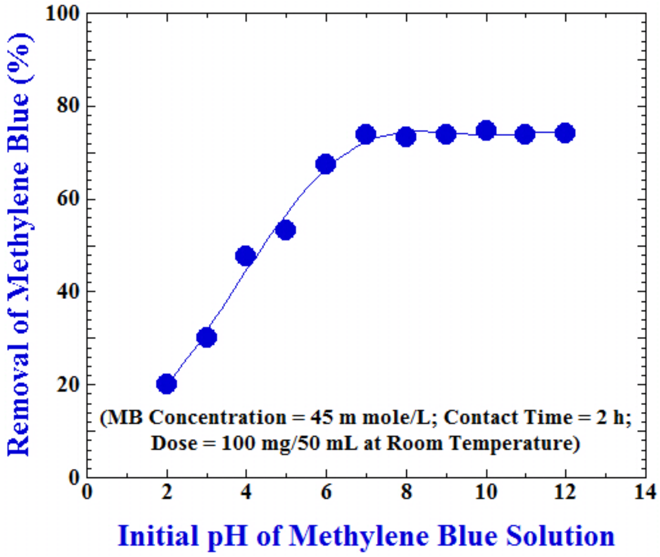

Figure2. *Effect of Initial Ph on the Removal of MB by the Bulk Clay Sample*

Figure 3 shows the removal percentage of the methylene blue by different clay sample specimens prepared after calcination of the bulk clay at different temperatures as a function of calcination temperature and grinding time at the given conditions. Removable amounts of MB by the clay samples significantly decreased with increasing calcination temperature at 573 K or high. This result revealed that the adsorption capacity of the clay sample is decreased with increasing the calcination temperature, probably due to the dehyroxylation of water molecules from the interlayer structure of the clay particles. In this context, present work is focused to increase BM removable capacity by grinding the calcined-bulk clay sample at the calcination temperature of 573 K.

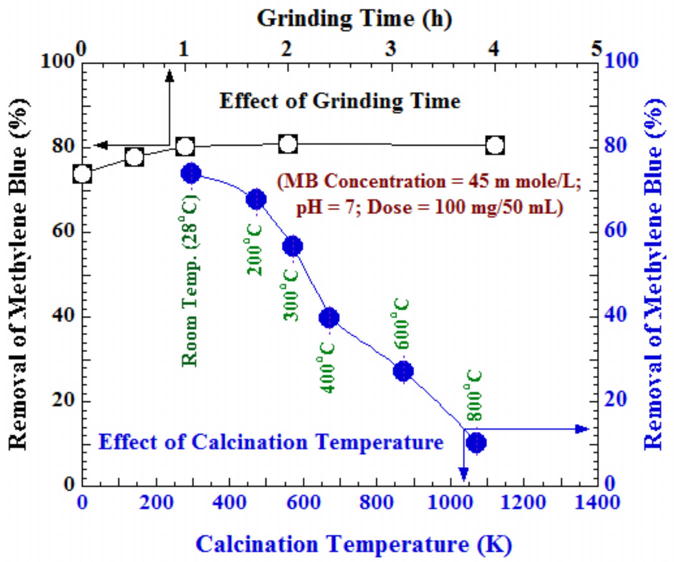

Figure3. *Effects of Grinding Time & Calcination Temperature on the Removal of MB*

3.2 Batch Adsorption Studies

To study the removable of MB by clay samples, Langmuir and Freundlich models were applied. Figure 4 shows the adsorption isotherm for the removable of MB by the calcined-bulk clay samples at the calcination temperature of 573 K without grinding and after dry grinding for ½ h, 1 h and 2 h at the given conditions. The result revealed that the removable capacity of MB from aqueous solution by the calcined-bulk clay sample at the calcination temperature of 573 K is significantly increased with dry grinding time up to 2 h and the removable capacity of the calcined-bulk clay sample after calcination at 573 K with dry grinding was almost same value as that for the bulk clay sample without calcination. Consequently, it can be said that the MB removable capacity of the calcined-clay minerals consisting mostly of vermiculite is decreased may be due to the decrease of internal surface areas of the vermiculite mineral for adsorption with calcination temperature and also increased the external surfaces of the clay minerals with increasing the grinding times.

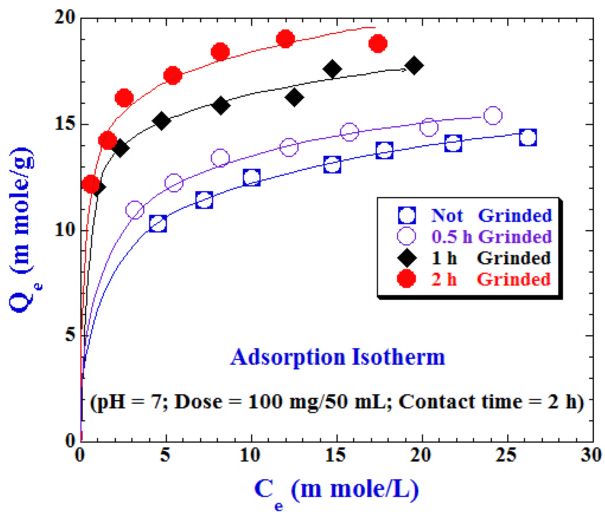

Figure4. *Adsorption isotherms for the removal of methylene blue by the calcined-bulk clay sample at the calcination temperature of 573 K and after dry grinding for different time periods*

Adsorption isotherms were evaluated using the linearized Langmuir and Freundlich isotherm equations (5) and (7), respectively, as mentioned. The Langmuir constants (i.e., Q_{max} and b) and Freundlich constants (K_F and n) were calculated from the linear plots of C_e / Q_e versus C_e as shown in Figs 5 and 6, respectively. The Langmuir and Freundlich constants and their linear coefficient of determination (R^2) were evaluated from the isotherm equations for differently treated clay samples are summarized in Table 1. The linear plots show that the removable of MB by the calcined-bulk clay specimens obeys both the Langmuir and Freundlich adsorption models. The high value of the linear coefficient of determination (i.e., R^2 = 0.9966 to 0.9995) as shown in Fig. 5 confirmed that the Langmuir isotherm is best fitted than the Freundlich isotherm. The linear correlation coefficient for Freundlich isotherm was found in the range of 0.9454-0.9853 as shown Fig. 6 and also summarized in Table 1.

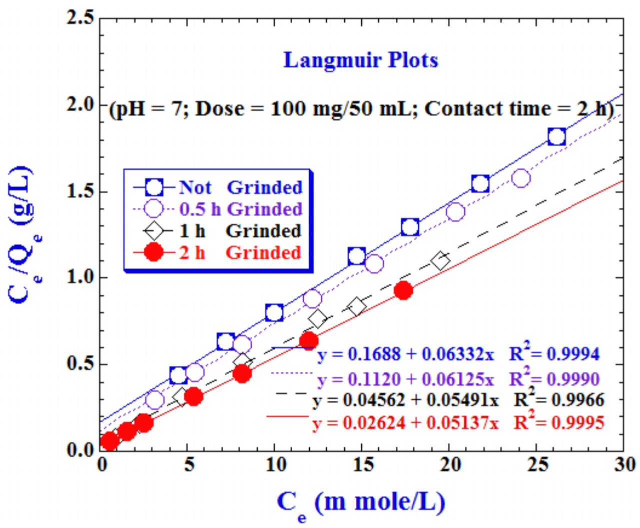

Figure5. *Langmuir plots for the removal of methylene blue by the calcined-bulk clay samples at the calcination temperature of 573 K and after dry grinding for different time periods*

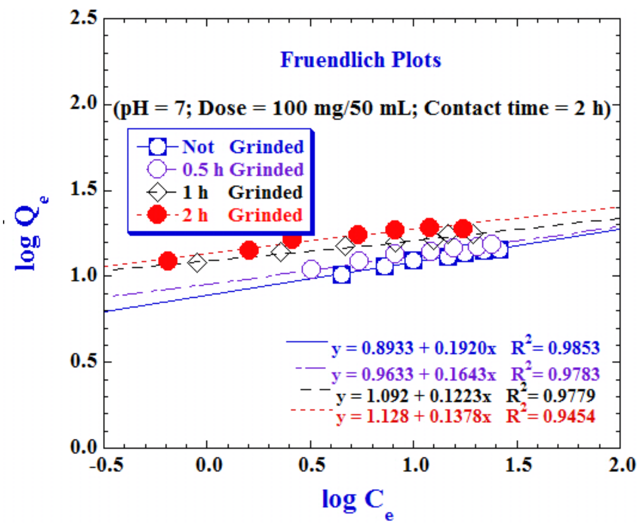

Figure6. *Freundlich plots for the removal of methylene blue by the calcined-bulk clay samples at the calcination temperature of 573 K and after dry grinding for different time periods*

Table1. *Langmuir & Freundlich constants for the removable MB by the calcined-bulk clay samples with and without dry grinding for different periods*

	Langmuir Constants			Freundlich Constants		
Modified Clays	Q_{max}	b	R^2	K_F	n	R^2
Bulk clay with dry grinding for 2 h [27]	19.47	3.2507	0.9977	15.10	10.87	0.9338
Calcinated at 573 K without grinding	15.79	0.3752	0.9994	7.82	5.21	0.9853
Calcinated at 573 K+dry grinding for ½ h	16.33	0.5468	0.9990	9.19	6.09	0.9783
Calcinated at 573 K+dry grinding for 1 h	18.21	1.2037	0.9966	12.36	8.18	0.9779
Calcinated at 573 K+dry grinding for 2 h	19.47	1.9574	0.9995	13.43	7.26	0.9454

The Q_{max} (maximum adsorption capacity) value for the removable of MB by the calcined- bulk clay sample at the calcination temperature of 573 K without grinding and after grinding for different times is in the range of 15.79 to 19.47 m mole/g using Langmuir model as summarized in Table 1 which is almost in the same range of Q_{max} value for the bulk clay sample without calcination [27]. On the other hand, the energy of adsorption (i.e., b) for trapping the MB by the calcinated-bulk clay sample without grinding and after grinding for different periods was found to be increased with dry grinding time as tabulated in Table 1. The Freundlich constants K_F and 1/n are related to the adsorption capacity and adsorption intensity, respectively. In the present study, the value of 1/n was found to be less than 1 which suggests the favorable adsorption behavior of MB onto the calcined-bulk clay sample at 573 K calcination temperature.

4. CONCLUSIONS

The bulk clay deposited in Kamerotar area of Bhaktapur district consisting of vermiculite, muscovite with admixtures of feldspars as well as quartz, was used to study the effect of the dry grinding in the calcined-bulk clay sample to remove the methylene blue from aqueous solution using Langmuir and Freundlich isotherms. The removable capacity of MB by the calcined-bulk clay sample at 573 K calcination temperature was increased with dry grinding which concluded that the adsorption capacity of the bulk clay can be improved by dry grinding of the calcined-Kamerotar bulk clay sample. Therefore, the clay sample from Kamerotar area of Bhaktapur with some modification like grinding can be used as an eco-friendly low cost adsorbent to removal the MB for the wastewater treatment to control the pollution problems created by dying industries.

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