

## Removal of Crystal Violet and Methylene Blue from Aqueous Solution using Soil Nano-Clays

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**Abstract**—This Environmental soil nano-clays are found in the pedosphere and their biogeochemical and ecological impacts are some of the fastest growing areas of research today. This study uses low-cost readily available soil nano-clays (particle size < 100 nm) to remove two different toxic cationic dyes, crystal violet (CV) and methylene blue (MB), from aqueous medium. The soil clays were characterized by measuring the BET surface area and XRD analysis. The adsorption of CV and MB dyes onto the soil clays was studied under different experimental conditions. Based on a kinetics study, dye adsorption on the soil clays could be separated into fast and slow reactions. The soil nano-clays adsorb both CV and MB dyes efficiently and could be employed as a low-cost alternative to remove cationic dyes in wastewater treatment.

**Keywords**—crystal violet; dyes; methylene blue; nanotechnology; nano-clay

### I. INTRODUCTION

Many industries, such as textile, dyestuff manufacturing, leather tanning, food preparation, paper production, and printing, use dyes that produce highly colored waste effluents. These dyes can consume the dissolved oxygen required by aquatic life and some of them are directly toxic to microbial populations and can even be carcinogenic to mammals.<sup>1</sup> In addition, dyes are resistant to light and moderate oxidative agents, so they cannot be completely removed by conventional biological treatment processes, such as activated sludge or anaerobic digestion.<sup>2</sup>

A wide range of methods has been developed and used for the removal of dye contaminants from wastewater. These technologies involve adsorption on inorganic matrices, decolorization by photocatalysis and/or oxidation, microbiological or enzymatic decomposition, and so on.<sup>3</sup> Adsorption has been recognized as the most popular treatment process for the removal of non-biodegradable organics from aqueous systems, with activated carbons being the most common adsorbent for this process because of their effectiveness and versatility.<sup>4</sup> However, the use of this type of adsorbent in wastewater treatment is still limited because of its high cost and difficulty in regeneration.<sup>5</sup>

In recent years, the use of soil clay materials to replace commercially available adsorbents has become popular because of their low cost, ready availability, lack of toxicity,

and potential for ion exchange.<sup>6</sup> Their unique properties, such as a high specific surface area and surface chemistry for example, give these materials a broad range of applications.<sup>7</sup> Naturally occurring clays have shown good results as adsorbents for the removal of various metals, organic compounds, and dyes.

Over the past two to three decades, nanoparticle research and development has brought about significant breakthroughs in many areas of basic and applied sciences.<sup>8</sup> In particular, nanoparticles smaller than 100 nm are important in natural systems because of their high surface area and surface reactivity and their associated properties of adsorbing or binding to organic and trace metal contaminants. However, collecting nanoparticles with high efficiency and in large quantities from either pure or natural systems is a challenge in nanoscience. In this study, we attempt to use nanotechnology (automated ultrafiltration device, AUD)<sup>9</sup> [United States Patent No. 7,501,063 B2] to collect soil nano-clay (< 100 nm) as an ecologically friendly alternative low-cost sorbent for the removal of cationic dyes from aqueous solutions.

This work examines the feasibility and efficiency of using soil nano-clay to remove cationic dyes from wastewater by measuring the adsorption data of crystal violet and methylene blue on soil nano-clays. Changes to the surface and structure of clays were characterized based on the analysis of the nitrogen isotherms and X-ray diffraction (XRD) analysis. The adsorption processes with respect to contact time, adsorbent dose, adsorbate concentrations, pH, ionic strength, and temperature were measured to provide more information about the adsorption characteristics of nano-clays. The equilibrium data were fitted into a Langmuir equation to determine the correlation between the isotherm models and experimental data.

### II. MATERIAL AND METHODS

#### A. Sampling

The black soil used was obtained from the Taitung Prefecture of eastern Taiwan (Shi-yu-san, SYS) and the low elevation of sample sites were between latitudes 23 ° 02'20''N to 23 ° 51'47''N and longitudes 121 ° 11'27''E to 121 ° 32'52''E.<sup>10</sup> In addition, the collected suspension (< 100

nm size fraction) was filtered by the AUD, using the Sigma ultrafiltration disk membrane to collect the size fraction of 1 – 100 nm. Details concerning the separation and collection of various particle-size fractions have been reported previously.<sup>13</sup>

### B. Characterization techniques

Samples of solid phase were analyzed by surface area, and XRD. Specific surface area analysis: samples of soil clays (< 2,000 nm and < 100 nm) were measured by the Brunauer-Emmett-Teller (BET) equation with a Nova 2000 analyzer.

### C. Adsorption studies

The adsorption of basic dyes onto the soil clays (i.e., < 2,000 and < 100 nm) was investigated in a batch system. Equilibrium experiments were carried out by containing 50 mg of clays with 50 mL of MB and CV solution of different initial concentrations (0.02 to 0.5 mM). A series of conical flasks was then shaken at a constant speed of 150 rpm in a shaking water bath. After 2 h, aliquots of 0.1 mL were withdrawn from the solutions, diluted, and centrifuged for 10 min at 12,000 rpm, and the absorbance of the supernatant solution was measured. The concentration of CV and MB were detected by a UV-vis spectrophotometer at the wavelengths of 590 and 665 nm, respectively. The data obtained in the batch mode studies were used to calculate the equilibrium dyes adsorption amount.

The effect of pH on the amount of dye removal was studied over the pH range from 4 to 9 for both dyes at 298 K. To optimize the solid/liquid ratio ( $\text{g L}^{-1}$ ) in terms of cost effect, batch experiments were conducted using different amounts of soil clays (< 2,000 nm and < 100 nm) between 0.05 and 0.20 g at pH 5. Sodium chloride (NaCl) was employed as a background electrolyte that varied between 0.01 and 0.2 mmole  $\text{L}^{-1}$  to investigate the influence of ionic strength on the dye removal. Kinetic experiments of dye adsorption on soil clays were conducted at four temperatures (i.e., 278, 288, 298 and 308 K) with 0.1 mmole  $\text{L}^{-1}$  of dye at pH 5 and monitored with a pH-stat. Adsorption data were fitted by the kinetic models, including zero-order, first-order, and second-order equations, and empirical models, such as two-constant, parabolic diffusion, and the Elovich equations.

## III. RESULTS AND DISCUSSION

### A. Characterization of the soil clays

Analyses by  $\text{N}_2$  adsorption/desorption presented specific surface areas of 22.1 and 87.3  $\text{m}^2 \text{g}^{-1}$  for the soil clays (< 2,000 nm) and soil nano-clays (< 100 nm), respectively. It can be clearly observed that the soil nano-clays (< 100 nm) have an X-ray poor crystalline structure of smectite materials ( $d = 1.25 \text{ nm}$ ). By contrast, the soil clay (< 2,000 nm) mineralogy showed that smectite ( $d = 1.26 \text{ nm}$ ), kaolinite ( $d = 0.72 \text{ nm}$ ), and quartz ( $d = 0.34 \text{ nm}$ ) are dominant in the black soil clays. The soil smectite was also characterized by XRD analysis with a saturation of Mg and glycerol salvation,

showing the expansion of 1.70 nm reflection peak in XRD analysis.<sup>14</sup>

### B. Effect of contact time

The amount of dyes adsorbed on soil clays increased with the increasing reaction time (Figure 1). The sequence of adsorption amount was: MB (< 100 nm soil clay, 80.77 to 113.13  $\text{mmol kg}^{-1}$ ) > MB (< 2,000 nm soil clay, 74.02 to 103.68  $\text{mmol kg}^{-1}$ ) > CV (< 100 nm soil clay, 67.13 to 94.14  $\text{mmol kg}^{-1}$ ) > CV (< 2,000 nm soil clay, 24.75 to 38.72  $\text{mmol kg}^{-1}$ ). Generally, the rate of dye adsorption in soil clays was speedy within the 0-30 min of the reaction period (fast reaction) and was relatively slow after 30 min (slow reaction), demonstrating that dye adsorption consists of multiple rate processes. This result is in agreement with Venkatraman Sethuraman and Raymahashay. By contrast, the adsorption amount was enhanced by using clay of a soil nanoparticle size.

### C. Effect of temperature on the adsorption amount

The amounts of CV and MB dyes adsorbed on each adsorbent increased with the increasing temperature of adsorption (Figure 2). This is because the diffusion of CV and MB molecules dyes in the aqueous phase is gradually faster with an increased temperature of adsorption and this thereby promotes the exchange interaction between the dye molecules and cations on the soil clay surface. Moreover, a similarly increasing degree in the amount of dyes adsorbed on each adsorbent was observed with an increasing temperature, suggesting that temperature has a similar influence on the adsorption amount of the soil clay (< 2,000 nm) (CV for 37.50 to 60.05 and MB for 98.28 to 117.89  $\text{mmol kg}^{-1}$ ) and soil clay (< 100 nm) (CV for 120.88 to 146.29 and MB for 201.39 to 224.12  $\text{mmol kg}^{-1}$ ).

## IV. CONCLUSIONS

The AUD (nano-technology) apparatus can be used to efficiently collect large quantities of soil and related environmental nano-particles to investigate the nanoscale, structural characteristics, and surface properties of these particles. In this study, the removal of CV and MB dyes from the aqueous solution was investigated using soil nano-clays. It was experimentally concluded that soil nano-clays could be used as low-cost and relatively effective adsorbents for the removal of CV and MB basic dyes from wastewater. Soil nano-clays have greater adsorption amount compared with untreated soil clay minerals (< 2,000 nm) because of the increased surface area and greater pore volume. The maximum CV and MB adsorption amount of soil nano-clays are about two to three times higher than those of soil clays (< 2,000 nm). Thus, soil nano-clays can be recommended as a friendly sorbent for CV and MB removal.

### ACKNOWLEDGMENT

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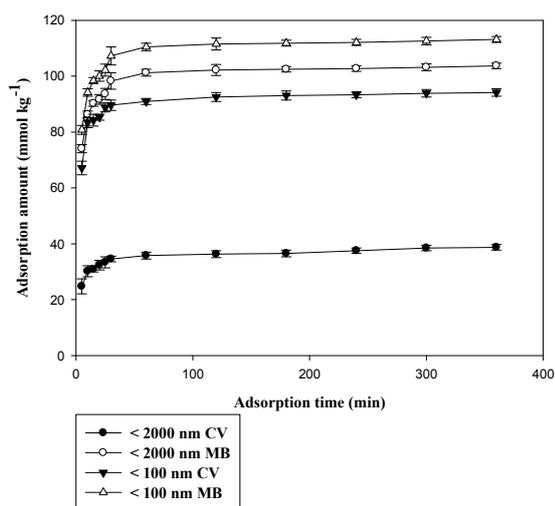


Figure 1. Equilibrium adsorption times of CV and MB dyes onto the clays.

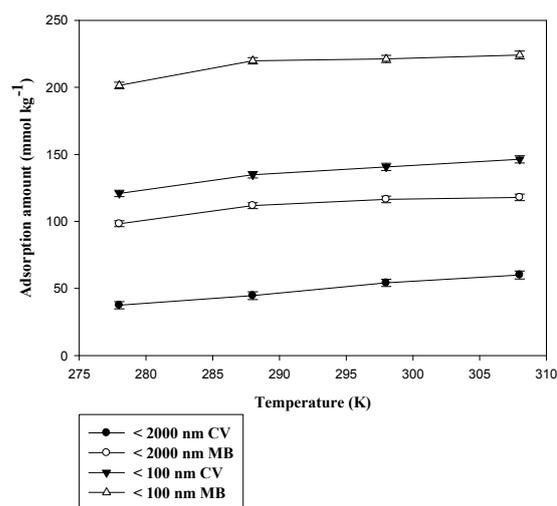


Figure 2. Effect of temperature on the adsorption of MB and CV to the clays.