

Bentonite Clay Adsorption Affinity for Anionic and Cationic Dyes

Elvis Fosso-Kankeu, Frans Waanders, and Corinne Fraser

Abstract—The incidence of dye pollution in South Africa is quite alarming, requesting effective and affordable techniques to curb further degradation of the limited water resource. Adsorption is an attractive technique due to a better removal efficiency of contaminants. Bentonite also known as montmorillonite clay, has a very large surface area, suitable for adsorption; however the availability of binding sites on the clay is dependent on the geochemical transformation undergone during the genesis, making the geographical source of the clay an important parameter determining his adsorption potential. This consideration has motivated the need to test the adsorption potential of local bentonite clay for the removal of anionic and cationic dye from solution. The clay was characterized using XRD, XRF and FTIR. The adsorption affinity was tested using isotherm and kinetic models. According to the FTIR spectroscopy profile, dyes attached to the clay through interaction between the cetonyl group of the clay and the amines-primary and -secondary functional groups of methyl orange (MO) and methylene blue (MB) respectively. The adsorption capacity values obtained from the pseudo-second order kinetic model indicate that our bentonite clay has higher affinity for MB ($q_e = 147.06$ mg/g) than MO ($q_e = 11.82$ mg/g). It therefore ensues that our clay is suitable for the removal of MB from polluted water, but will require activation to improve the affinity for MO.

Keywords—Cationic- and anionic-dyes, dye removal, adsorption affinity, bentonite clay

I. INTRODUCTION

THOUSANDS of dyes are reported to contaminate surface waters around the world. Most of these dyes are from paper, leather tanning, food and textile industries [1]. The occurrence of dyes in surface waters causes ecological problems, affecting the health of humans who may drink the untreated water. Dye removal from unclean water is a requirement to increase the quantity of usable water and to improve the living quality of humans over the world.

There are ecological and cost related challenges with regard to the treatment of dye polluted wastewater using conventional techniques. These techniques or paths that are usually followed to clean the wastewater include reverse

osmosis, ultrafiltration, oxidation, chlorination, biological treatment, sedimentation, precipitation and many more [2, 3]. Among the different approaches investigated for wastewater treatment over the years, adsorption seems to be a more favourable technique due to a better removal efficiency of contaminants.

Adsorbents such as activated carbon are mainly used, because of their high removal efficiency [4], but the use of activated carbon is costly, hence the need to explore alternative adsorbents that are more affordable [2]. Bentonite, also known as montmorillonite clay, is an affordable adsorbent clay and readily available in various countries [5] including South Africa. Bentonite has favourable properties that make it a more suitable adsorbent, which include a greater surface area; high plasticity and bentonite can swell numerous times in comparison to its original size [6]. However dyes such as methylene blue and methyl orange exhibit different chemical and physical characteristics, which can determine their interactions with any adsorbent.

In this study the affinity and the suitability of bentonite clay from the North West Province as adsorbent for the removal of these dyes from solution will be investigated..

II. METHODOLOGY

A. Materials

Bentonite clay was used during the course of the experiments. The raw clay was ground using a mortar and pestle, then the powder was sieved. The various desired particle sizes were: -212 μm ; -150 μm ; -106 μm and -75 μm , which were sieved out from the initial ground sample. The two dyes used during the investigation were methylene blue (MB) and methyl orange (MO). The corresponding wave lengths were obtained from a previous study (Fosso-Kankeu and Simelane, 2013) performed on these dyes and was determined to be 663nm and 470 nm. This information was used in the calibration process of the spectrophotometer to determine the amount of dye adsorbed.

B. Characterization of the clay

The mineralogical composition of the clay was determined through X-ray diffractometer (XRD); The diffractometer used was the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017°. The elemental composition of the clay was

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determined using the X-ray fluorometer (XRF) which was performed on the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland); a rhodium(Rh) anode was used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

The ATR-FTIR (Perkin-Elmer Spectrum 100 spectrometer) to ascertain the different functional groups of the clay in the spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} .

C. Dye adsorption

The adsorption experiment was carried out in the batch system; bentonite was added to 100 ml of synthetic solution of dyes and mixed on an orbital shaker at 160 rpm. Four parameters were considered to assess the adsorption capacity of the bentonite clay; these included the adsorbent particle size (-212 μm ; -150 μm ; -106 μm and -75 μm), adsorbent dosage (0.05 g, 0.1 g, 0.15 g, 0.3 g), initial dye concentrations (10 mg/L, 20 mg/L, 30 mg/L, 50 mg/L, 75 mg/L, 100 mg/L) and contact time (5 min, 10 min, 20 min, 30 min, 60 min, 100 min) of the clay with the dye solutions.

D. Isotherm and kinetic models

Langmuir and Freundlich isotherms were used to determine the adsorption affinity of the bentonite clay for the dyes: The linear expression of the Langmuir model is as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (1)$$

where: C_e is the dyes' equilibrium constant in (mg/L), q_e is the amount of adsorped dye at equilibrium in (mg/g), q_m is a Langmuir constant associated with the adsorption capacity in (mg/g), b is a Langmuir constant associated with the energy releasing during adsorption in (L/mg)

The linear expression of the Freundlich model is as follow:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (2)$$

where: q_e is the concentration of the dye at equilibrium in its solid form (mg/g), C_e is the concentration of the dye at equilibrium in the solution (mg/L), k_f is the adsorption capacity measured (mg/g), n is the intensity of adsorption

The pseudo-first order is expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where: q_e is the adsorped amount of dye at equilibrium in (mg/g), q_t is the adsorped amount of dye at a certain time t (mg/g), k_1 is the rate constant for the first order adsorption in (min^{-1})

The pseudo-second order can be described by the following

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

equation: where: q_e is the adsorped amount of dye at equilibrium in (mg/g), q_t is the adsorped amount of dye at a certain time t (mg/g), k_2 is the rate constant for the second order adsorption in ($\text{g/mg} \cdot \text{min}^{-1}$)

III. RESULTS AND DISCUSSION

A. Mineralogical and elemental composition of the clay

The X-ray diffraction of the clay allows identifying the phase composition and as expected the bentonite fraction was dominant, representing more than 63% of the clay which also contained quartz and kaolinite.

TABLE I
XRD RESULTS PERFORMED ON RAW BENTONITE CLAY

Phase name	Figure of merit
Quartz	0.533
Bentonite	3.229
Montmorillonite	3.205
Kaolinite	3.335

The elemental composition was determined through X-ray fluorescence analysis; alongside alumina and silicate generally found in alluminosilicates, elements such as Na, Mg, Ca, Cl, Mn, Fe and Ti were dominants and possibly poisoning the binding sites.

B. Binding sites on the clay

Infrared spectra of the raw bentonite and the loaded bentonite are shown in Figure 1.

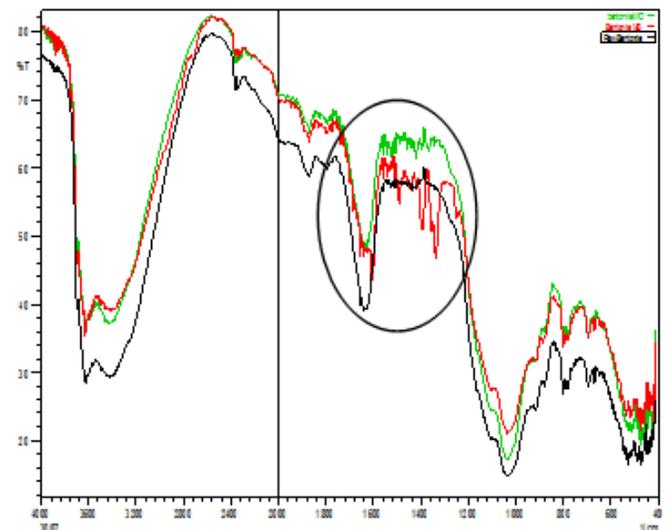


Fig 1 FT-IR analyses for raw bentonite, bentonite loaded with MB and bentonite loaded with MO

It can be observed that the pattern of the spectra differ for the loaded and the raw bentonite, especially in the region 1700 – 1200 where changes of certain bands can be observed. In this region interaction can occur between the cetonyl group of the clay and the amines-primary and secondary functional group of methyl orange and methylene blue respectively; however it can be observed that the changes is most pronounced in clay loaded with methylene blue, implying a higher affinity of the bentonite clay for the latter.

C. Clay adsorption behavior

To determine the adsorption behavior of the clay, the Langmuir isotherm model was applied for the analysis of data [7] and the plot between C_e/q_e and C_e is shown in Figures 2a and 2b for the adsorption of MB and MO respectively, with

the values of q_m and k presented in Table 1. The values were calculated from the slope and intercept of the line with the y-axis of the plot. From Figures 2a and 2b it is clear that the graphs exhibit different patterns with the line for the adsorption of MB having a positive slope while the line for the adsorption of MO has a negative slope. The R^2 value obtained from the fit of the data to the theory for the adsorption of MB was much better than for the case of the adsorption of MO, implying that the Langmuir model was suitable only for the prediction of the adsorption of MB on the clay, which therefore bind at the surface; the parameters determined are shown in Table 1.

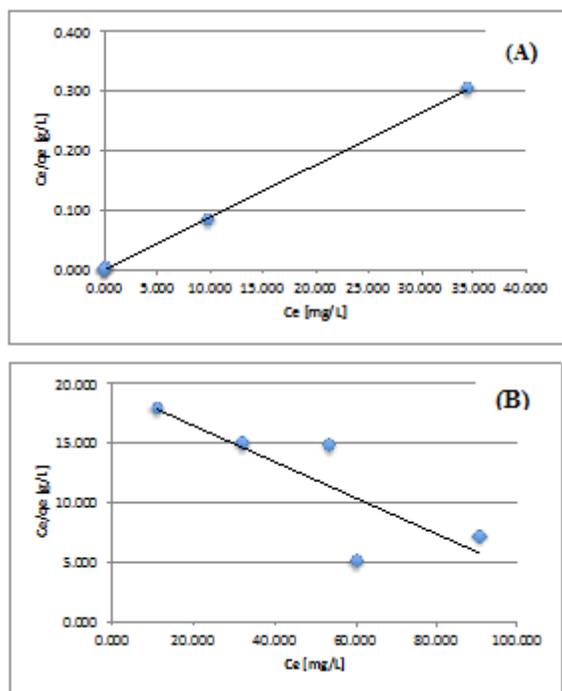


Fig 2 Fit of Langmuir isotherm data for the adsorption of (A) MB and (B) MO onto bentonite clay

The pseudo-first order model did not fit the description of data for the adsorption of methyl orange and was therefore not suitable to compare the potential of both dyes.

The pseudo-second order model is widely used [8] and was applied for the kinetic study of the adsorption of the dyes on the clay. The plot of t/qt vs. t shows an acceptable fit for the adsorption of both MB and MO onto the clay as indicated by Figures 3a and 3b, with results shown in Table 1.

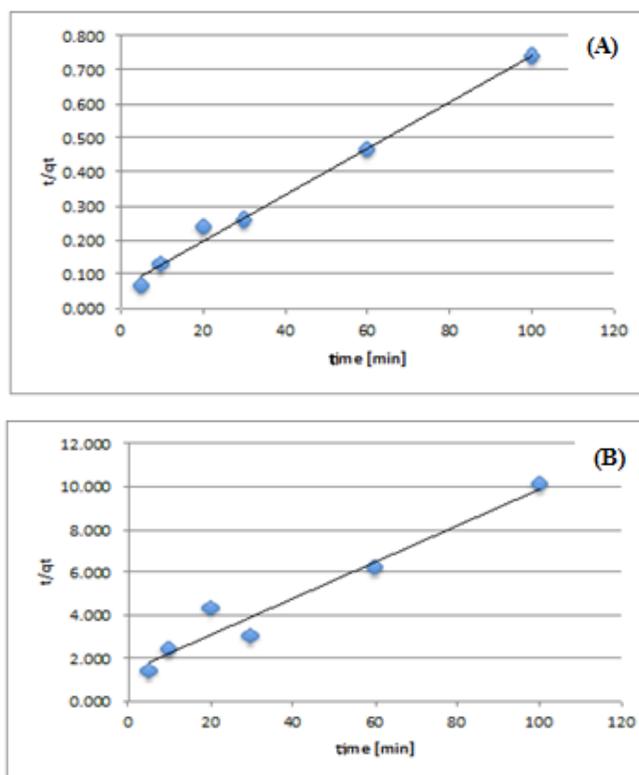


Fig 3 Pseudo second order kinetic plots for (A) the adsorption of MB and (B) MO

It can be observed that the adsorption capacity of MB ($q_e = 147.059$ mg/g) is very high compared to that of MO (11.82 mg/g) which clearly implies that the bentonite clay has more affinity for the MB dye. Previous studies have reported similar trends when adsorbing cationic and anionic dyes onto clays [9, 10] where the electrostatic force contributes to the interaction between clay and dye. It therefore ensues that the negative net charge of the bentonite clay is suitable for the attraction of a cationic dye such as methylene blue (MB).

TABLE II
ISOTHERM AND KINETIC PARAMETERS FOR THE ADSORPTION OF MB AND MO ONTO BENTONITE CLAY

Model	Parameters	MB	MO
Langmuir	q_m	113.636	NF
	k	-29.333	NF
	R^2	0.999	0.6598
Pseudo first order	k_1	0.036	NF
	q_e	81.096	NF
	R^2	0.978	0.6254
Pseudo second order	$k_2 \times 10^{-2}$	0.077	0.517
	q_e	147.059	11.820
	R^2	0.991	0.947

NF: no fit

IV. CONCLUSION

The adsorption affinity of the local bentonite clay for the cationic and anionic dyes has been successfully assessed using the pseudo second order kinetic and it was found that the specific bentonite clay is suitable for the removal of methylene blue from solution. The relative high adsorption capacity of the clay indicates that it can be effectively used in a treatment plant for the restoration of the water quality.

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