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Evaluation of adsorptive capacity of natural and burnt kaolinitic clay for removal of congo red dye

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ABSTRACT

The performance of natural and burnt kaolinitic clay were studied to evaluate their capacities for the removal of a reactive dye [Congo Red: sodium 3, 3'-(1E, 1E)-biphenyl-4, 4'-diylbis(diazene-2,1-diyl)bis(4-aminonaphthalene-1-sulphonate)] from aqueous solution at room temperature (25°C) via batch adsorption. The effect of pH, adsorbent dosage and contact time on the removal of Congo red dye from aqueous solution was also investigated. The concentration of the dye in the solution at equilibrium was determined by spectrophotometry. The equilibrium data seemed to follow both Freundlich and Langmuir models. Maximum adsorption of CR dye was achieved between pH 5 and 9. The burnt kaolinitic clay showed greater capacity for the adsorption of CR dye with maximum adsorption capacity value of 172.4148mg/g as compared to 45.8930mg/g for the natural kaolinitic clay.

Keywords: Adsorption, Clay, Congo red, Kaolinitic, Spectrophotometry.

INTRODUCTION

Treatment of dye-manufacturing and textile industries wastewater is currently a major challenge for environmental managers. This is mainly due to the fact that coloured effluents are composed of non-biologically oxidizable components because of the molecular size and structure of the dye-stuff. Dyes are chemicals which on binding with a material, gives it colour. Coloured dye wastewater arises from the production of the dye and also as a consequence of its use in the textile and other industries. The rapid growth in the use of reactive dyes is as a result of the increasing use of cellulosic fibres and the technical and economic limitations of other dyes used for these fibres (1).Adsorption techniques for treatment of effluent have become increasingly popular due to their efficiency in the removal of pollutants too stable for biological methods. Adsorption is a physico-chemical process with great potential for effluent treatment, in that effluents are rendered in a safe and reusable form (2). The most widely used adsorbent in industrial concerns for effluent treatment is activated carbon.

However, there are certain drawbacks associated with its use especially the expensive nature of high quality activated carbon. As such, there has been increasing interest in research into cheaper and more readily available adsorbents (3). Some biological adsorbents have also been studied for the adsorption of reactive dyes; these include amongst others; apple pomace and wheat straw, corncob and barley husk, maize cob, wood and rice husk. These adsorbents were found to be efficient in binding with basic dyes rather than acid dyes (4).

In recent years, clay minerals have been accepted as one of the most appropriate low cost adsorbents (3). Investigations have been carried-out to evaluate the adsorption of dyes onto a wide range of clay minerals. Some workers (4) carried-out an investigation into the use of an open burnt clay for the removal of a reactive dye (CR). They reported that the open burnt clay could serve as a cheap alternative to activated charcoal for the removal of the dye.

This work seeks to determine and compare the adsorptive capacities of natural and burnt kaolinitic clay for the reactive dye Congo Red (CR). It also seeks to determine the effect of pH, adsorbent dosage and contact time on the adsorption process.

MATERIALS AND METHODS

The clay sample was obtained from local mining sites in kankara, Katsina State, Nigeria. The clay deposit has been reported by other workers (5) to be kaolinitic. The clay sample is dispersed in the deionized water contained in a 20 liter plastic bucket. The dispersed clay is stirred vigorously and allowed to settle. The upper layer which consists of insoluble impurities and plant particles are sieved-off. The process of stirring and sieving-off is repeated with the lower layer until it becomes free from suspended particles. The dispersed clay is then allowed to settle for 24 hrs to allow the sedimentation process since different clay particle sizes are present. The top layer was collected via decantation and the remainder was washed with deionized water, allowed to settle for 24 hrs (for further sedimentation) and decanted to collect the top layer.

The prepared clay is dried in an oven (Gallenkamp, England) at 105°C for 6hrs and then stored in a dessicator. The burnt clay used was prepared using the method described by Mumin *et al.*, 2007. All chemicals used were of Analytical grade and distilled water used for all preparations except otherwise stated. A UV-Vis spectrophotometer (Thermo Fisher, England) and pH meter (KENT, England) were used for this study.

Preparation of standard curve

0.25g of Congo red (CR) dye was accurately weighed and transferred quantitatively into a 250ml volumetric flask. It was dissolved then made to mark with distilled water. From this stock, the following concentrations 20, 40, 60, 80, 100 and 120mg/L were prepared via serial dilution. The absorbance of each concentration was determined via UV spectrometry, and then the standard curve plotted (Figure 1).

Batch adsorption studies

1.00g of adsorbent was transferred into 50ml of the adsorbate and the mixture agitated for 3hrs. the mixture was then filtered, and the absorbance taken using the UV spectrometer at a wave length of 499nm and 1cm path length.

RESULTS AND DISCUSSION

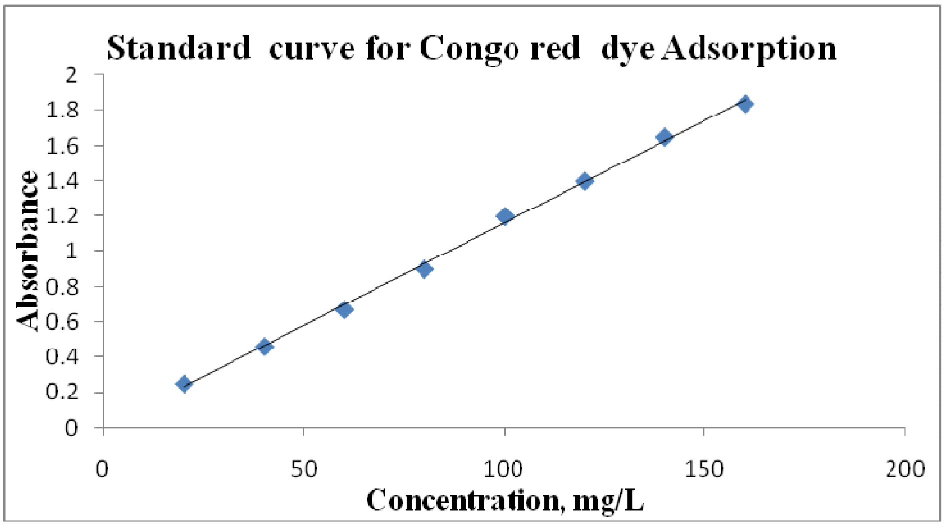

Figure 1: Standard curve for CR dye adsorption

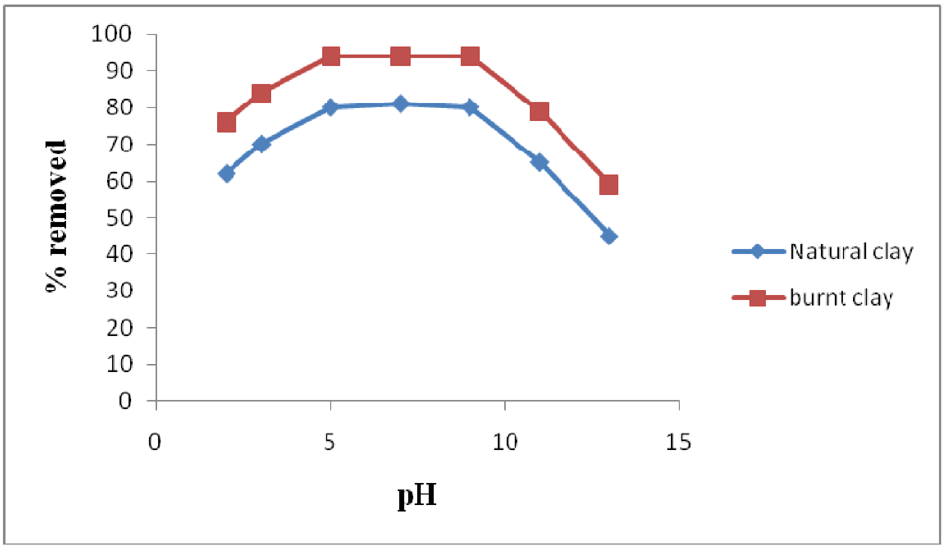

Figure 2: Plot showing the effect of pH on the adsorption of CR dye onto natural and burnt kaolinitic clay.

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of CR (20mg/L) concentration onto both natural and burnt kaolinitic clay was studied by varying the pH from 2 to 13. The amount of dye adsorbed per unit mass of adsorbent at equilibrium (i.e. % removed)as shown in Figure 2, increased as pH was increased from 2-5 for both the natural and burnt kaolinitic clay, reaching a maximum at pH 5 with adsorption efficiency of 84% and 94% for natural and burnt kaolinitic clay respectively. The amount of dye adsorbed per unit mass of adsorbent remained constant with increasing pH until pH 9 was attained, thereafter, adsorption decreased with increasing pH.

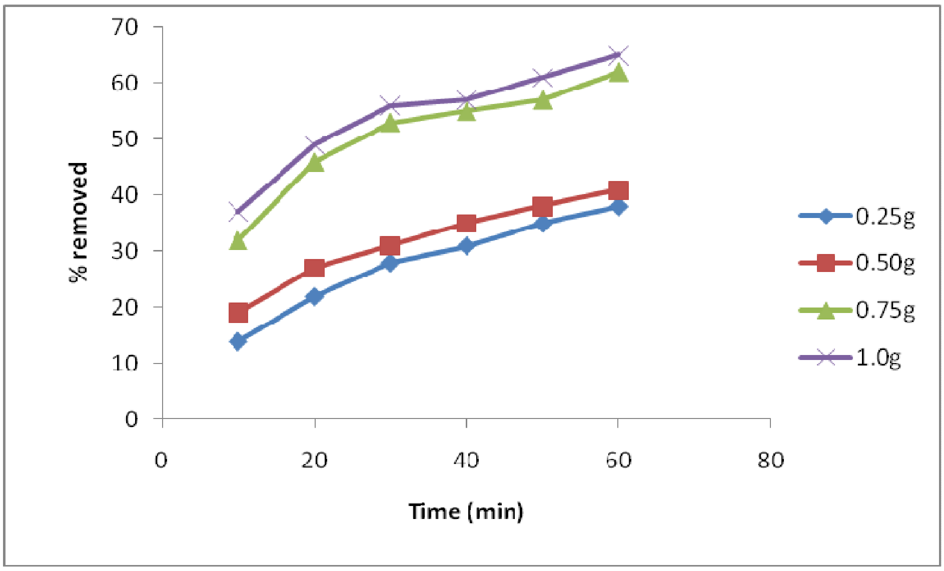

Figure 3: Plot showing the effect of adsorbent dosage and contact time on the adsorption of CR dye onto natural kaolinitic clay.

The above scenario can be attributed to the changes in the polarity of the electric double layer on both the silica and alumina contents of the clay from positive to negative. These changes enhance the removal of the cationic dye from its aqueous solution by attracting the dye cations. In addition, the acid-base dissociation of the hydroxylated oxides of the clay followed by ion exchange with the dye cations could be responsible for the maximum removal of the cationic dye from its alkaline solution.

Above pH 9, the negative charge density on the surface of the adsorbent decreased, this led to a gradual decline in the removal ability of the clay. However, between pH values 5 and 9, the plateau observed indicates that the presence of high concentrations of hydronium ions does not influence the kinetics of adsorption and consequently, the removal is at its maximum.

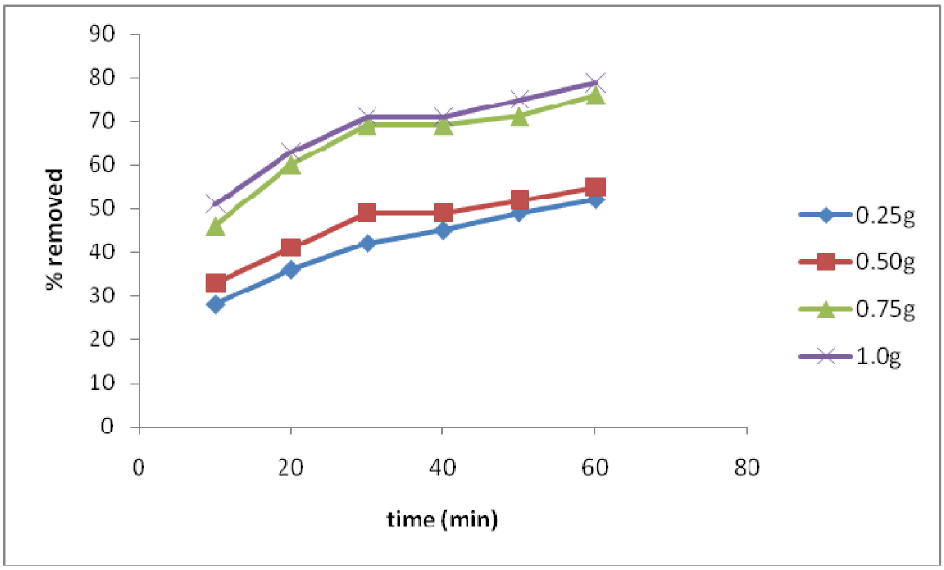

Figure 4: Plot showing the effect of adsorbent dosage and contact time on the adsorption of CR dye onto burnt kaolinitic clay.

Adsorbent dosage is another important parameter due to its strong effect on the capacity of an adsorbent at a given initial concentration of the adsorbate. Influence of adsorbent dosage on the amount of CR adsorbed by the clays is shown in Figures 3 and 4. It can be seen that by increasing the adsorbent dose from 0.25-1.0 g (for initial dye concentration 40 mg/L, solution volume 50 mL and at a pH=8, room temperature) the removal efficiency increases from 28% to 51% at time, t = 10min. This is likely due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent (6). Also, it can be seen that at the conditions listed above, i.e. initial dye concentration, volume etc., there was significant increase in removal efficiency as time, t, was gradually increased to 60 min. This resulted from the fact that there were still active sites in each clay dosage under investigation; therefore, an increase in contact time would result in increased removal efficiency until the sites are saturated. It can also be seen that the removal efficiency of the burnt clay was higher for each clay dosage under investigation than that for the natural clay. For example at t = 60min removal efficiency of 0.25g and 1.0g doses were 52%, and 79% respectively for burnt clay, while it was 38% and 65% respectively for natural clay. This is due to the fact that thermal treatment of the clays results in an opening of the pores (increased surface area).

Adsorption isotherm models

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Congo red dye on both natural and open burnt clay was modeled using Freundlich and Langmuir adsorption isotherms.

Freundlich isotherm

This isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto theheterogeneous surface of an adsorbent (7). The linear form of Freundlich equation is expressed as:

$\log q_e = 1/n \log C_e + \log K_F$

where K_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and C_e is the equilibrium concentration (mg/L) (8).

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as:

$Ce/qe = 1/K_L q_m + C_e/q_m$

where K_L is the Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mg/g) (8, 9).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation (10):

$R_L = 1/ (1+ K_L C_o)$

where C_o (mg/L) is the initial concentration of adsorbate, and K_L (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for the adsorption of CR onto both natural and burnt kaolinitic clay (Table 2) are observed to be in the range 0–1, indicating that the adsorption was a favorable process. The equilibrium data were further analyzed using the linearized form of Freundlich isotherm, by plotting log q_e versus log C_e (Figures 5 and 6). The calculated Freundlich isotherm constants (K_F, n) and the corresponding coefficient of correlation, R^2 are shown in Table 1.

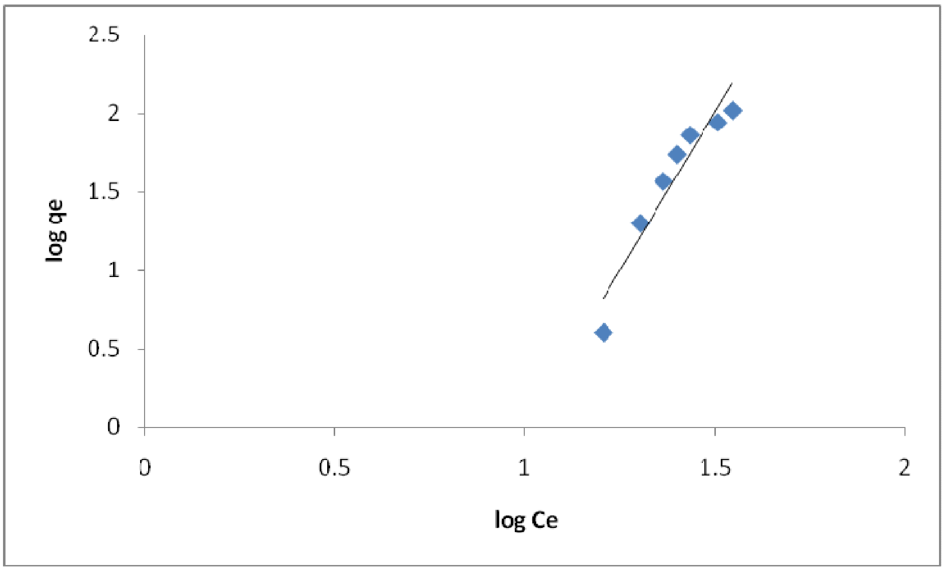

Figure 5: Freundlich Isotherm plot for adsorption of CR dye onto natural kaolinitic clay.

The coefficient of correlation $R^2 = 0.9743$ and 0.9045 as shown in Table 1. This indicates that the adsorption obeyed the Freundlich adsorption isotherm.

The coefficient of correlation for adsorption of CR on burnt kaolinitic clay is ($R^2 = 0.9743$). The result shows that the value of n is greater than unity (n = 1.2009) indicating that the dye is favorably adsorbed on burnt clay, which is in great agreement with the calculated R_L value. This magnitude of Freundlich constant indicates easy uptake of CR from aqueous solution onto the burnt clay. Whereas, the coefficient of correlation for adsorption of CR on natural clay is (R^2= 0.9045). The result also shows that the value of n is less than unity indicating that the adsorption of the CR dye onto natural clay is less favourable than that of the burnt kaolinitic clay.

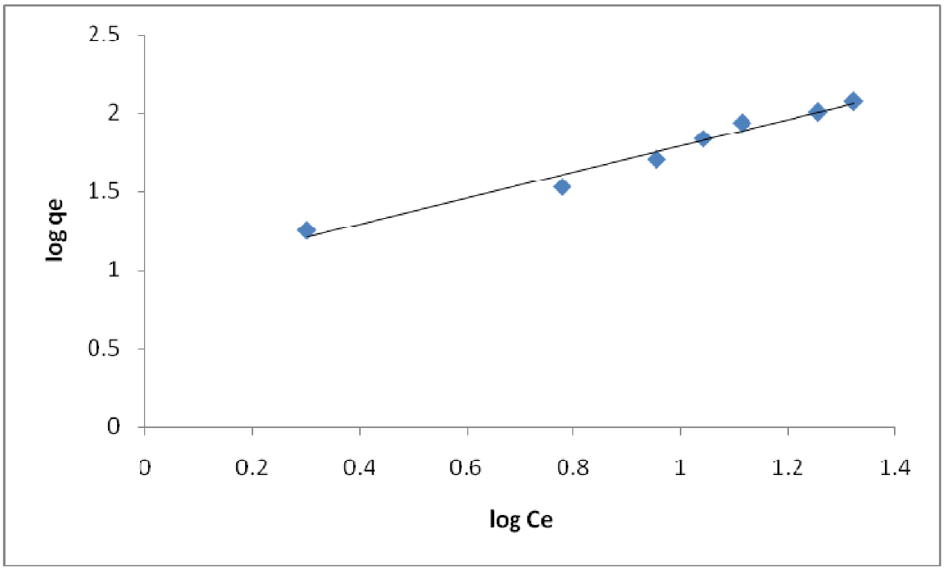

Figure 6: Freundlich Isotherm plot for adsorption of CR dye onto burnt kaolinitic clay.

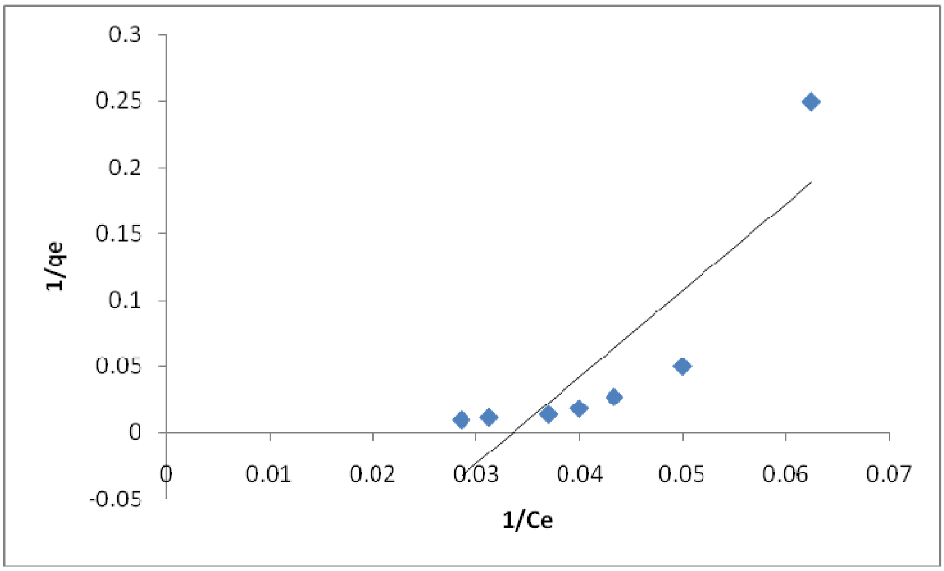

Figure 7: Langmuir Isotherm plot for adsorption of CR dye onto natural kaolinitic clay.

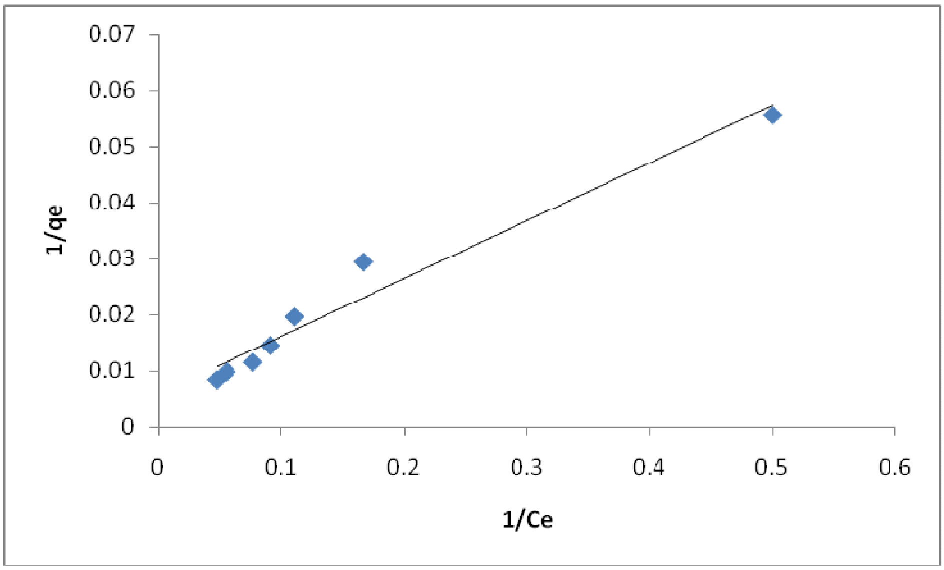

Figure 8: Langmuir Isotherm plot for adsorption of CR dye onto burnt kaolinitic clay.

Table 1: Showing Freundlich Adsorption Parameters

Freundlich Adsorption Parameters	Congo red onto natural clay	Congo red onto burnt clay
K_F	1.3921	0.0404
n	0.2485	1.2009
R^2	0.9045	0.9743

Table 2: Showing Langmuir Adsorption Parameters

Langmuir Adsorption Parameters	Congo red onto natural clay	Congo red onto burnt clay
q_m	45.8930	172.4148
K_L	0.0335	0.0563
R_L	0.5988	0.4704
R^2	0.7488	0.9624

CONCLUSION

This study has evaluated the adsorptive capacities of natural and burnt kaolinitic clay for the uptake of a reactive dye (CR). Even though the equilibrium data obtained showed that adsorption in both cases seemed to follow both Freundlich and Langmuir models with the exception of the data for natural clay which poorly fitted the Langmuir model; nevertheless, the correlation coefficient values showed that the adsorption data better fitted the Freundlich model. Maximum removal of CR dye was obtained between pH 5 and 9 with removal efficiency of 84% and 94% for natural and burnt clay respectively. The burnt clay with a monolayer (maximum) adsorption capacity (q_m) of 172.4148mg/g as compared to 45.8930mg/g for the natural, has greater capacity for the uptake of the CR dye.

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