

ADSORPTION AND OPTIMIZATION STUDIES OF CONGO RED FROM SOLUTION USING MONTMORILLONITE-SILICA NANOCOMPOSITE

ABSTRACT

Congo red was removed on Montmorillonite-silica nanocomposite from solution by adsorption process. The adsorption parameters studied were adsorbent dose, initial concentration and contact time. The optimum adsorption parameters were found to be 2mg/L, 1.5g and 40 minutes for initial concentration, adsorbent dose and contact time respectively with removal percentage of 84.10%. Pseudo first and second order kinetics were used for the studies. Pseudo second order best fit the adsorption process with $R^2 = 1$ than the Pseudo first order which has $R^2 = 0.933$. Experimental data was best fitted by the Langmuir Isotherm with $R^2 = 0.9024$ other than the Freundlich Isotherm, $R^2 = 0.568$. The R_L of 0.994 of the Langmuir isotherm shows the favourability of the adsorption process. The maximum adsorption capacity by Langmuir isotherm was found to be 172.40 mg/g.

Key words: Adsorption, Congo Red, Nanocomposite, Optimization

1.0 INTRODUCTION

Dyes are used in various industries such as pharmaceutical, cosmetic, paper, leather, food stuff, plastics, and textile etc. The dye effluents are discharged into environment either water or land. The discharge of these effluents into the receiving environments results in hazardous health problems as most of these dyes have carcinogenic effects on the living organisms [1-6]. Due to the toxicity (carcinogenic or mutagenic) of the dye pollutants, when discharge into the environments it cause serious problem with respect to aquatic life and human health [7]. In other words, toxic nature of the dye effluents lead to death of soil microorganisms when they are used for irrigation purposes and this affects agricultural productivity [8]. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. There are different methods of treatment of dye contaminated wastewater which includes; Biological treatment, Chemical oxidation, Ozonation, membrane filtration, electrochemical method, Coagulation and flocculation, Liquid-liquid extraction, and Adsorption. But adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation

and insensitivity to toxic substances [9-11]. Nanocomposite is a multiphase material where one of the phases has one, two, or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material [12].

The aim of the present work was the optimization of adsorption conditions for the effective removal of Congo red using Montmorillonite-Silica Nanocomposite. Thus, the adsorption conditions evaluated includes adsorbent dose, contact time and initial concentration of Congo red. Also, Kinetic and equilibrium isotherm models were applied to establish the rate of adsorption and adsorption capacity.

2. MATERIALS AND METHODS

2.1. Preparation of solution / reagents

M H₂SO₄: A 5.3ml of concentrated sulphuric acid was pipetted and poured into 30ml distilled water in a 100ml volumetric flask and diluted with distilled water to the mark.

1MHCl: A measuring cylinder was used to measure 30.9ml of concentrated HCl. It was then transferred into a 100 ml volumetric flask and diluted to the mark with distilled water.

2.5M NaOH: An accurately weighed 100g of sodium hydroxide was placed in 1000 ml volumetric flask, distilled water was added up to the mark.

1000mg/L Methylene blue stock solution: One gram methylene blue was weighed and placed in 100 ml volumetric flask. Distilled water was added and mixture thoroughly shaken until the methylene blue dissolved. It was then made up to the mark with distilled water.

2.2. Sample Collection and Preparation

Both montmorillonite clay and rice husk samples were collected at Talasse, Balanga Local Government Area of Gombe state, Nigeria. The 1000g rice husk was washed thoroughly with tap water for about six times and rewashed with distilled water three times to remove the adhesive dirt. It was dried overnight and subsequently oven dried at 95°C and kept for ashing.[13]

The clay (1000g) was washed several times with tap water, and rewashed further with distilled water four times. The washed sample was air dried and then oven dried for four hours at 110°C. The clay was ground and sieved using a 250µm sieve. A weighed of 250g of the powdered clay was refluxed with 500 ml of 1M HCl for 1 hour at 120°C. It was then washed with distilled water five times to remove the acid. The clay was then dried in an oven at 105°C for six hours until a constant weight was obtained. It was then ground and kept for further synthesis of the montmorillonite –silcanano composite, [14-16].

2.3. Preparation of rice husk ash

Rice husk ash was prepared according to [4]. A 500g portion of dried rice husk was refluxed with 1000ml hydrochloric acid for 1hour at 95°C to remove some metallic impurities. After completion, it was washed thoroughly with distilled water five times, dried in an oven for five hours at 110°C. The treated rice husk was calcined in a muffle furnace for 7 hours at 650°C. The white rice husk ash was

66 obtained and kept for further preparations.

67 2.4. Synthesis of Montmorillonite-silicananocomposite

68 A 20g of white rice husk ash (WRHA) was refluxed with 2.5M NaOH solution for 1 hour with
69 constant stirring at 200°C and then filtered, where a clear sodium silicate solution was obtained. A
70 weighed amount of 80g of acidified clay was added into 200ml solution of the sodium silicate obtained
71 with constant stirring. It was then precipitated with 1M H₂SO₄ drop wise and measuring the pH until it
72 is equal to 8.9, it was then kept for 24 hours and then washed five times with distilled water until the
73 pH was observed to be 7. It was then oven dried for five hours, ground and sieved with a 250µ sieve,
74 [17-19].

75 2.5. Adsorption studies

76 All the experiments in these studies were carried out in 500ml conical flask both containing 200ml
77 methylene blue. After adding the amount of adsorbent, the flasks were agitated using magnetic stirrer
78 while studying the parameters such as; the effect of adsorbent dose, initial concentration and contact
79 time.

80 After the adsorption process, the flash content was filtered using whattman filter paper. The filtrate
81 obtained was analyzed using UV/Visible spectrophotometer (Model JENWAY 6300) at the wavelength
82 of 497 nm. The adsorption percentage of the adsorbate and the amount of adsorbed, q_e (mg/g) were
83 calculated according to the following equation;

$$85 \quad \text{Adsorbate removal \%} = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

$$86 \quad \text{Amount adsorbed, } q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

87
88 Where, C_o = initial concentration of Congo red solution in mg/L, C_e = equilibrium concentration of
89 Congo red solution in mg/L, m = mass of the adsorbent in grams, V = volume of Congo red test
90 solution in liters(L).

91 3.0 RESULT AND DISCUSSION

92 3.1 Effect of adsorbent dose

93 The effect of adsorbent dose for Congo red dye, is shown in Table 1, it was observed that there was
94 an increase in the removal percentage from an adsorbent dosage of 0.5g – 1.5g which decreases
95 thereafter, Figure 1. This scenario is against the report by [20-23] where the removal percentage
96 increases with increase in adsorbent concentrations. However, a similar case was reported by [24], in
97 which removal percentage increases with increase in adsorbent dose and thereafter has a sharp
98 decrease. And the authors reported that this may be due to aggregation of adsorption sites resulting
99 in decrease in total adsorbent surface area of particles available to adsorbate and an increase in
100 diffusion path length. This observation was in agreement with previous investigation by [25]. Thus, the
101 optimum adsorbent dose was found to be 1.5 g with a percentage removal of 74%.

Table 1; Effect of adsorbent dose table for Congo Red

Adsorbent dose(g)	Absorbance	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	%Removal
0.5	0.027	2	0.780	1.220	61.00
1.0	0.024	2	0.694	1.306	65.30
1.5	0.018	2	0.520	1.480	74.00
2.0	0.019	2	0.549	1.451	72.55
2.5	0.021	2	0.607	1.393	69.65

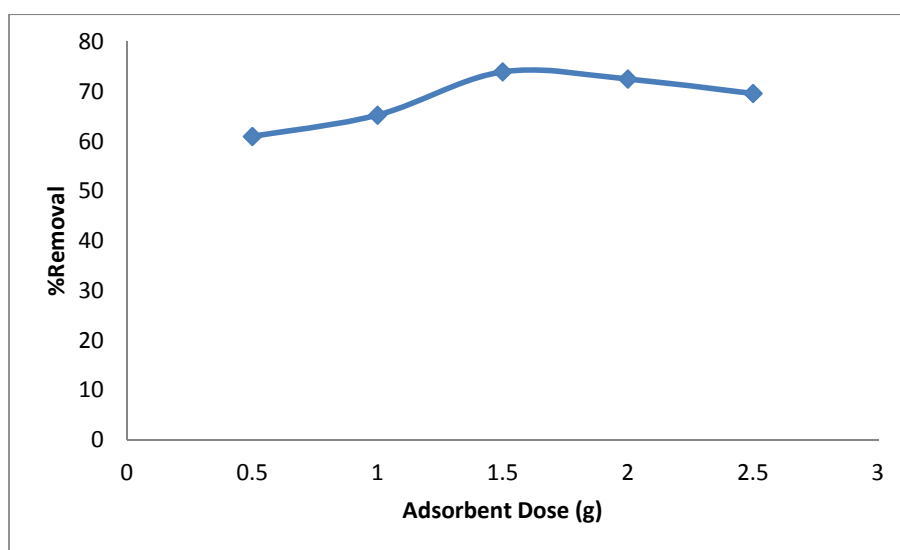


Figure 1; Effect of adsorbent dose graph for congo red at adsorbate conc. Of 2mg/L, contact time of 60 (min), and varied dosage of 0.5, 1.0, 1.5, 2.0 and 2.5g.

3.2 Effect of initial concentration of adsorbates

The adsorption of Congo red dye on montmorillonite-silica nanocomposite was studied at different initial concentrations from 1mg/L to 5mg/L. The result was represented in Table 2 and Figure 2, it was observed that there was high removal percentage increase from 1mg/L to 2mg/L. Beyond this concentration, the percentage removal decreases very slightly. This scenario is against the report by [20-23] where the removal percentage increases with increase in initial concentrations. However, a similar case was observed in an investigations by [24, 25] where removal percentage increases with increase in initial concentration and thereafter have a sharp decrease. The optimum initial concentration was observed to be 2mg/L with percentage removal of 79.80%.

Table 2; Effect of initial concentration for congo red

Adsorbent dose(g)	Absorbance	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	%Removal
1.5	0.011	1	0.3179	0.6821	68.21
1.5	0.014	2	0.4046	1.5954	79.80
1.5	0.029	3	0.8381	2.1619	72.06
1.5	0.040	4	1.1560	2.844	71.10
1.5	0.049	5	1.4161	3.5839	71.67

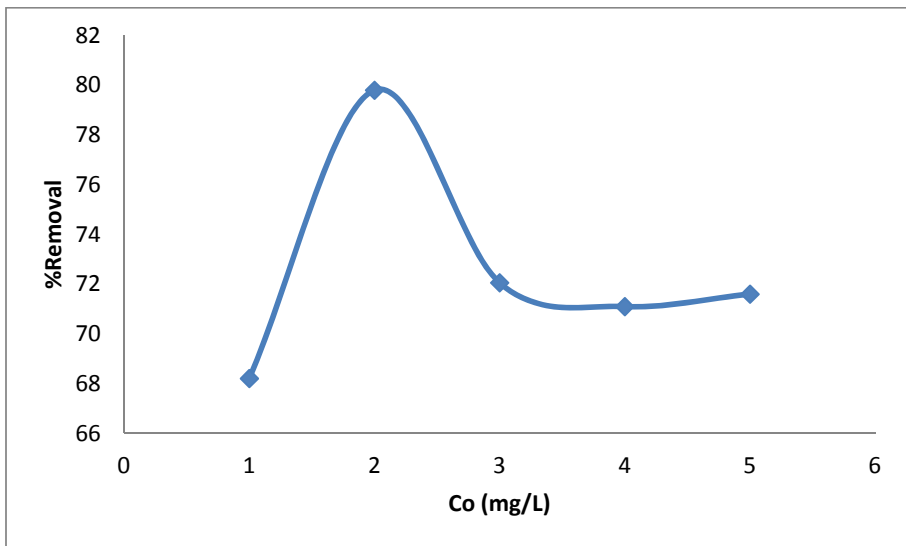


Figure 2; Effect of initial concentration graph for congo red ay varied conc. of 1, 2, 3, 4and 5mg/L, Contact time of 60 (min) and adsorbent dose of 0.5g

3.3 Effect of contact time

The experimental results of effect of contact time obtained from the batch adsorption process of Congo red dyes; Table 3 and Figure 3, these shows that the effect of contact time plays an important role as the percentage removal of the dye increases rapidly with the increase of the contact time from 10 to 40 minutes. The percentage removal increases rapidly and then decreases significantly as the contact time for the adsorption increase. Similar observation was reported by [25] with even formation of plateau. Also, two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature [26,27,28]. These two stage sorption mechanism lead to plateau formation and thus, this behavior gives away a slow approach to equilibrium [28]. Hence, the optimum contact time was obtained to be 40 minutes with the percentage removal of 84.10%.

Table 3; Effect of contact time for Congo red

Time (min)	Adsorbent dose (g)	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	% Removal
10	1.5	2	0.6936	1.3064	65.32
20	1.5	2	0.6358	1.3642	68.21
30	1.5	2	0.4046	1.5954	79.77
40	1.5	2	0.3179	1.6821	84.10
50	1.5	2	0.3757	1.6243	81.22
60	1.5	2	0.5202	1.4798	73.99

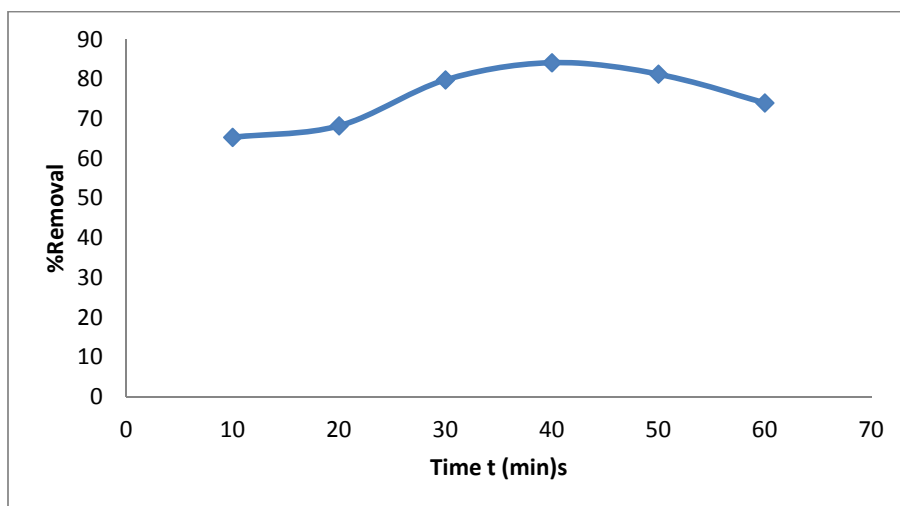


Figure 3; Effect of contact time graph for congo red at adsorbent dose of 1.5g, varied contact time of 10, 20, 30, 40, 50 and 60min and adsorbate conc. of 2mg/L

3.4 Adsorption isotherm study

The experiment data studied in this adsorption process were analyzed using only two models namely: Langmuir isotherm model and Freundlich isotherm model

3.4.1 Langmuir isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the absorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phase, the Langmuir isotherm is valid for monolayer adsorption on to a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. For liquid adsorbates however, the Langmuir isotherm is usually expressed as follows;

$$q_e = \frac{(q_{max}C_e)}{(K_l + C_e)} \dots \dots \dots (4)$$

For correlation purposes, the equation is rearranged as follows;

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} \cdot C_e \dots \dots \dots (5)$$

Where

- C_e = the equilibrium concentration of adsorbate (mg/L).
- q_e = Is the equilibrium value of adsorbate adsorbed per unit weight of adsorbent (mg/g).
- q_{max} =Is the maximum amount of adsorption corresponding to monomolecular layer coverage (mg/g).
- K_L = Is the Langmuir constant and is related to measure of affinity of the adsorbent (l/mg).

A linearized plot of $\frac{C_e}{q_e}$ against C_e yields a straight line graph which has an intercept and slope which correspond to $\frac{1}{K_L q_{max}}$ and $\frac{1}{q_{max}}$ respectively, from which the q_{max} and K_L can be calculated.

To confirm the favourability of an adsorption process to Langmuir isotherm, the essential features of the isotherm can be expressed in terms of a dimensionless constant known as the separation factor or equation parameter R_L, which can be calculated by the following equation;

$$R_L = \frac{1}{K_L q_{max}} \tag{6}$$

Where, C₀ is the initial concentration.
 The value of R_L indicates whether the isotherm is irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1), or unfavourable (R_L>1). Hence, from Table 4, the R² of 0.9 shows the fitness of the experimental data and the maximum adsorption capacity was found to be 172.40 mg/g. The R_L of 0.994 of the Langmuir isotherm shows the favourability of the adsorption process.

Table 4: Langmuir Isotherm Data table

DYE	ISOTHERM	CONSTANT	VALUES (mg/g)
Congo Red	Langmuir	q _{max}	172.40
		R ²	0.9024
		b	0.0002
		R _L	0.994

3.4.2 Freudlich isotherm

The freundlich isotherm is an empirical equation employed to describe heterogeneous system, it assumes that the adsorption energy of a solution or ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied.

The freundlich equation is written as;

$$\text{Log} q_e = \text{Log} K + \frac{1}{n} \text{Log} C_e \tag{7}$$

Where, q_e and C_e are the equilibrium adsorption capacity of the adsorbent and the equilibrium concentration in the aqueous solution respectively.

K and n are the Freundlich constants related to adsorption capacity. And the plot of Logq_e against LogC_e gives the Freundlich isotherm graph. And the parameters; n and K were also obtained from the slopes and intercept of the graph.

For the Freundlich isotherm Table 5, the parameters were also obtained from the slopes and intercept of the graph of the plot of $\log q_e$ against $\log C_e$ and R^2 values obtained was observed to be 0.568.

Table 5: Freundlich Isotherm

DYE	ISOTHERM	CONSTANT	VALUE
Congo Red	Freudlich	K_F	0.39
		R^2	0.568
		n	0.49

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3.5 Kinetic adsorption study

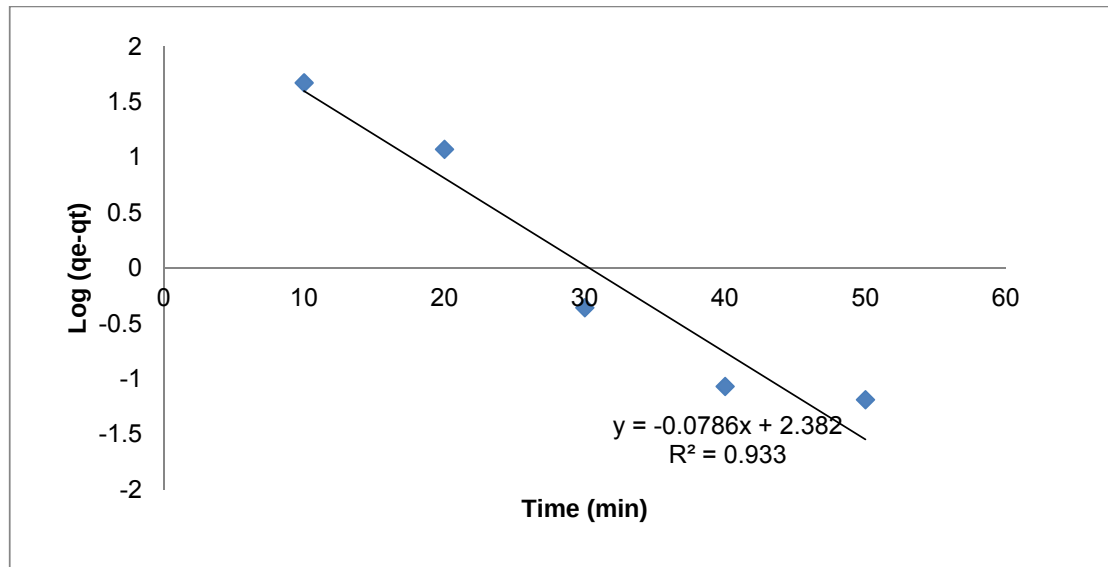
The pseudo-first order and the pseudo-second order kinetics are the only kinetics studied for this experimental adsorption process.

The pseudo-first order equation is represented as follows:

$$\log(q_e - q_e) = \log q_e + \frac{K_1 t}{2.303} \dots \dots \dots (8)$$

Where, K_1 is the Lagergren rate constant of adsorption (1/min).

The plot of $\log (q_e - q_t)$ against t , gives linear relationship from which q_e and K_1 are determined from the intercept and slope of the plot respectively. The data for pseudo first order is shown in Figure 4 and the R^2 values indicate that the data fit the process.



220
221

Figure 4: Pseudo first order kinetic graph

The pseudo-second order equation can be represented by the following linear form.

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (9)$$

Where, K_2 is the second order rate constant of adsorption (g/mg min). The values of K_2 and q_e are determined from the intercept of the plot of t/q_t against t . The data for pseudo second order is shown in Figure 5 and the R^2 values indicate that the data fit the process than the pseudo first order.

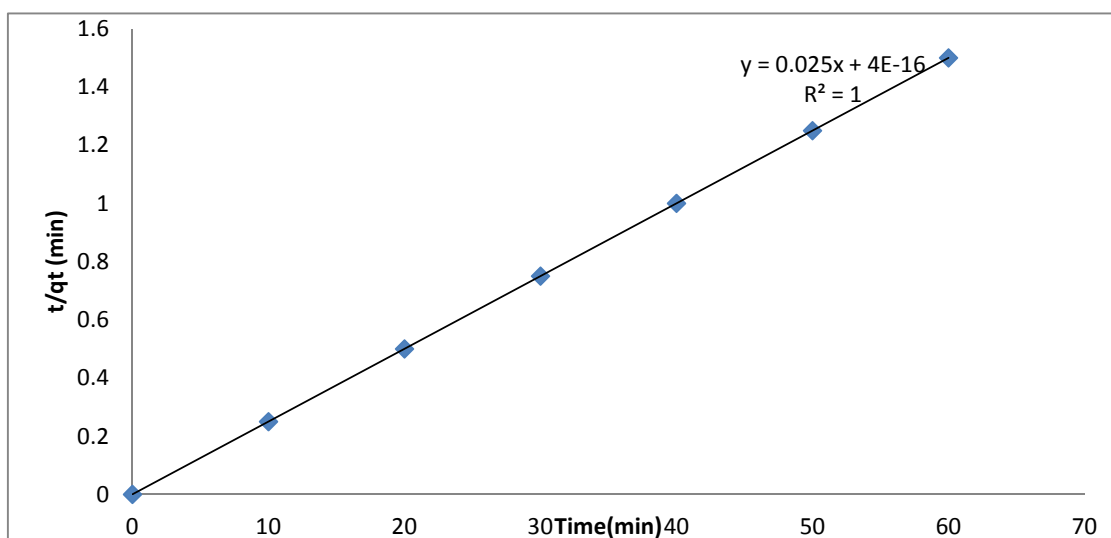


Figure 5: Pseudo second order kinetic graph

CONCLUSION

The adsorption process of Congo red was carried out using Montmorillonite silica nanocomposite. From the experimental data the percentage removal of 84.10% obtained at optimum initial concentration of 2mg/l, optimum adsorbent dose of 1.5g and optimum contact time of 40 minutes. Experimental data was best fitted by the Langmuir Isotherm with $R^2 = 0.9024$ other than the Freundlich Isotherm, $R^2 = 0.568$. The pseudo second order kinetic with $R^2 = 1$ best fit the adsorption process other than the pseudo second order kinetics, $R^2 = 0.933$.

Therefore, Mmontmorillonite- silica nanocomposite obtained from montmorillonite clay and Rice husk ash can serve as a cost effective adsorbent in the removal of Congo red dye.

RECOMMENDATION

The authors recommend that further work should be carried with full characterization of the adsorbent With FTIR, SEM, TEM, and XRD etc in order to understand the adsorption mechanism for this particular work as well as to derive a good conclusion.

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