

## ADSORPTION OF CONGO RED FROM AQUEOUS SOLUTIONS USING CLAY– CORN COB–FeCl<sub>3</sub> COMPOSITE

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### ABSTRACT

Dyes constitute major wastes from textile, dye manufacturing, pulp and paper industries. Some amounts of these dyes are transferred into water systems. In this research, Clay–Corn cob–FeCl<sub>3</sub> composite (adsorbent) was prepared from clay, corn cob, FeCl<sub>3</sub> and lime. The adsorbent was used for the effective removal of Congo red from aqueous solutions. The adsorbent was characterised using Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Nitrogen adsorption/desorption isotherm. Effects of pH, contact time, initial concentration of Congo red and temperature on the adsorption capacities were investigated using batch adsorption experiment. The optimum pH of 2 and equilibrium time of 1 h were observed for the adsorption process. The pseudo–second order model was the best model for description of the kinetic data out of four models (pseudo first order, pseudo second order, Elovich and intra-particle diffusion). The equilibrium data was evaluated using Langmuir, Freundlich and Temkin models. The Freundlich model gave the best fit of the equilibrium data. The maximum adsorption capacity calculated from the Langmuir model was 1000.00 mg/g. Thermodynamic parameters such as standard Gibbs free energy, standard enthalpy and standard entropy were evaluated. Congo red adsorption from aqueous solutions was spontaneous and exothermic. It showed that adsorbent prepared and used in this study was efficient for removal of Congo red from aqueous solutions. The adsorbent can be used for treatment of industrial effluents.

**keywords:** Congo red, Adsorption, Equilibrium, Kinetics, Freundlich, Pseudo–second order model

### INTRODUCTION

Dyes are utilised in many industries such as textiles, rubber, paints, food and beverages, pharmaceuticals, plastics, paper, printing, leather, cosmetics, photography, among others, for production of coloured products (Adebayo *et al.*, 2014; Cardoso *et al.*, 2011). A good percentage of the dyes present in water systems originate from textile industries. Effluents containing dyes being released into water bodies are toxic and affect not only the aquatic organisms but also human beings. Succinctly, dyes prevent penetration of sunlight into the water bodies, and hinder photosynthetic

activities of aquatic plants (Galán *et al.*, 2013; Rovani *et al.*, 2014). The presence of dye in aqua system is a vital concern because it poses a serious health threat to mankind and water quality. Among the consequential effects of dyes on human beings include skin irritation, cancer, allergic, dermatitis, and mutation (Cardoso *et al.*, 2011; Machado *et al.*, 2014).

A number of treatment methods, such as sono-chemical degradation, Fenton biological treatment, photo-catalytic degradation, biodegradation, integrated chemical biological process, electrochemical, adsorption, chemical

coagulation-flocculation, precipitation, and so on, have been developed and explored for remediation of dyes in the wastewater (Adebayo *et al.*, 2014; Muthuraman, 2011; Doumic *et al.*, 2015; Adebayo *et al.*, 2012a; Adebayo *et al.*, 2012b; Olasehinde *et al.*, 2018). Adsorption process is an effective and efficient method among the available techniques. Adsorption is a prominent technique because of its cheapness, simplicity, and rapidness. Similarly, adsorbents can be regenerated easily and reused after adsorption experiments (Thue *et al.*, 2016; Bazzo *et al.*, 2016). A number of adsorbent materials have been studied and used for removal of dyes from aqueous solutions; these adsorbent materials include carbon nanotubes (Machado *et al.*, 2014), alumina (Domic *et al.*, 2015), coffee waste (dos Santos *et al.*, 2014; dos Santos *et al.*, 2015), cocoa pod husks (Bello and Ahmad 2011; Ribas *et al.*, 2014), mesoporous material (Umpierres *et al.*, 2017), sludge (Puchana-Rosero *et al.*, 2016), Bacury shell (Saucier *et al.*, 2015a) and so on.

Congo red is a diazo dye. It is a valuable textile dye that can be applied directly on cotton (Steensma, 2001; Purkait *et al.*, 2007). Congo red also finds its application in wood pulp and paper industries and could be used as a laboratory testing aid for free hydrochloric acid in gastric contents, as pH indicator, in the diagnosis of amyloidosis and as a histological stain for amyloid. Congo red dye can be synthesised by coupling two molecules of naphthionic acid with tetrazotised benzidine (Purkait *et al.*, 2007). Congo red is red in the pH range of 5 to 10, however, its colour changes from red to blue at acidic media (< pH 5). This blue colour of Congo red could be linked to the resonance among charged canonical structures (Purkait *et al.*, 2007). Congo red dye is carcinogenic and must be removed from water systems. Among the adsorbents that have been used for removal of Congo red from aqueous solutions include activated carbon (Purkait *et al.*, 2007), activated carbon from *Imperata cylindrica* leaf (Bello and Banjo 2012), bentonite (Toor *et al.*,

2015), activated carbon/surfactant (Cheng *et al.*, 2015), wheat straw (Zhang *et al.*, 2014), and nanotubes (Guo *et al.*, 2014).

In this work, a composite was prepared from clay, corn cob (agricultural waste) and iron(III) chloride (activating agent). The composite material tagged clay–corn cob–FeCl<sub>3</sub> composite (CCCF) was successfully utilised for adsorption of Congo red from water systems. Corn cobs are agricultural wastes that are discarded in the environment after consuming maize. These corn cobs litter the environment, accumulate and decompose. The decomposition of these wastes contaminates our so-called safe environment. It is of good concern, as shown in this research, to convert the corn cob waste into useful material that can decontaminate toxic Congo red from aqueous solutions.

## MATERIALS AND METHODS

### Reagents and Solutions

Congo red (molecular weight: 696.67 g/mol) was furnished by Aldrich Chemical Company and used without further treatment. All other reagents used in the study were of analytical grade and used without further purification. Cleaning and preparation of solutions were done using Milli-Q water. A 5 g/L (stock solution) of Congo red was prepared and experimental solutions were prepared by diluting the stock solution using Milli-Q water.

### Collection of Samples and Preparation of Adsorbent

The corncob was collected from Oja-oba, Akure, Ondo State, Nigeria. The corncob was sundried for a week to drive off the moisture, oven-dried at 100 °C for 24 h, and subsequently burnt in a furnace between 300 and 400 °C. The residue from the corncob was ground, sieved to get a smooth and smaller materials (106 µm) and kept securely until use. Clay soil was gotten from Apatapiti, Akure, Ondo State, Nigeria, and was

identified at Soil Laboratory at Federal University of Technology, Akure, Ondo State, Nigeria. The clay was oven-dried at 100 °C for 48 h, crushed with mortar and pestle, sieved to get a smaller particle (106 µm) of the clay soil and properly stored until needed.

A 50 g of corn cob was weighed and mixed with a 50 g of clay. A 80 g of iron(III) chloride was dissolved in 300 ml of water. The corn cob and clay were added to the solution of FeCl<sub>3</sub>. A 20 g of lime was weighed and added to the mixture. The inclusion of lime was to ensure smooth and proper mixing of the components (Ribas *et al.* 2014; Saucier *et al.*, 2015a; Saucier *et al.*, 2015b). Iron (III) chloride was used as activating agent. The mixture was put on a magnetic stirrer for 1 h at 80 °C and solution was brought to pH ≈ 9 using NaOH solution. The solution was allowed to age for 24 h. The clear solution was decanted and the adsorbent was washed with Milli-Q water several times to drive out the inorganics used during the preparation. The resulting material (adsorbent) was oven dried and sieved with a 106 µm mesh sieve. This adsorbent was named clay–corn cob–FeCl<sub>3</sub> composite (CCCF) and stored in an air-tight plastic bottle until usage. The ratio of precursor (corn cob and clay) to inorganics (FeCl<sub>3</sub> and lime) was 1:1. Adsorbents with different ratios of precursor to inorganics (1:2, 2:1, 2:3 and 3:2) were also prepared. The preliminary experiments in this study revealed that CCCF with ratio 1:1 (precursor : inorganics) gave the best adsorption capacity (data not shown). This adsorbent was used for further adsorption study.

### Characterisation of the Adsorbent

The CCCF adsorbent was characterised using Fourier Transform Infra-Red Spectroscopy (FTIR) (Perkin Elmer 2000 FTIR spectrophotometer). The adsorbent and KBr were dried in an oven at 393 K for 10 h, stored in airtight flasks and kept in a vacuum desiccator prior analysis. The FTIR spectrum of the CCCF

was recorded between 4000 and 650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

The micrograph of CCCF was taken using Scanning Electron Microscope (SEM) (Zeiss DSM 982 Gemini).

The N<sub>2</sub> adsorption-desorption isotherm of the adsorbent was done at liquid nitrogen boiling point (77 K) using a surface analyser (Nova Station A Equipment). The specific surface area and pore size distribution of the adsorbent were evaluated using BET (Brunauer, Emmett and Teller) multipoint technique and BJH (Barret, Joyner and Halenda) (Gregg and Sing, 1982).

### Adsorption Studies

Batch experiment was used to study the adsorption of Congo red dye on the CCCF. The influences of pH, contact time, initial concentration of Congo red and temperature on the adsorption capacity were investigated. All batch adsorption studies were carried out in various 20 mL of Congo red solutions (200 – 2000 mg/L) and 50 mg CCCF in the pH range of 2.0 to 10.0. The adsorbent-adsorbate mixtures were agitated at 160 rpm and equilibrated at an appropriate time (from 2 min to 8 h) in a thermostatic shaker (25 – 50 °C). After equilibration at specific conditions, the mixtures were filtered using Whatmann No. 1 filter paper. The concentration of un-adsorbed dye was measured using UV/Visible spectrophotometer. The right wavelength maximum for measurement of absorbances was obtained by running spectra of diluted dye (taking into consideration the pH) before taking the absorbance of un-adsorbed dye from aqueous solutions. An aliquot of the residual concentration of dye in the supernatant was diluted when necessary before spectroscopic measurements. Each experiment was carried out in duplicate.

The amount of Congo red adsorbed and percentage of adsorption (%A) were calculated using Eqs (1) and (2), respectively, for all experiments carried out.

$$q_e = (C_o - C_e) \cdot m^{-1} \cdot V \quad (1)$$

$$\%A = \frac{(C_o - C_e)}{C_o} \cdot 100 \quad (2)$$

where  $q_e$  is the amount of Congo red adsorbed onto the adsorbent (mg/g),  $C_o$  is the initial Congo red concentration (mg/L),  $C_e$  is the equilibrium concentration of the Congo red solution (mg/L) after adsorption,  $V$  is the volume (L) of the aqueous phase;  $m$  is the dry weight (g) of the adsorbent used.

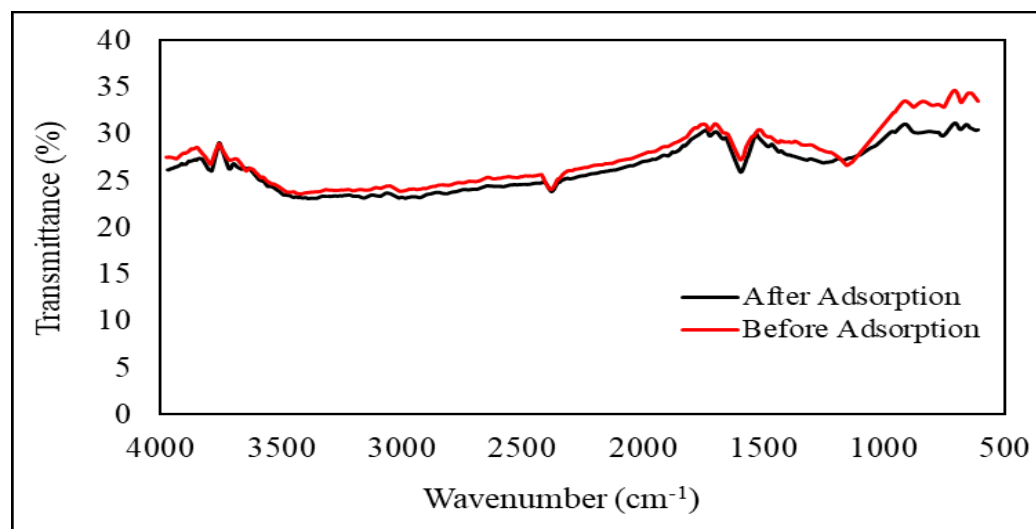
## RESULTS AND DISCUSSION

### Preparation and Characterisation of Adsorbent

The preliminary experiments (data not shown) showed that the adsorption capacity of CCCF was better than those of native Corn cob

and clay for removal of Congo red. Iron(III) chloride played a substantial activation role. Iron salts have been employed previously as activating agents (Leal *et al.*, 2012; Saha *et al.*, 2011).

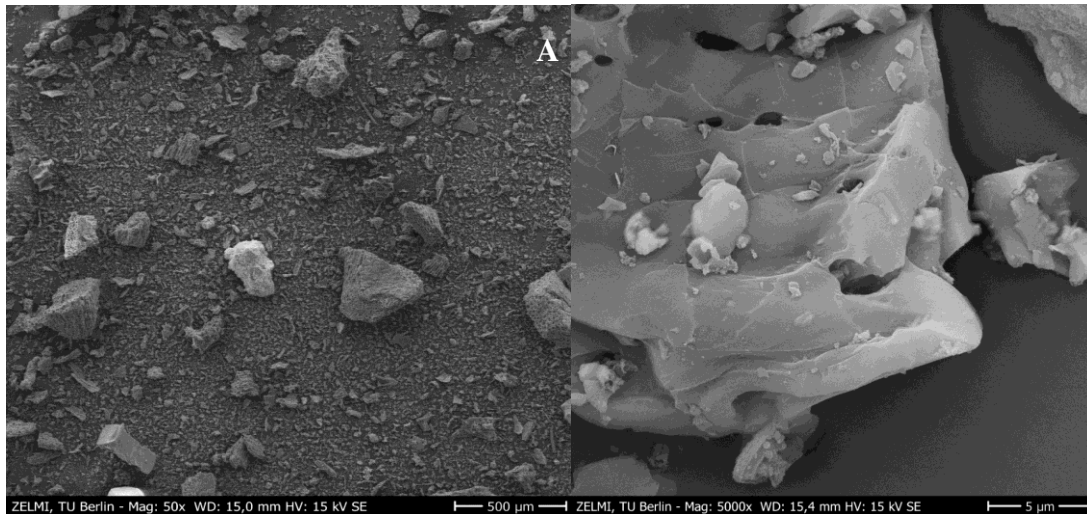
To obtain the functional groups on the surface of the CCCF, FTIR analysis was carried. This analysis provides valuable information on the chemical composition adsorbent materials and the functional groups responsible for binding and removal of pollutants from aqueous solutions (dos Reis *et al.*, 2016; dos Reis *et al.*, 2017). The prominent peaks and functional groups assignments of the CCCF spectrum (**Figure 1**) are  $3793 \text{ cm}^{-1}$  (–OH),  $2383 \text{ cm}^{-1}$  (–C=C),  $1597 \text{ cm}^{-1}$  (–C–O),  $1156 \text{ cm}^{-1}$  (C–O stretching of alcohol and phenol, and the Si–O stretching of silicates) (dos Reis *et al.*, 2017). There are noticeable differences in the peaks of CCCF before and after adsorption. The peaks of CCCF after adsorption of Congo red (**Figure 1**) are  $3756 \text{ cm}^{-1}$  (–OH),  $2373 \text{ cm}^{-1}$  (–C=C), and  $1598 \text{ cm}^{-1}$  (–C–O).



**Figure 1: FTIR spectra of CCCF before and after adsorption of Congo red**

Surface information such as the shape and size of the particles can be obtained from the SEM micrographs. The adsorbent (**Figure 2**) has rough and coarse surface that can adsorb dyes from aqueous solutions. The activating agent created pores that can adsorb the Congo red molecules

from solutions. The Barrett-Joyner-Halenda (BJH) model was used to calculate the pore size distribution; the pore radius of the adsorbent is  $17.26 \text{ \AA}$  while the total pore volume is  $26.88 \text{ cm}^3/\text{g}$ . The specific surface area, using BET technique, of CCCF is  $88.93 \text{ m}^2/\text{g}$ .



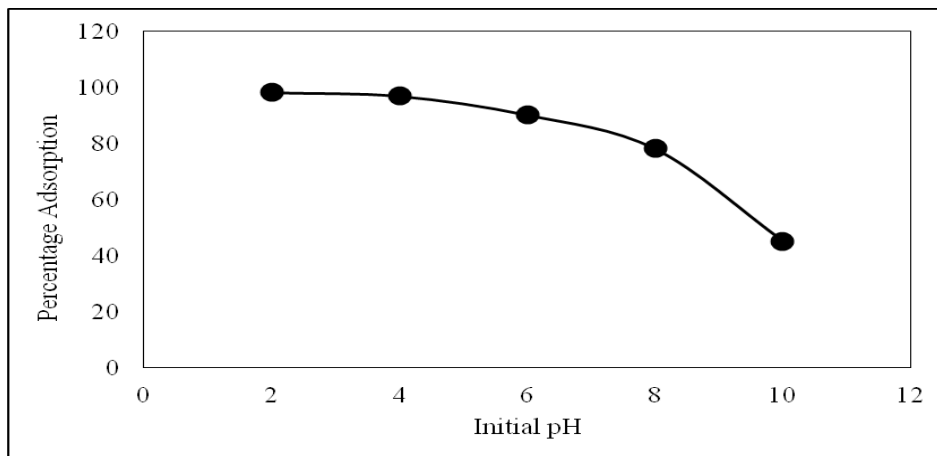
**Figure 2:** the SEM micrographs of CCCF at different magnifications A) 50X and B) 5000X

### Batch Adsorption Studies

#### Effect of pH on the Adsorption Efficiency of CCCF

A determining parameter in adsorption studies is the effect of acidity of the medium (Adebayo *et al.*, 2014; Rovani *et al.*, 2014; Bazzo *et al.*, 2016). Different adsorbing materials show different characteristics at various pH values. Removal of Congo red dye using CCCF was evaluated within the pH range of 2 to 10 as shown in **Figure 3**. For this adsorbent, the highest

percentage removal of 98.22% was observed at pH 2.0 while the lowest removal of 45.27% was observed at pH 10.0. In brevity, the adsorption capacities decrease as pH values increase and interaction of CCCF with Congo red is highly pH dependent, which is quite similar to what have been reported earlier (Gupta *et al.*, 2011; Rovani *et al.*, 2014; Saucier *et al.*, 2015a; Puchana-Rosero *et al.*, 2016). The optimum pH for the removal of Congo red by CCCF is 2, therefore, the pH of adsorbate solution was fixed at pH 2.0 for other aspects of the work.



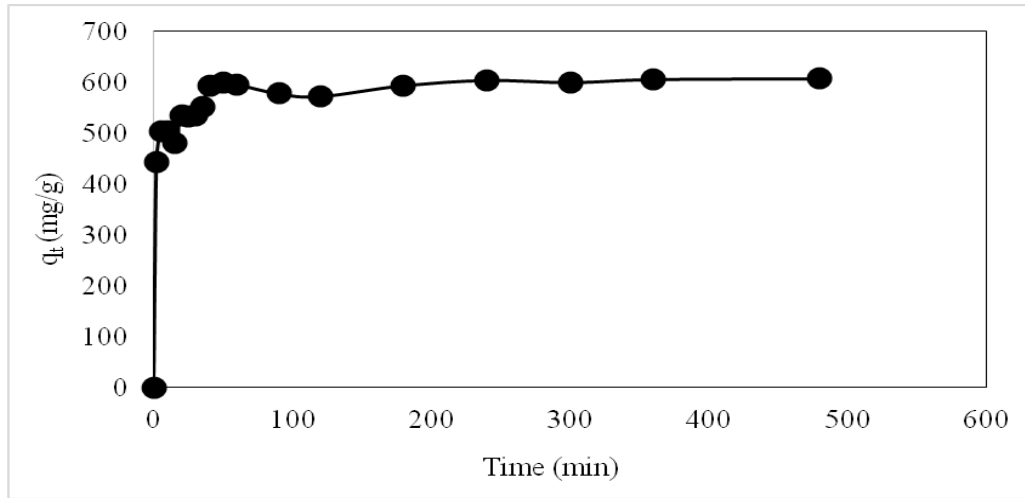
**Figure 3:** the effect of pH on the removal of Congo red using CCCF. *Conditions: temperature = 25 °C; contact time = 2 h; agitation speed = 160 rpm; initial Congo red concentration = 600 mg/L.*

Adsorption of adsorbate from aqueous solutions is a function of surface properties adsorbent (Thue *et al.*, 2016). The initial pH of adsorbate solution is important for the sorption capacity of the adsorbate if the mechanism of adsorption is electrostatic attraction. The surface of CCCF is readily available for adsorption of Congo red at acidic pH values. However, protonation of Congo red is weakened as pH values increase (basic pH values) due to

electrostatic repulsion between CCCF and Congo red molecules (da Farias *et al.*, 2018).

### Influence of Contact Time on Adsorption and Kinetic Models

The effect contact time is shown in **Figure 4**. It is clear that the extent of adsorption was rapid at the initial stage of the experiment. A steady state equilibrium was achieved at 1 h (equilibrium time) for CCCF.



**Figure 4:** influence of contact time on the removal of Congo red from aqueous solutions using CCCF. Conditions: temperature = 25 °C; contact time = 2 – 480 min; agitation speed = 160 rpm; initial Congo red concentration = 600 mg/L.

Four kinetic models were employed for analysis of time dependent data. The models are pseudo-first order, pseudo-second order, Elovich and Intraparticle diffusion models; the corresponding equations for these models are shown in Eqs (3) – (6).

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

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

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

$$q_t = k_{id} t^{0.5} + C \quad (6)$$

where  $q_t$  is the amount of Congo red adsorbed at time (t) (mg/g);  $q_e$  is the amount of Congo red adsorbed at equilibrium (mg/g);  $k_1$  is the pseudo first order rate constant ( $\text{min}^{-1}$ ),  $k_2$  (g/mg) is the pseudo-second reaction rate constant;  $\alpha$  is the initial adsorption rate (mg/g);  $\beta$  is related to the extent of surface coverage and the activation energy for chemisorption (g/mg);  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg}/(\text{g min}^{0.5})$ ).

The parameters of the four models used for kinetic analysis are presented in **Table 1**. The linear fitting of the pseudo-first order model (**Figure 5A**) exhibited low correlation value ( $R^2$ ), showing poor fit of the model while pseudo-second order model (**Figure 5B**) gave an ideal fit

for CCCF at 25°C as proven by the high  $R^2$  value ( $R^2 = 0.9998$ ). Similarly, the calculated equilibrium adsorption capacity ( $q_{e(cal)}$ ) and the experimental one ( $q_{e(exp)}$ ) agree closely for pseudo-second order model. The pseudo second order model gave better fit than the Elovich model. According to Elovich model in (Figure 5C), the initial adsorption rate is  $1.029 \times 10^8$  mg/g while the value of  $\beta$  that is related to the extent of surface coverage and the activation energy for chemisorption is 0.033974 g/mg.

The plot of the intra-particle diffusion model mechanism of the Congo red adsorption onto CCCF (Figure 5D), signify that the whole-time range could not be fitted by a straight line, but it could be separated into two linear regions, which imply that the Congo red adsorption onto CCCF is governed by more than one adsorptive process. The first region (fast phase) is related to the external surface adsorption or boundary layer diffusion while the second linear region (slow phase) is related to intraparticle diffusion through smaller pores of adsorbent (Galán *et al.*, 2013; Ribas *et al.*, 2014; dos Santos *et al.*, 2015).

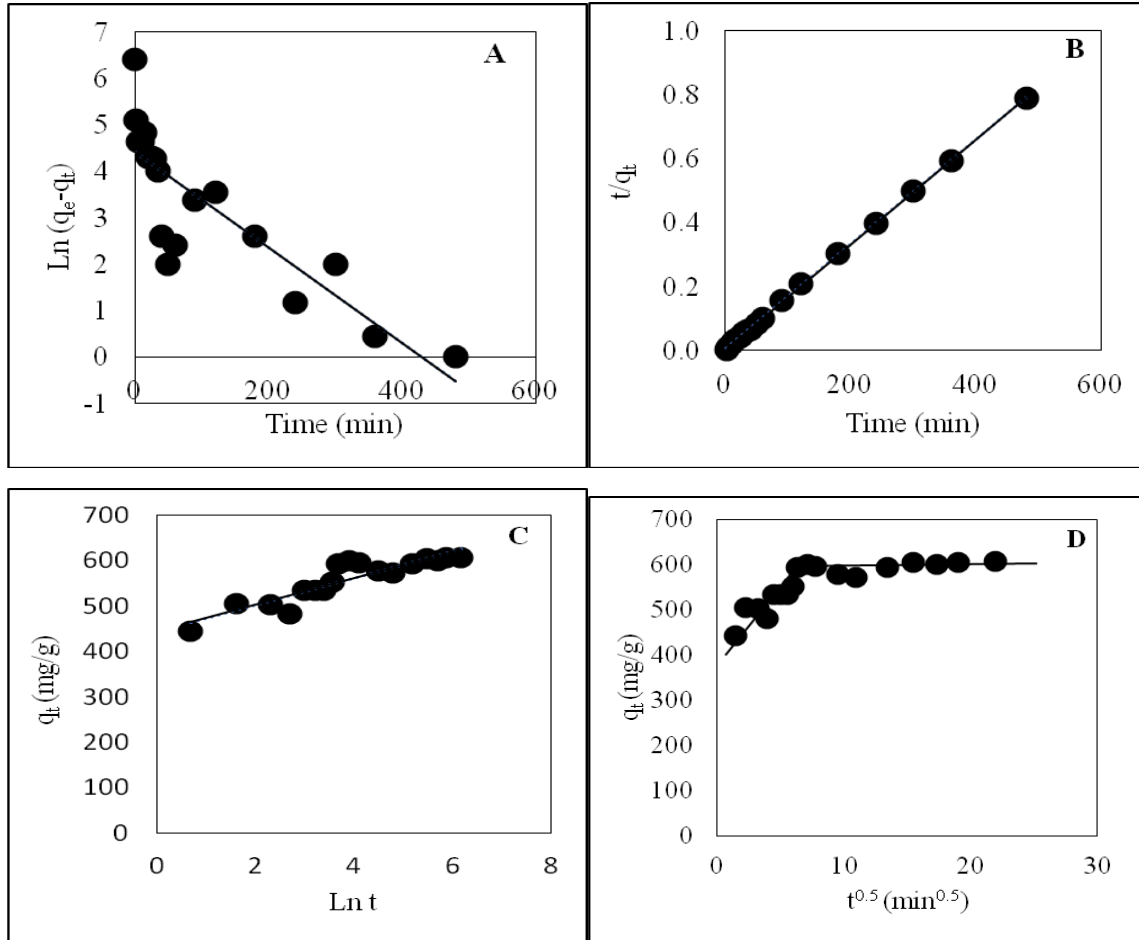
**Table 1: kinetic parameters of the adsorption of Congo red onto CCCF**

| <b>Pseudo First Order</b> |         |
|---------------------------|---------|
| $k_1$                     | 0.0103  |
| $q_e (cal)$               | 82.574  |
| $q_e (expt)$              | 607.383 |
| $R^2$                     | 0.7237  |

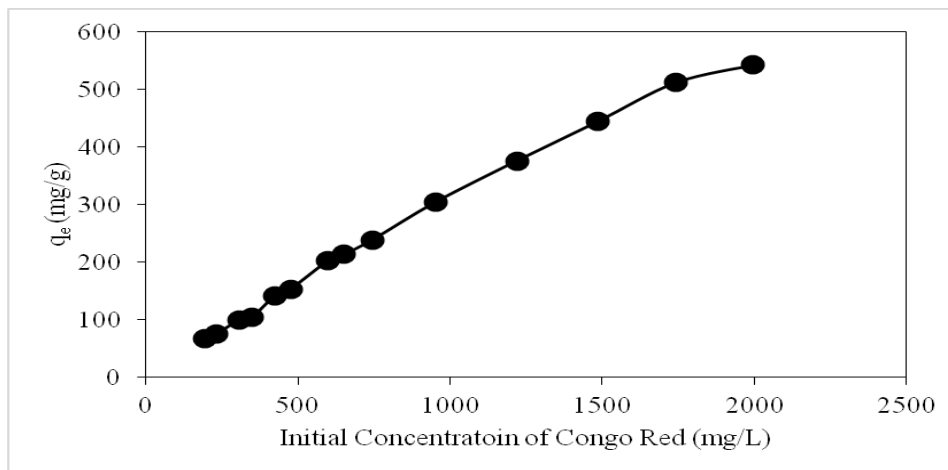
| <b>Pseudo Second Order</b>     |                     |
|--------------------------------|---------------------|
| $k_2$                          | 0.0005545           |
| $q_e (cal)$                    | 625.000             |
| $q_e (expt)$                   | 607.383             |
| $R^2$                          | 0.9998              |
| <b>Elovich</b>                 |                     |
| $\beta$                        | 0.033974            |
| $\alpha$                       | $1.029 \times 10^8$ |
| $R^2$                          | 0.814               |
| <b>Intraparticle diffusion</b> |                     |
| $k_{id}$                       | 6.2544              |
| $C$                            | 502.13              |

### **Effect of Initial Concentration of Congo Red on Adsorption and Application of Equilibrium Models**

The effect of initial Congo red concentration on the adsorption capacity was investigated at pH 2 using 50 mg of CCCF and 20 ml of Congo red solution. The dye-binding capacity of an adsorbent is related to the initial concentration of dye, which depends on the available binding sites on an adsorbent surface (Daneshvar *et al.*, 2014). Therefore, as shown in of Figure 6, the percentage of dye removal increases as the initial concentration increases because of the unsaturation of adsorption sites on the adsorbent surface. Higher adsorption capacity was obtained at the higher initial concentrations of Congo red.



**Figure 5:** the kinetic plots of adsorption of Congo red onto CCCF A) pseudo first order kinetic; B) the pseudo second order kinetic; C) the Elovich; and D) the intra-particle diffusion. *Conditions: temperature = 25 °C; contact time = 2 – 480 min; agitation speed = 160 rpm; initial Congo red concentration = 600 mg/L.*



**Figure 6:** dependence of initial dye concentration on removal of Congo red from aqueous solutions using CCCF. *Conditions: temperature = 25 °C; contact time = 2 h; agitation speed = 160 rpm; initial Congo red concentration = 200 – 2000 mg/L.*



Equilibrium relationships between dye molecules and adsorbent can be obtained from isothermal studies. The parameters of the equilibrium models provide explanation for mechanism of adsorption, affinity of the adsorbents for adsorbates and surface properties of adsorbents (dos Santos *et al.*, 2014). The adsorption characteristics CCCF were evaluated using Langmuir isotherm (Langmuir, 1918), Freundlich isotherm (Freundlich, 1906), and Temkin model (Tempkin, and Pyzhev, 1940). The Langmuir, Freundlich and Temkin models are depicted using Eqs (7), (8), and (9), respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (7)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

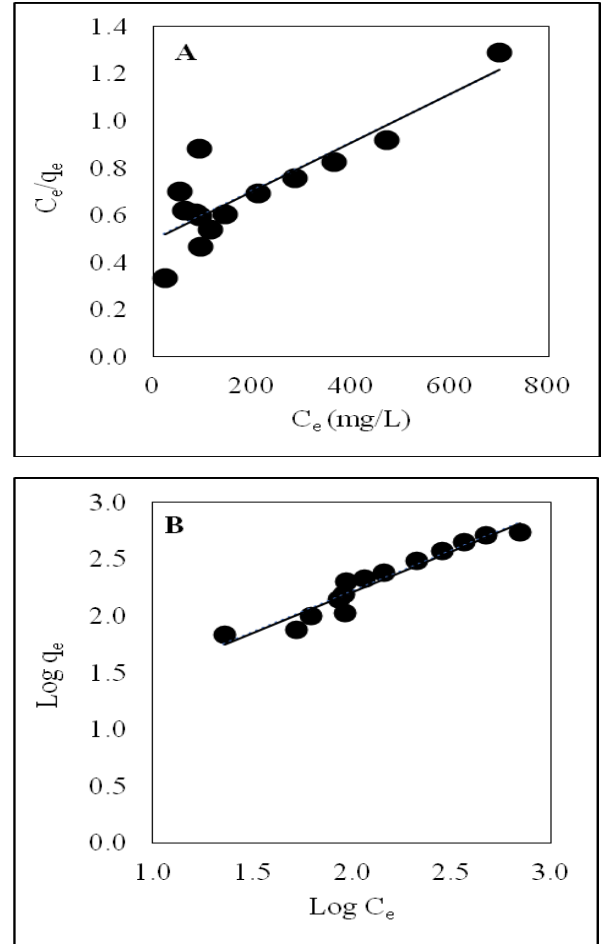
$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \quad (9)$$

where  $q_e$  is the equilibrium amount of Congo red adsorbed (mg/g);  $C_e$  the equilibrium concentration of the Congo red (mg/L);  $q_m$  is the monolayer adsorption capacity of the adsorbent (mg/g);  $K_L$  is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.  $K_F$  and  $n$  are Freundlich constants, which are characteristics of the adsorption system and related to adsorption capacity and adsorption intensity;  $A_T$  is the Temkin isotherm equilibrium binding constant (L/g);  $b_T$  is the Temkin isotherm constant related to heat of sorption (J/mol),  $R$  is the universal gas constant (8.314 J/mol K);  $T$  is Temperature (K).

The Langmuir, Freundlich, and Temkin adsorption isotherms at 25°C are shown in **Figures 7A, B, and C**, respectively. **Table 2** shows the parameters of the three models. The data at 25°C and other temperature values used in this study show that adsorption isotherm of Freundlich were followed because Freundlich model successfully fit the experimental isothermal

data based on the value of  $R^2$  in **Table 2**. The CCCF has both micropore and mesopore surfaces.

The maximum adsorption capacity ( $q_{max}$ ) value of CCCF at 25°C for Congo red is 1000 mg/g. From the Freundlich model, the values of  $n$  of the lie between 1 and 10, which indicates that the surface CCCF is heterogeneous (Kadirvelu and Namasivayam, 2000).



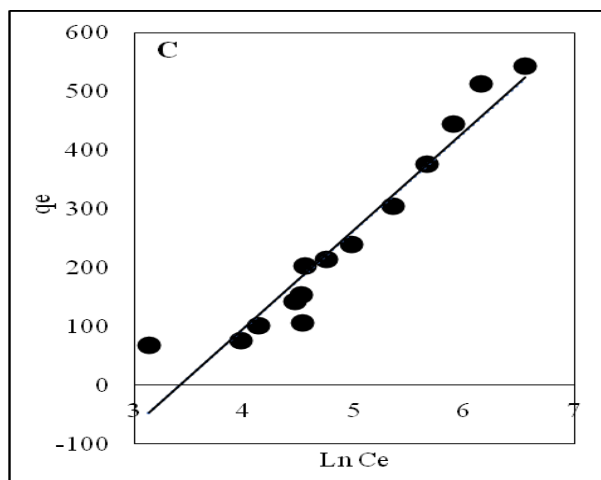


Figure 7: Equilibrium models of removal of Congo red using CCCF A) Langmuir plot; B) Freundlich plot; and C) Temkin plot. Conditions: temperature = 25 – 50 °C; contact time = 2 h; agitation speed = 160 rpm; initial Congo red concentration = 200 – 2000 mg/L.

Table 2: Equilibrium parameters of adsorption of Congo red using CCCF

|                   | 25°C     | 30°C                   | 35°C     | 40°C    | 50°C                   |
|-------------------|----------|------------------------|----------|---------|------------------------|
| <b>Langmuir</b>   |          |                        |          |         |                        |
| $q_m$             | 1000.000 | 476.190                | 588.235  | 526.316 | 252.462                |
| $K_L$             | 0.002008 | $5.181 \times 10^{-5}$ | 0.007784 | 0.0179  | $2.422 \times 10^{-5}$ |
| $R^2$             | 0.7381   | 0.8814                 | 0.8081   | 0.9669  | 0.7924                 |
| <b>Freundlich</b> |          |                        |          |         |                        |
| $n$               | 1.390    | 3.308                  | 0.2528   | 3.956   | 3.821                  |
| $K_F$             | 5.911    | 42.766                 | 75.405   | 70.502  | 75.370                 |
| $R^2$             | 0.9252   | 0.9991                 | 0.9257   | 0.9665  | 0.9463                 |
| <b>Temkin</b>     |          |                        |          |         |                        |
| $K_T$             | 0.03299  | 0.317                  | 1.701    | 0.930   | 1.574                  |
| $b_T$             | 14.853   | 43.394                 | 46.583   | 37.754  | 48.326                 |
| $R^2$             | 0.9188   | 0.676                  | 0.6275   | 0.8653  | 0.8700                 |

### Thermodynamic Studies

A good indicator of the nature of adsorption is temperature. The effect of temperature was investigated in this work (Figure

8A). The adsorption capacity increased with increasing temperature from 25 to 40 °C, then decreased at 50 °C. The removal of Congo red

using the CCCF adsorbent is temperature dependent.

The thermodynamic parameters in **Table 3** were calculated using Eqs (10) – (12). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept, respectively, of van't Hoff plot (**Figure 8B**) using Eq. (12).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

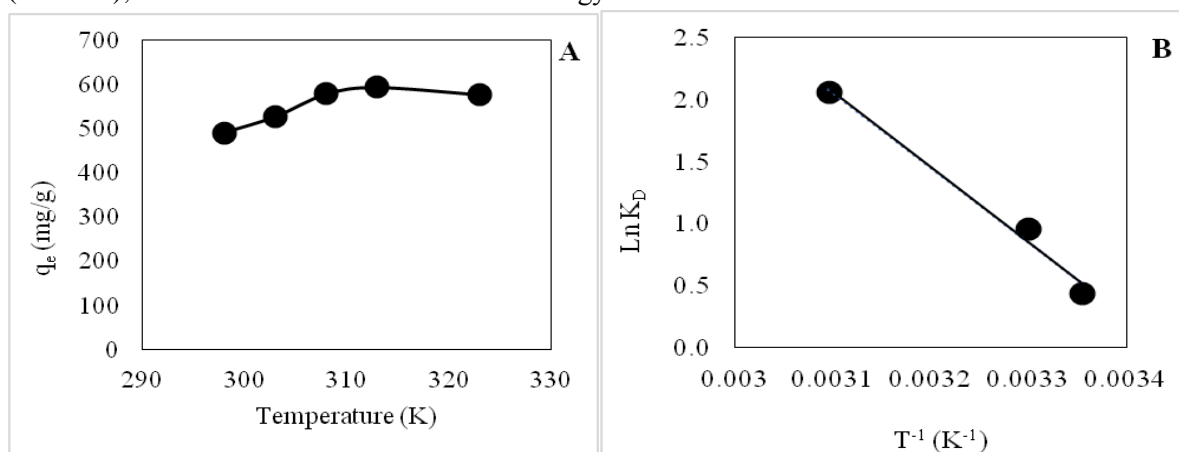
$$\Delta G^\circ = -RT \ln K_D \quad (11)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where  $\Delta H^\circ$  is the standard enthalpy change (kJ/mol);  $\Delta S^\circ$  is the standard entropy change (J/mol K);  $\Delta G^\circ$  is the standard Gibb's free energy

(kJ/mol); R is the universal gas constant (8.314 J/K) mol; T is temperature (K); and  $K_D$  is equilibrium adsorption constant of the isotherm fits (which must be converted to SI units using the molecular mass of the dye).

The negative values of  $\Delta G^\circ$  imply that the Congo red adsorption onto CCCF is a favourable and spontaneous process at all experimental temperatures. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  obtained in this study are  $-50.087$  kJ/mol and  $172.374$  J/mol K, respectively. The interaction between CCCF and Congo red was an exothermic process. There was an increase in randomness at the solid/liquid interface because  $\Delta S^\circ$  has positive value.



**Figure 8:** A) effect of temperature on the removal of Congo red using CCCF; and B) van't Hoff plot. Conditions: temperature = 25 – 50 °C; contact time = 2 h; agitation speed = 160 rpm; initial Congo red concentration = 1000 mg/L.

**Table 3:** thermodynamic parameters of adsorption of Congo red onto CCCF

| Temperature (K) | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol K) |
|-----------------|---------------------------|---------------------------|----------------------------|
| 298             | -1.0826                   |                           |                            |
| 303             | -2.4010                   | -50.087                   | 172.374                    |
| 323             | -5.5327                   |                           |                            |

## CONCLUSION

Clay–Corn cob–FeCl<sub>3</sub> composite was prepared and used as adsorbent for removal of Congo red from aqueous solutions. The adsorbent

was characterised using FTIR spectroscopy, SEM, and Nitrogen adsorption/desorption isotherm. The optimum pH for adsorption of Congo red onto CCCF was pH 2 while the equilibrium time for the adsorption process was 1 h. Four kinetic models

were used to test the kinetic data. The pseudo-second order model gave the best fit. The equilibrium data was evaluated using Langmuir, Freundlich and Temkin models. The best isotherm model that described the interaction of Congo red with CCCF was the Freundlich model. The maximum adsorption capacity ( $Q_{max}$ ) was 1000.00 mg/g. Thermodynamic studies calculations suggested that the Congo red adsorption from aqueous solutions using CCCF was spontaneous and exothermic. The CCCF adsorbent was effective for removal of Congo red from aqueous solutions.

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