

KINETICS AND SORPTION MODELS FOR ADSORPTION OF CONGO RED DYE FROM AQUEOUS SOLUTION ONTO *PENICILLIUM NOTATUM*-BASED CHITOSAN

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Abstract

The kinetics and sorption models for the adsorption of Congo red dye from aqueous solution onto *P. notatum*-based chitosan were studied. The adsorption process was carried out in a batch system as a function of contact time and initial concentration of dye. The results showed that optimum removal efficiency of 84.6% was attained at initial dye concentration of 40mg/L at equilibrium time of 140 minutes. The pseudo second order model had a better description of the adsorption kinetics with a coefficient of determination (R^2) of 0.9814 and rate constant of 0.1936 gm/g.min. The diffusion model shows that the adsorption of Congo red dye onto chitosan was governed by both intraparticle and film diffusion. The adsorption isotherm was fitted more to Langmuir isotherm with maximum monolayer adsorption capacity of 1.6108mg/g.

Keywords: Chitosan, Congo red dye, *Penicillium notatum*, adsorption capacity, decolourisation

Introduction

Dyes are the major water pollutants in most of the fabric and textile industries. Congo red dye is one of the popular water-soluble azo dyes commonly used for dyeing variety of materials such as nylon, wool and silk in the textile industries. It is also greatly used in biological and chemistry laboratories. Congo red is a toxic chemical considered as a serious health threat to humans because its ingestion can irritate

eye, skin, mucous membrane and upper respiratory tract. The harmful consequences of Congo red dye are severe headache, nausea, water-borne diseases such as dermatitis and loss of bone marrow leading to anaemia (Marandi *et al.*, 2011). It is capable of causing carcinogenic effects in living things changing the biological life of organisms exposed to it (Kumar *et al.*, 1998). The chemical structure of Congo red dye is shown in Figure 1.

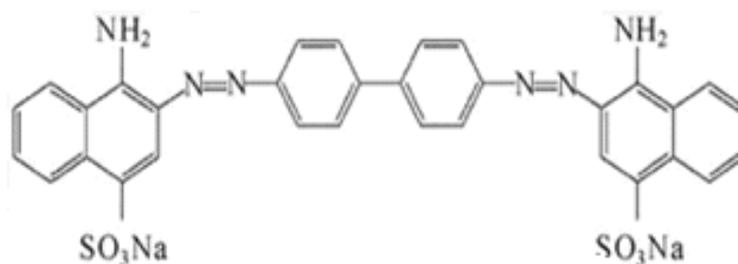


Figure 1: Chemical structure of Congo red

Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) with formula: $C_{32}H_{22}N_6Na_2O_6S_2$. The Congo red molecule is symmetric and consists of two identical amino-substituted naphthalene-sulphonate groups connected by azo linkages to a central biphenyl group (Ojala *et al.*, 1995). The poly-aromatic rings character of Congo red dye correlate with the elongated phobicity of the molecules, which favours self-assembling. Congo red binds to proteins not as a single molecule but as a ligand represented by a group of self-assembled dye molecules (Stopa *et al.*, 2003).

Chitosan is a natural polysaccharide comprising of copolymers of glucosamine and N-acetylglucosamine. It can be obtained by the partial deacetylation of chitin. Chitosan in its crystalline form is insoluble in aqueous solutions above pH7; however, the protonated free amino groups on glucosamine facilitate solubility of the molecule in dilute acids (pH6.0) (Martino *et al.*, 2005). Chitin is a natural polysaccharide of major importance among the families of biological

macromolecules. Chitin and chitosan are the second-most abundant high molecular-weight and environmentally friendly biopolymers (Abdulkarim *et al.*, 2013). Chitin is the main component of crustacean shells (crab, prawn etc.) and the cell walls of fungi such as *Penicillium* species (Latha, 2013; Ahila *et al.*, 2014). Chitosan is obtained from chitin by demineralisation, deproteination and deacetylation processes. Being that fungal mycelia have lower levels of inorganic materials compared to crustacean shells, therefore, no demineralization treatment is required during processing (Wu *et al.*, 2005).

Various methods of removing colour from industrial wastewater include coagulation, adsorption, photo-oxidation, filtration and biological treatment (Patil *et al.*, 2011). Adsorption has an edge over other treatment methods due to its sludge free operation, and thorough removal of dyes even from dilute solutions (Negrulescu *et al.*, 2014). Adsorption is usually described by isotherms which show how much solute can be adsorbed by the adsorbent at given conditions. Adsorption isotherms (Freundlich and Langmuir) relate the concentration of

solute on the surface of the adsorbent to the concentration in solution.

The Langmuir isotherm is an empirical isotherm where molecules of adsorbate are deposited only on the free surface of the adsorbent. The linearized form of Langmuir equation is given in equations (1) (Mittal *et al.*, 2007).

$$\frac{1}{q_e} = \frac{1}{Q_s} + \frac{1}{Q_s k_L C_e} \quad (1)$$

Where, C_s is the equilibrium concentration of adsorbate (mg/L).

q_s is the amount of solute adsorbed per gram by the adsorbent at equilibrium (mg/g).

Q_s is maximum monolayer coverage capacity (mg/g).

K_L is Langmuir isotherm constant (L/mg).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant, also referred to as separation factor.

$$R_L = \frac{1}{1 + (K_L C_0)} \quad (2)$$

where C_0 is initial concentration. The value of R_L indicates the shape of the isotherm to be linear ($R_L=1$), unfavourable ($R_L>1$), irreversible ($R_L=0$) and favourable ($0<R_L<1$) (Dada *et al.*, 2012).

The Freundlich equation is one of the earliest empirical equations used to describe adsorption equilibrium data. This model can be applied to non-ideal sorption. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-to-solute interactions.

The linear form of the equation is given as:

$$\text{Log}q_e = \text{Log}k_F + \frac{1}{n}\text{Log}C_e \quad (3)$$

where k_f and n are sorption capacity and intensity respectively (Piccin *et al.*, 2011).

Decolourisation of dye in aqueous solution by chitosan occurs via adsorption process. Though other low price adsorbents such as banana and orange peels (Annadurai *et al.*, 2002), and rice husks (Ong *et al.*, 2009) have been used in adsorption processes; not all the adsorbents have been effective in colour removal (Negrulescu *et al.*, 2014). Therefore, this study is focused on the decolourisation of Congo red dye in aqueous solution using *P. notatum*-based chitosan.

2.0 Materials and Methods

2.1 Materials

Penicillium notatum biomass was sourced from the Department of Plant Biology and Biotechnology, University of Benin, Benin city, Nigeria. All reagents and chemicals used in this study were of analytical grade. Congo red dye, an anionic dye with molecular weight of 696.67g/mol was obtained from Department of Chemistry, University of Benin, Benin city, Nigeria.

2.2 Methods

Preparation and Characterisation of *P. notatum*-based chitosan

The *P. notatum* powder was dried at 60°C in an oven, and then mixed with 1M sodium hydroxide solution in the ratio of 1:30w/v and autoclaved at 121°C for 15 minutes to remove the protein content. The mixture was centrifuged, and the insoluble particles were collected and washed with distilled water. The particles were then mixed with 2% hydrochloric acid and heated at 95°C for 6 hours. The mixture was centrifuged, and the supernatant was adjusted to pH 9 using 2M sodium hydroxide to precipitate

the chitosan in the supernatant. The resulting solution was centrifuged and the residue (chitosan) was washed with distilled water and dried at 60°C to constant weight (Ebrahimzadeh *et al.*, 2013; Wu *et al.* 2005). The prepared chitosan was characterised using Fourier transform infra-red (FTIR) (Shimadzu 8300BX) analysis

Decolourisation of Congo red dye in aqueous solution (Adsorption process)

Various initial concentrations (20 to 100 mg/L) of dye solution were prepared by dissolving appropriate quantity of Congo red dye in distilled water. The adsorption study was conducted in a batch system. 200ml of dye solutions were dispensed into separate Erlenmeyer flasks containing 100mg of chitosan. The mixture was agitated at room temperature (28-30°C) in an orbital shaker (model THZ-82) at a speed of 160 rpm for three hours. Samples (20ml) were withdrawn at pre-determined time interval and filtered. The absorbance of the filtrate was measured in a UV/VIS spectrophotometer (T-80 model) at a wavelength of 530nm. A standard curve relating absorbance to dye concentration was used to determine the residual concentrations of the samples. The effects of contact time and dye concentration on adsorption capacity were determined from the data obtained. The percentage decolourisation of the dye, the amount of dye adsorbed at time *t* and equilibrium,

$$\% \text{ decolourisation} = \frac{C_o - C_t}{C_o} \times 100 \tag{4}$$

$$q_t = \frac{(C_o - C_t)V_d}{W_c} \tag{5}$$

$$q_e = \frac{(C_o - C_e)V_d}{W_c} \tag{6}$$

where, C_o = initial dye concentration (mg/L), C_t = dye concentration at time t (mg/L), C_s = dye concentration at equilibrium (mg/L), V_d = volume of dye solution (L), W_c = weight of chitosan (g).

3.0 Results and Discussion

3.1 Characterizations of chitosan

Fourier transform infrared (FTIR) spectroscopic analysis was carried out to determine the functional groups present in *P. notatum*-based chitosan powder. Figure 2 shows the FTIR spectrum characterised by various absorption bands of different functional groups. The band at 3435.22cm^{-1} in the range of $3000\text{-}3600\text{cm}^{-1}$ is characteristic of O-H stretch bond, corresponding to hydroxyl group, it is

indicative of the presence of carbohydrate, alcohols and/or phenols. The peaks in the range of $1537\text{-}1641\text{cm}^{-1}$ characterise C=C and N-H bonds showing the presence of carbonyl amides groups. The peak around 1261cm^{-1} gives a C-O stretch band which occurs as a result of esters and anhydrides present in the powder. The bands in the range of $2850\text{-}3000\text{cm}^{-1}$ are characteristic of C-H stretch attributed to alkyl groups (Dawood, and Li, 2013).

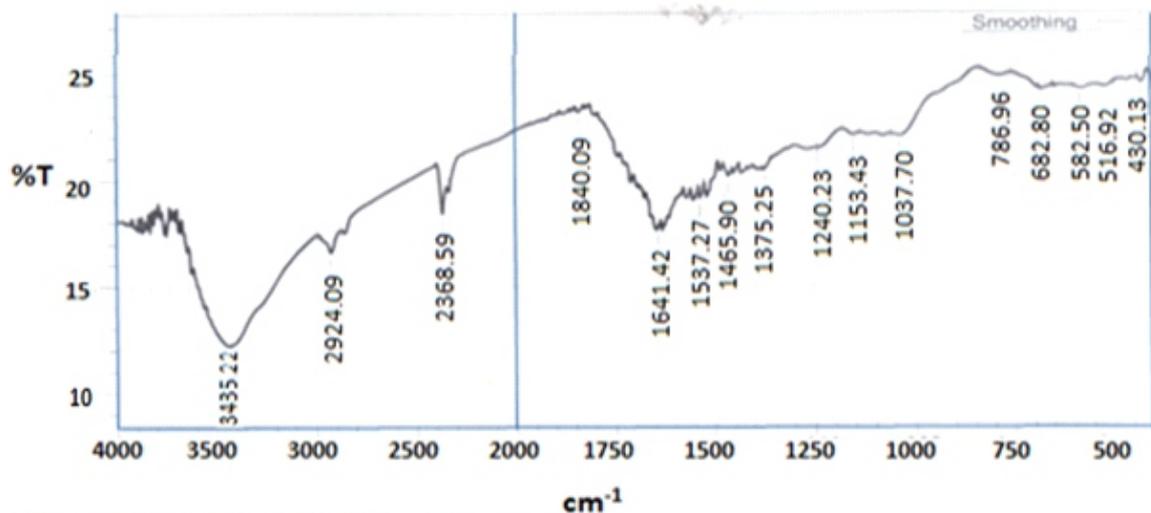
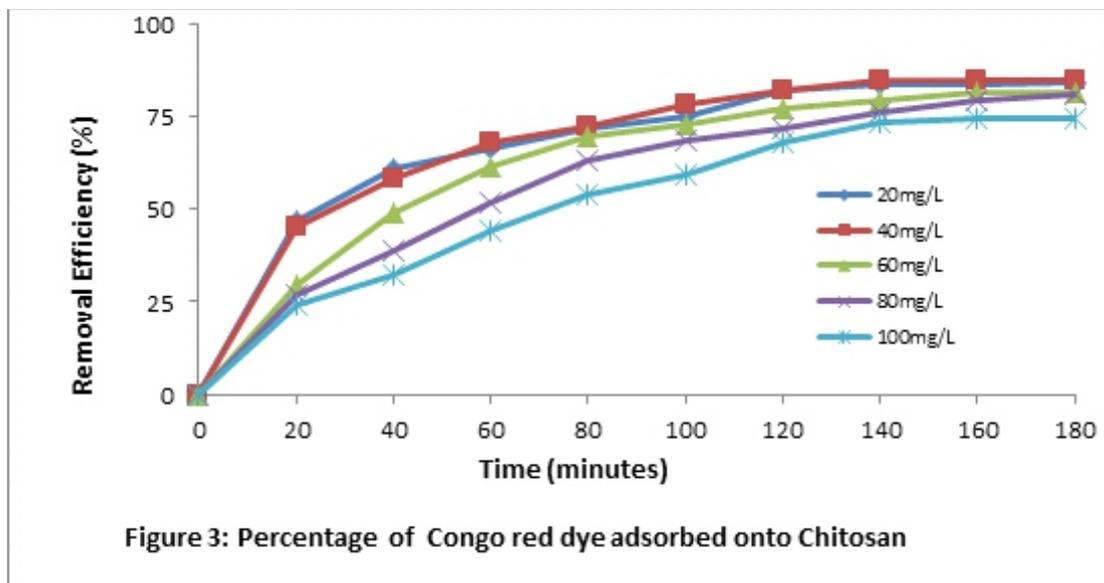


Figure 2: FTIR spectrum for chitosan from *P. notatum*

Effect of contact time

The percentage of Congo red dye removed at different initial concentrations as a function of contact time is presented in Figure 3. The results obtained under constant conditions of 100mg/L chitosan dosage, pH 7 and room temperature (28-30°C) revealed that the percentage removal of dye increases with increasing time. The

adsorption started quite rapidly at the initial time and then progressed steadily at a slower rate and finally attained equilibrium at an average time of 140 minutes. The percentage removal of Congo red dye ranges from 74.5% to 84.6 with the maximum percentage removal occurring at 40mg/L.



Effect of Initial Dye Concentration

The effect of initial concentration for the adsorption of Congo red dye is presented in Figure 4. The results showed that the amount of dye removed depends on the initial dye concentration. It was noticed that percentage removal was higher at the lower initial concentration, and decreases as the concentration increases. From Figure 4, the removal efficiency of 83.8% , 84.6% , 81.2% , 79.3% and 74.5% were attained at initial concentration of 20mg/L, 40mg/L,

60mg/L, 80mg/L and 100mg/L, respectively. This observation may be due to the fact that sufficient surface active sites of the adsorbent were available for the relatively fewer number of dye molecules at lower concentrations (Patil *et al.*, 2011). Higher dye concentrations are capable of affecting the chemical equilibrium between dye molecules in the liquid phase and the ones adsorbed onto the adsorbent surface (Marandi *et al.*, 2011).

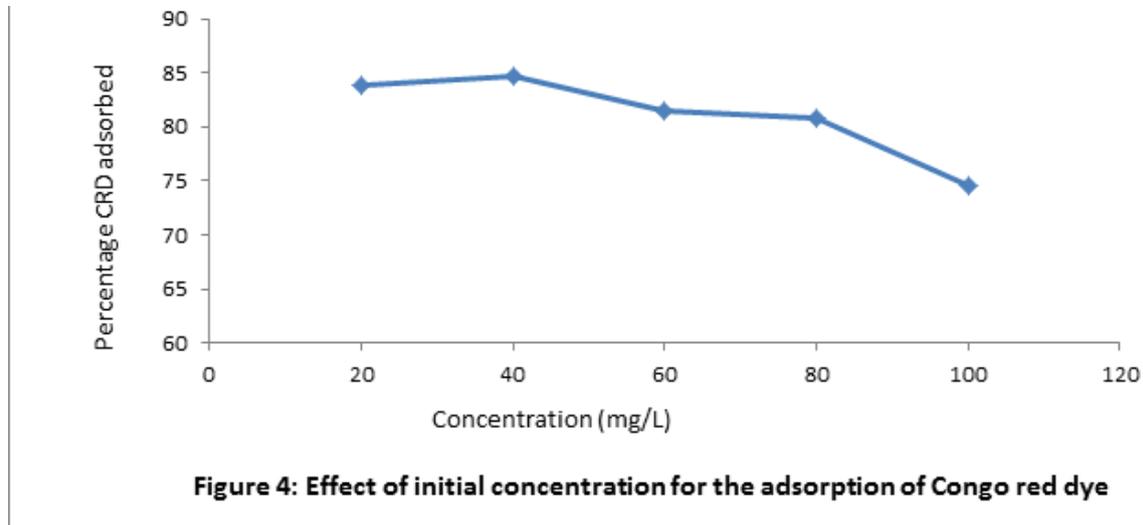


Figure 4: Effect of initial concentration for the adsorption of Congo red dye

3.2 Kinetics model equations

In order to study the rate of decolourisation of Congo red dye in aqueous solution, the most widely used kinetic models namely pseudo first order, the pseudo second order, and the intra-particle diffusion (Gerente *et al.*, 2007) were employed. Figures 5, 6 and 7 show the linear representation of pseudo-first order, pseudo-second order and intra-particle diffusion models for the adsorption of Congo red dye on chitosan. Adsorption kinetics is influenced by sorption reactions and mass transfer steps that govern the transfer of solutes from the bulk of the solution to the sorption sites on the surface

of the adsorbent particles. These mechanisms depend on the physical form and intrinsic structure of the adsorbent, the molecular weight and nature of the solute as well as the process conditions under which the adsorption was carried out (Gerente *et al.*, 2007).

Pseudo First Order Model

Pseudo first order was the first rate equation employed for sorption of liquid/solid system based on the solid capacity (Ho and McKay, 1999). The Lagergren rate equation for pseudo first order is given as:

$$\frac{d_q}{d_t} = K_1(q_e - q_t) \quad (7)$$

K_1 (min^{-1}) is a pseudo first order sorption rate constant.

Equation (7) is linearized to give:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (8)$$

The values of K_1 for the adsorption of Congo red dye at various initial concentrations are shown in Table 1. It was observed that K_1 reduces from 0.0125 min^{-1} to 0.0100 min^{-1} as the initial concentration increases from 20 mg/L to 80 mg/L . Further increase in concentration to 100 mg/L slightly increased K_1 to 0.011 min^{-1}

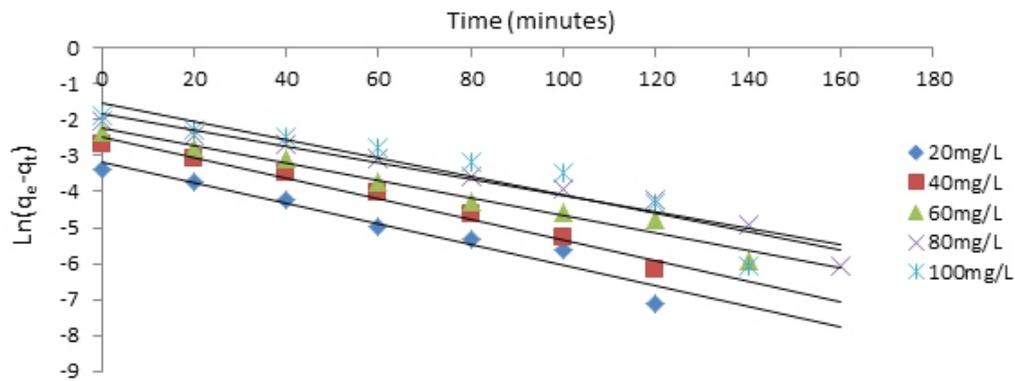


Figure 5: Pseudo-first order model for Adsorption of Congo red dye on chitosan

Pseudo Second Order Model

The adsorption mechanism was also subjected to pseudo second order chemisorption kinetics rate equation expressed as:

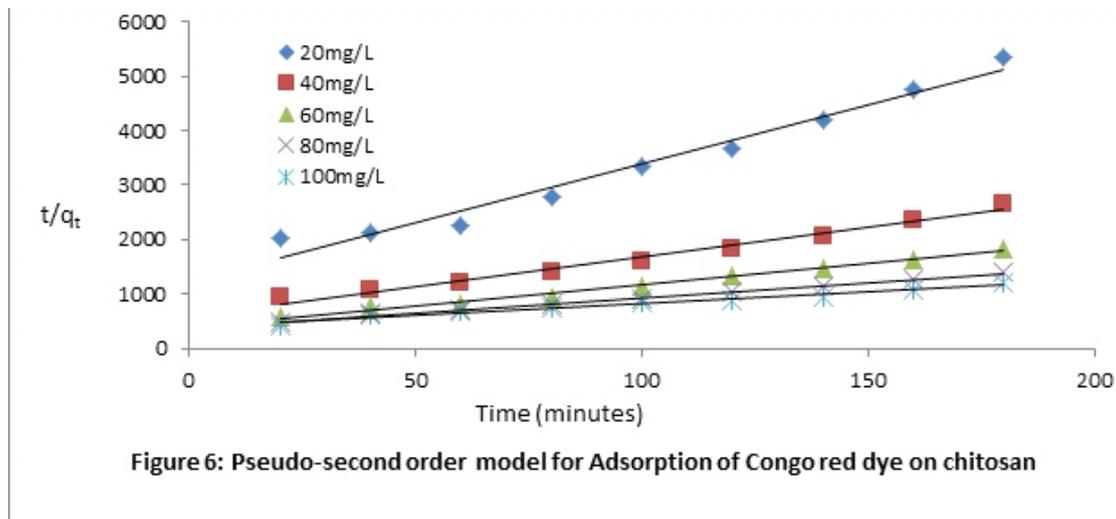
$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{9}$$

K_2 (g/mg.min) is the pseudo second order sorption rate constant. The linear form of the equation is given by:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

The kinetics parameters for the pseudo second order equation are shown in Table 1. The rate constant (K_2) decreases from 0.3868 g/mg.min to 0.0487 g/mg.min as the initial concentration increases from 20 mg/L to 100 mg/L . This observation suggests that more adsorption sites were available for fewer molecules of the dye at lower concentration. The R^2 and K_2 values were quite higher in pseudo second order model than the pseudo first order for all the

concentrations tested. This is an indication that the adsorption kinetics of Congo red dye from aqueous solution onto chitosan was better fitted to the pseudo second order rate model than the first order. This result is in conformity with the investigations carried out by Perju and Dragan (2010) and Mincea *et al.* (2013), where it was stated that pseudo second order better described the removal of azo dyes from aqueous solution using chitosan based composite hydrogel.



Intra particle diffusion-controlled sorption

To investigate the internal diffusion mechanism during adsorption, the intra-particle diffusion equation was used considering that adsorption is usually controlled by an external film resistance and/or intra-particle diffusion (Gerente *et al.*, 2007). The intraparticle diffusion model equation as proposed by Crank (1970) is given as follows:

$$q_t = K_{id} t^{0.5} \quad (11)$$

The coefficient K_{id} is determined from the initial linear slope of q_t versus $t^{0.5}$.

According to previous work by Perju and Dragan (2010), if the plot of intraparticle diffusion equation is not completely linear, and does not pass through the origin, then the intra particle diffusion cannot be said to be the only rate limiting step involved in the transport process, then equation (11) becomes:

$$q_t = K_{id} t^{0.5} + C_{id} \quad (12)$$

where C_{id} is intraparticle diffusion constant (mg/g), which is directly proportional to the boundary layer of the process. In addition to the linearity of the plot, the sorption mechanism is assumed to be intra particle diffusion if the following conditions are met: (1) High coefficient of determination (R^2) to ascertain applicability, (2) Straight line which passes through the origin and (3) Intercept $C_{id} < 0$. Deviation from (2) and (3) shows that the mode of transport is affected by more than one rate limiting step (Itodo *et al.*, 2010). The intraparticle diffusion constants are shown in Table 1. It was observed that all the boundary layers except the initial concentration of 100 mg/L were greater than zero which indicates that both intra-particle diffusion and external mass transfer (film diffusion) are considered as rate limiting steps, and that the values of C_{id} are directly related to the thickness of the boundary layer (Ho and McKay, 1999).

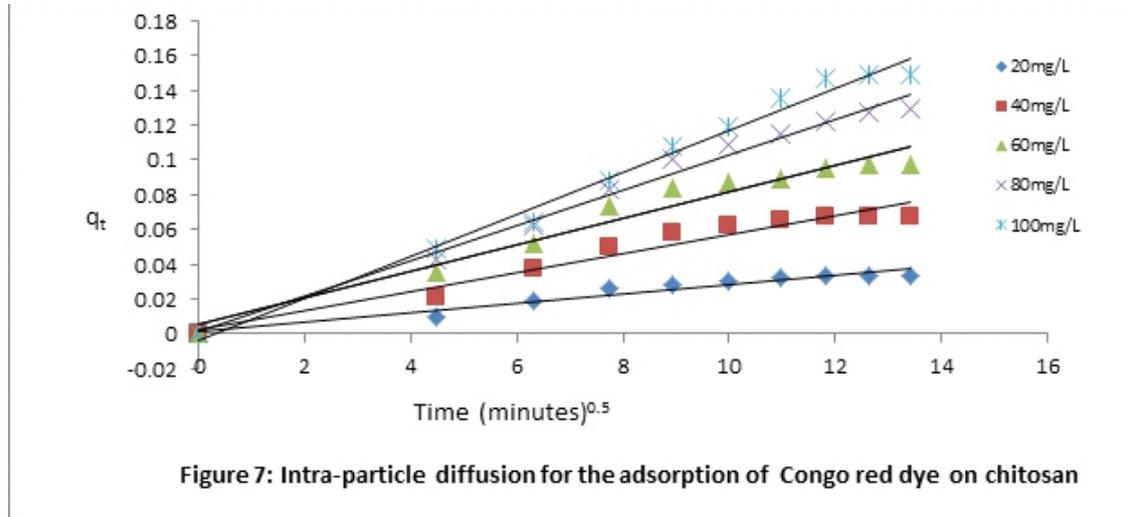


Table 1: Kinetics parameters for the adsorption of Congo red dye onto chitosan

| Concentration of dye (mg/L) | Pseudo-first order | | Pseudo-second order | | Intra-particle diffusion | | |
|-----------------------------|----------------------------|----------------|---------------------|----------------|-------------------------------------|-----------------|----------------|
| | K_1 (min ⁻¹) | R ² | K_2 (g/mg.min) | R ² | K_{id} (g/mg.min ^{0.5}) | C_{id} (mg/g) | R ² |
| 20 | 0.0125 | 0.9475 | 0.3868 | 0.9729 | 0.0027 | 0.0013 | 0.9441 |
| 40 | 0.0124 | 0.9797 | 0.1936 | 0.9814 | 0.0055 | 0.0024 | 0.9534 |
| 60 | 0.0105 | 0.9732 | 0.1607 | 0.9911 | 0.0077 | 0.0052 | 0.9590 |
| 80 | 0.0100 | 0.9516 | 0.0812 | 0.9944 | 0.0101 | 0.0014 | 0.9856 |
| 100 | 0.0110 | 0.8580 | 0.0487 | 0.9715 | 0.0121 | -0.0032 | 0.9868 |

3.3 Adsorption isotherms

Considering the adsorption of Congo red dye onto chitosan, the data obtained were fitted into Langmuir and Freundlich isotherm models.

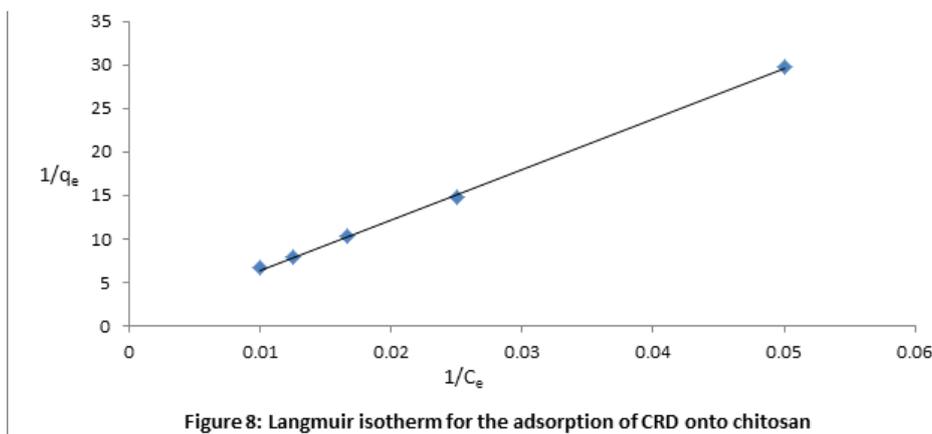
Langmuir isotherm

The values of maximum monolayer coverage, Q_0 (1.6108 mg/g) and Langmuir isotherm constant, K_L (0.011 L/mg) were computed using the slope and intercept of Figure 8. From the study of Okuo *et al.* (2009) and Piccin *et al.* (2011), it was observed that Q_0 depends on temperature

and other factors like chemical structure of solute and adsorbent, molecular size and nature of the adsorbent. The values of the separation factor (R_L) at different initial concentrations are presented in Table 2, and are between zero and one, given an indication that the adsorption process was favourable. It was also observed that R_L decreases from 0.8197 to 0.4761 as the initial concentration increases from 20 mg/L to 100mg/L. A similar trend was observed by Amenaghawon *et al.* (2014) where R_L values also decreases with increasing initial concentration.

Table 2: Values of R_L at different initial concentrations

| Initial concentration (mg/L) | R_L |
|---------------------------------|--------|
| 20 | 0.8197 |
| 40 | 0.6944 |
| 60 | 0.6024 |
| 80 | 0.5319 |
| 100 | 0.4761 |



Freundlich isotherm

The constants associated with the Freundlich isotherm model are sorption capacity (k_F) and sorption intensity (n) which provide information about the adsorption capacity and favourability of the system, respectively (Piccin *et al.*, 2011). The values of n and k_F as obtained from Figure 9 are presented in Table 3. Freundlich isotherm demonstrates that the

adsorption of Congo red dye is favourable because the values of n fell within the range of 1 and 10 (Okieimen and Osarumwense, 2006). The Freundlich equation does not consider all sites on the adsorbent surface to be equal; it is assumed that, once the surface is covered, additional adsorbed species can still be accommodated, that is, multilayer adsorption is predicted by this equation (Van Loon and Duffy, 2005).

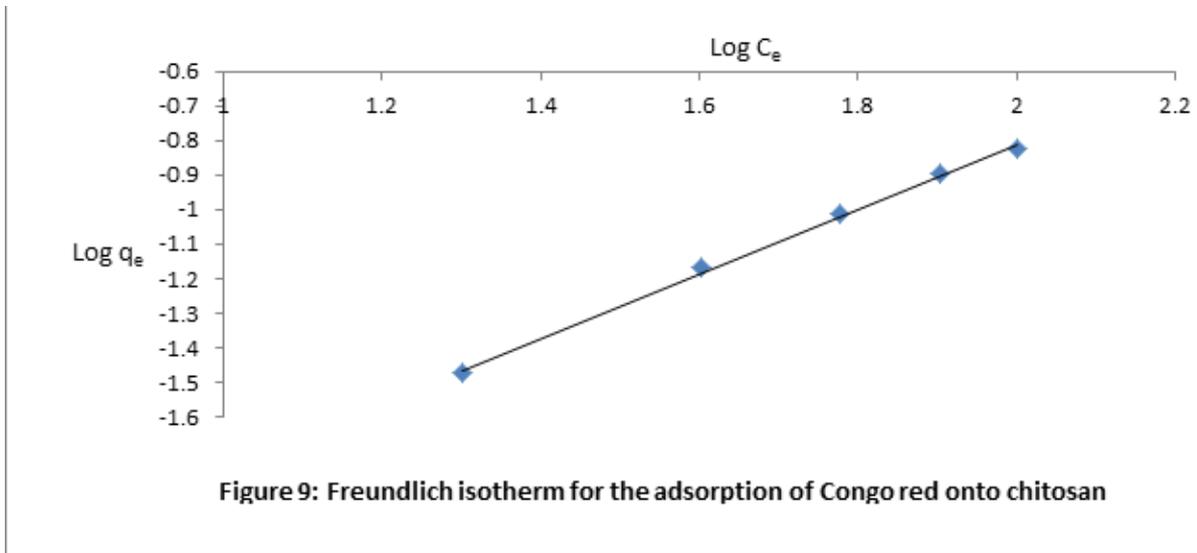


Figure 9: Freundlich isotherm for the adsorption of Congo red onto chitosan

Table 3: Isotherm parameters for adsorption of Congo red dye onto chitosan.

| Langmuir | | | Freundlich | | | |
|-----------------|-----------------|--------|-----------------|--------|-------|--------|
| K_L (L/mg) | Q_0 (mg/g) | R^2 | K_F (mg/g) | $1/n$ | n | R^2 |
| 0.011 | 1.6108 | 0.9993 | 0.021 | 0.9336 | 1.071 | 0.9977 |

4.0 CONCLUSION

The decolourisation of Congo red dye was carried out in a batch adsorption process as a function of contact time and initial concentration of the dye using chitosan prepared from *Penicillium notatum* biomass. FTIR analysis revealed that *P. notatum*-based chitosan contains several functional groups which include hydroxyl, carbonyl amide and alkyl groups. The kinetics and adsorption equilibrium were well described by the pseudo second order and the Langmuir isotherm models, respectively. The diffusion mechanism shows that the adsorption of Congo red dye onto chitosan was governed by both intraparticle and film diffusion. The study has proven that *P. notatum*-based chitosan is a good adsorbent for the removal of Congo red dye from aqueous solution.

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