ADSORPTION OF CONGO RED DYE UNTO *Luffa cylindrica* FIBERS: KINETIC AND THERMODYNAMIC STUDIES

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Abstract: Adsorptive removal of Congo Red dye from aqueous solution with *Luffa cylindrica* fibers was investigated. The effects of various experimental parameters such as the contact time, solution pH, temperature, biosorbent dosage and particle sizes were studied. Modelling of the kinetics data showed that pseudo-second order kinetic model provided the best fit for the process and increasing the adsorbent dosage increased the uptake of Congo Red dye. An optimum pH and contact time of 7.0 and 180 min were respectively used for the adsorption process in this study. The spectra obtained from Fourier Infrared Spectroscopy (FTIR) used for characterization of the adsorbent (*Luffa cylindrica*) revealed basic cellulosic functional groups which are good sites for adsorption. The adsorption process is endothermic with change in enthalpy ($\Delta H°$) =13201.04 KJ/mol; change in entropy ($\Delta S°$) = 26.3032 J/K/mol and positive values of Gibb's free energy for all temperatures used in the study. This study revealed that *Luffa cylindrica* cellulose could be used for removing Congo red dye from wastewater in an environmentally friendly way.

Keywords: Adsorption, thermodynamics, kinetic models, Congo Red dye, *Luffa cylindrica*

Introduction

"Colour the earth and kill it with sweet and subtle poison" is my slogan for the enormous havoc the use of dye has cause or created in our ecosystem. Dye is any organic compound with the ability to impact colour to other materials such as plastics, textile fibers, pulp and paper and dyestuffs, being a coloured substance itself. Dye application is today a massive industries and its usage in industries like textile mills, food, carpets, cosmetics, rubber, paper and a host of other industries where dyes are used to colour their products cannot be under-estimated (Kant, 2012).

As a result of the widespread use of dye in various industries, there are more than 10,000 available dyes for different purposes. Due to its origin and complex aromatic structure, dyes are stable and very difficult to biodegrade (Eren and Acar, 2006). From textiles mills alone, an approximate value between 8 – 20% of unutilized dyes and auxiliary chemicals were reported to be discharged into waste streams (Markandeya *et al.,* 2017; Al-Ghouti *et al.,* 2003; Pearce *et al.,* 2003). The discharge of millions litres of coluored effluent containing these hazardous toxic wastes is a significant cause of degradation to the environment and human illnesses. Components in dyes can accumulate in sediments and soils of the surrounding areas where the effluents are discharged and subsequently be leached into the ground water system if not directly discharged into the water bodies (Namasivayam and Sumithra, 2005). The accumulation of organic products in the environment is a topical problem for man because of the various adverse effects they produce or have on all forms of life; some dyes are mutagenic and carcinogenic and can cause severe damage to vital organs and systems in the human body. They lead to dysfunction of the kidney, brain, liver, reproductive system and the central nervous system (Kadirvelu e*t al.*, 2003).

Therefore, wastewater containing dyes should be given adequate treatment before discharge into the environment. Various treatment techniques such as Fenton process, ozonization, membrane separation, electrocoagulation, ion exchange resins, photochemical degradation, co precipitation, reverse osmosis and adsorption using different adsorbents have some associated disadvantages such as of high capital and operational cost (Ebraheim *et al.,* 2017; Kasiri *et al*., 2013; Shukla *et al.,* 2014). As promising as adsorption appears to be as a method for decolourization and removal of toxic components from dye wastewater, its use has been limited by the cost of commercial activated carbon. The removal of dye in an economical viable way has necessitated researches and studies on the use of plant fibers as possible low cost, renewable and readily available adsorbents for the treatment of dye wastewater. Studies have been carried out on the use of rice hull ash, sugarcane bagasse, sawdust, pine needle, mango seed kernel powder for the removal of dyes (Sud *et al.*, 2008; Salleh *et al.,* 2011) but very few are devoted to the study of the *Luffa cylindrica* fibers, hence the idea of directing a study in this direction.

Oladoja *et al.* (2009) used the *Luffa cylindrica* to remove Methylene Blue dye from aqueous solution and reported that the Freundlich Isotherm model favoured the theoretical adsorption capacity more than the Langmiur model; and that Pseudo second order kinetic model was fitted well to the experimental data for the entire process. Demir *et al.* (2008) reported that the adsorption of Methylene Blue onto *Luffa cylindrica* fibers will be relatively irreversible with an adsorption capacity of 49 mg/g; the second order kinetic model best explained the process, the reaction was exothermic with enthalpy as – 20 kJ/mol while the thermodynamic parameters revealed that the adsorption will be spontaneous without the need for high activation energy. Abdelwahab (2008) worked on the use of activated carbon obtained from *Luffa cylindrica* fibers for the removal of Orange Red dye from aqueous solution and reported an optimal pH of 1 and adsorption capacities of 38.8 and 50 mg/g for the different activated carbons he prepared. Pseudo-first order kinetic model provided the best mechanism for the process while from the thermodynamic point of view, the reaction was spontaneous and exothermic. Congo Red is a type of acid dye that is widely applied in the industries because of its wide colour range and ability to absorb light. It is a symmetric anionic sulfonated azo dye with structural formula [$C_{32}H_{22}N_6Na_2O_6S_2$].

Luffa cylindrica belongs to the family curcubitacea and is commonly grown in Japan, China, Asia, and in some parts of Africa. In Nigeria, its use as local sponge has been largely replaced synthetic sponge for bathing and washing of dishes. The sponge is a lignocellulosic material composed mainly of cellulose, hemi-cellulose and lignin with vascular fibrous tissues which permit the removal of pollutants in water (Segun *et al.,* 2014; Demir *et al.,* 2008).

This work is focused on the removal of Congo Red dye from water using a locally available agricultural material, *Luffa*

cylindrica as adsorbent in batch adsorption studies. The mechanism of adsorption was studied using the kinetics and thermodynamics involved in the process. The effects of different experimental conditions such as pH, adsorbent dose, temperature, particle size and time, on the adsorption process were examined.

Materials and Methods

Experimental

Adsorbent preparation

Dried *Luffa cylindrica* fruits (that is the sponge) used were sourced from Oye Ekiti in Ekiti State, Nigeria. The collected *Luffa* was dehusked and the seeds were removed before the fibers were washed clean with water to remove any water soluble contaminants and debris attached to it.

The washed *Luffa* fibers were sun dried for two days and later dried in an oven at a temperature of 80ºC for six h. The dried *Luffa* was then pound in a local metal mortar (Agate mortar) in order to obtain finer but non homogenous pieces of different undetermined sizes. The pounded *Luffa* was sieved through different mesh sizes of the USA standard sieve (150, 425, 600 and 1180 µm) from which particular sieve size (600 µm) was used for this research work (Oladoja *et al.*, 2009; Demir *et al*., 2008). FTIR absorption spectra (before and after the sorption experiments) were obtained using Nicolet iS10 Model Fourier Transform Infra-Red Spectrometer in order to be able to characterize the adsorbent.

Preparation of dye solution

Stock solution (500 ppm) of Congo Red was prepared by dissolving 0.5 g of Congo Red dye powder (C.I number=22,120; MW= 696.7 g/mol and λmax = 497 nm) obtained from Fine Chemicals, India, in deionized water in a 500 mL volumetric flask and made to the mark. The stock solution was diluted to the working concentrations required for this work using serial dilution. pH of the solution was adjusted by adding drops of HCl (0.1 M) and NaOH (0.01M) where necessary and monitored with a pH meter (model 15, Fisher Scientific).

Adsorption experiments

The adsorption experiments carried out in triplicates involved contacting a known mass (0.2 g) of the *Luffa* fibers with a certain volume (20 ml) of the prepared dye of desired concentration (20 ppm) in conical flasks and agitated vigorously at 165 rpm for 180 min. At the end of the predefined time the suspension was centrifuged and the supernatant was analysed using a UV/Visible spectrophotometer (Shimadu UV1601, UV/VIS) at maximum absorption wavelength of 497 nm. The quantity or amount of Congo Red adsorbed (mg/g) was calculated using Equation 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad 1$$

Where: C_0 and C_e (C_t) are the initial and final concentrations of dyes (mg/L), respectively; Vis the volume of the solution (L); m is the mass of the *Luffa* fibers used (g).

The experiments were performed at temperature (28 ± 2^0C); the experimental variables considered were in the following ranges: pH of dye solution 1 – 8; *Luffa* fibers dose 0.1 – 1.5 g; contact time 5 – 360 min, adsorbent particle size 150 - 1180 µm (Gedam *et al.*, 2019).

Results and Discussion

Characterization

The FTIR Spectroscopic analysis was done on both the Fresh and Spent *Luffa* fibers samples using the Nicolet iS10 Model Fourier Transform Infra-Red Spectrometer. The FTIR spectra presented in Fig. 1 showed the peak at 600 cm^{-1} are due to stretching vibration of S–O groups; while those at 901 cm^{-1} was due to C–C stretching; vibration due to C-O group was obtained at 1102 cm^{-1} . The deformation at 1048 cm^{-1} is related to C–O–H; the band at 1375 cm^{-1} could be attributed to COO^- symmetric stretching vibration; the presence of the peaks at 1635 and 1439 cm^{-1} indicate the presence of COO of carboxyl group and stretching of carbon double bond carbon (C=C) in aromatic rings, respectively. The band at 2902 and 2358 cm^{-1} indicate aliphatic group (C-H) stretching vibration and the broad absorption band at 3428 cm^{-1} corresponds to the stretching vibration of hydroxyl group (OH) (Tanobe *et al*., 2005; Chakraborty *et al*., 2003; Pathania *et al*., 2017). These surface functional groups on the *Luffa cylindrica* fibers are good point of interaction for Congo Red Dye molecules.

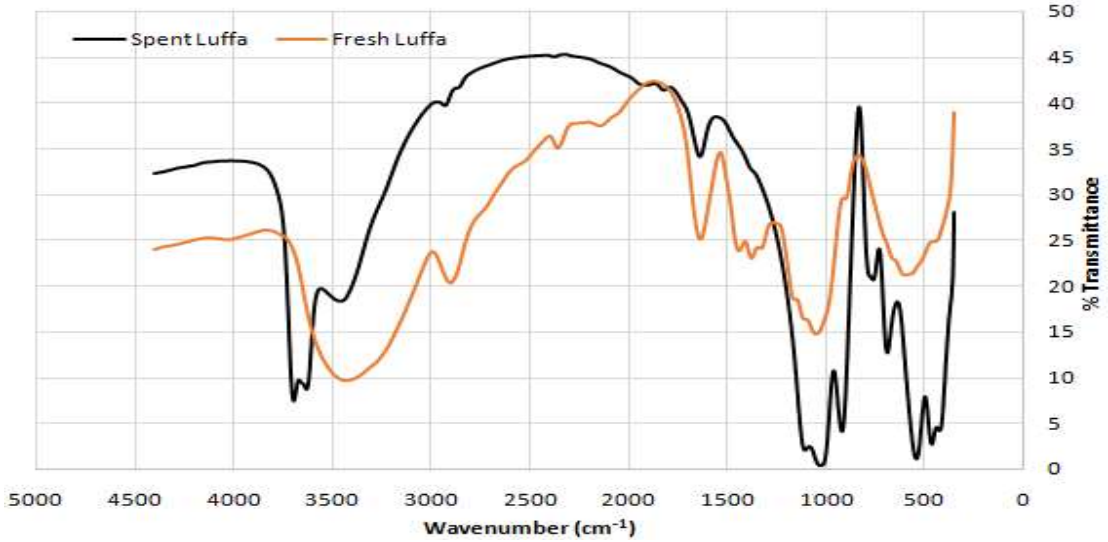


Fig. 1: FTIR Spectra of *Luffa cylindrica* fibers before and after adsorption of Congo Red Dye

Effects of pH on adsorption

The pH is a crucial parameter controlling parameter in the biosorption. This is possibly due to its impact on both the surface binding sites of the biosorbent and ionization status of the Congo Red (CR) dye molecule in water (Boudechiche *et al*., 2016). The percentage adsorption increase with an increase in initial pH of the system due to its influence on the surface properties of *Luffa cylindrica* and ionization and dissociation of the Congo red molecule. The effect of pH on Congo red dye sorption by *Luffa cylindrica* is very important

in establishing the optimum sorption of dye molecules at the solid/liquid interphase. Ionization and solubility of dye molecules during sorption is pH dependent because at low pH, the adsorbent surface become more protonated which allow for the anionic dye to bind with the binding sites at the surfaces more easily while at higher pH, hydroxyl ion increases and thus competition with the anionic dye for sorption site occurs (Adelaja *et al.,* 2019; Babalola *et al.,* 2019a).

The result obtained from this aspect of the study is presented in Fig. 2, from where it is shown that a reduced adsorption of about 49.5 to 61.8% of Congo red dye was removed at pH range 1.0 to 3.0, it increased gradually to pH 7.0 and remained fairly constant at pH 8. At pH 7, which is the optimum for this work, 67% dye removal was recorded. As we approach neutral pH an increase in H^+ ion and OH^- ion concentration in the system was observed, and the surface of the *Luffa cylindrica* Powder acquires both positive and negative charge. As the *Luffa cylindrica* powder become temporarily neutral, the equal competition rate between H^+ ion and OH^- ion on the absorptive leads to high binding, rapid and electrostatic attraction with the anionic dye molecule, leading to maximum adsorption of dye (Uddin *et al*., 2017). As the pH of the system increases and the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the *Luffa cylindrica* does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion while attraction occurs with the positively charged site (Gupta and Lataye, 2017). Furthermore, lower adsorption of the Congo Red dye at the alkaline medium is also due to the competition from excess OH^- ions with the anionic dye molecule (Raval *et al*., 2016) for the adsorption sites. The result obtained by Nadaroglu *et al*. (2018) and Gedam *et al.* (2019) recorded the optimum pH of 8.0 and 6.0, respectively for the removal of Congo Red by teak leaf powder.

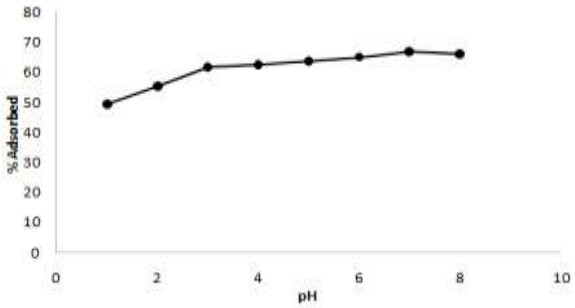


Fig. 2: Effect of pH on Congo Red dye adsorption

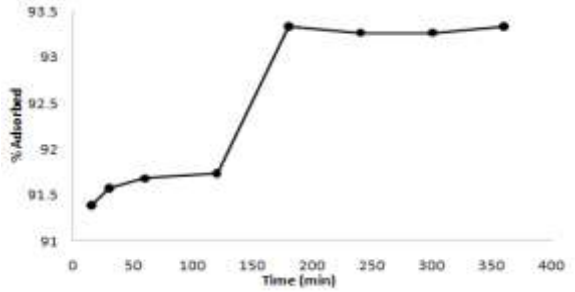


Fig. 3: Time study of the adsorption of Congo Red dye unto *Luffa cylindrica*

Kinetics of the adsorption of Congo Red dye unto Luffa cylindrica

In order to optimize the adsorption of Congo Red unto *Luffa* fibers, it is necessary to establish the optimum time required for the adsorption and also to establish the kinetic model that is well suitable to explain the mechanisms involved during the process. In view of these, contact time experiment was carried out and the result obtained shown in Fig. 3 revealed that initial rapid adsorption process removed a large fraction of the dye within the first 120 min of contact. The initial rapid dye adsorption observed may be due to the availability of more adsorption binding sites on the surface of the adsorbent at the initial stage (Ngaha *et al.,* 2019).

Thereafter, there was a noticeable increase in adsorption up to 180 min after which the adsorption remains fairly constant for the remaining period investigated. Thus, 180 min was used for all other investigation done in this work. Data obtained from the Contact time study was subjected to various kinetic model, pseudo first order, pseudo second order and intra particle diffusion in order to determine which model is most suitable.

The linear form of the pseudo first order kinetic is expressed in Equation 2.

$$\ln(q_e - q_t) = \ln q_e - kt \qquad 2$$

Where: q_e and q_t(mg/g) are the quantity of Congo Red dye adsorbed at equilibrium and at any time *t* respectively; k is the pseudo first order kinetic model rate constant (min^{-1}).

The rate constant and the coefficient of correlation R^2 obtained from the plot of *ln (qe –qt)* against *t* in Fig. 4 are shown in Table 1.

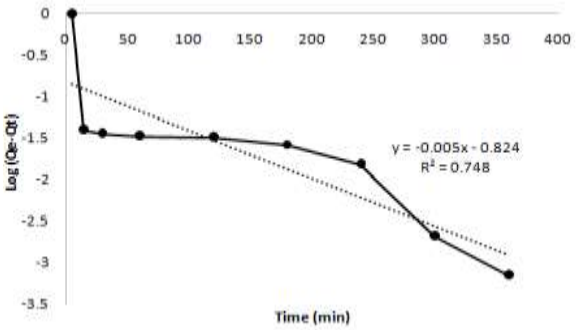


Fig. 4: Pseudo first order kinetic model for the adsorption of Congo Red dye on *Luffa cylindrica*

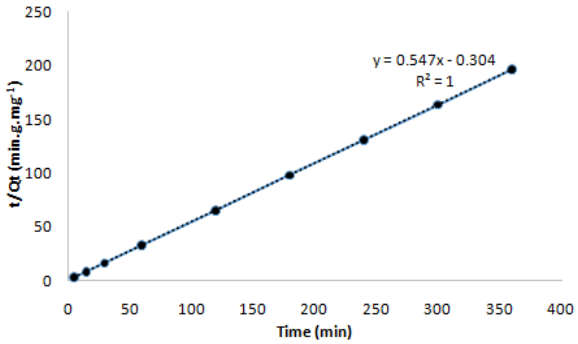


Fig. 5: Pseudo second order kinetic model for the adsorption of Congo Red dye on *Luffa cylindrica*

From the Table, we see that the value of R^2 (0.7481) obtained did not give a good correlation for the process (Segun *et al*., 2014). The Pseudo second order kinetic model is expressed in its linear form in Equation 3.

$$\frac{t}{q_t} = \frac{1}{q_e k^2} + \frac{t}{q_e} \qquad 3$$

Where: q_e and q_t(mg/g) represented the same quantities as mentioned in Pseudo first order model while *k* stand for the rate constant for the pseudo second order model.

Fig. 5 showed the plot of t/q_t versus *t* from which *k* and q_e can be obtained from the intercept and slope, respectively; values obtained for each of these parameters and the correlation coefficient are shown in Table 1.

Table 1: Kinetic parameters for the adsorption of Congo Red Dye unto *Luffa cylindrica* fibers

Kinetic Parameters	Pseudo First Order kinetic model	Pseudo Second Order Kinetic model	Intra-particle diffusion
k	0.0058/min	-0.983g/mg/min	-0.0026 mg/g/min$^{1/2}$
q	e-0.8243 mg/g	1.8275 mg/g	--------
R^2	0.7481	1	0.9563

These values implied that the second order model fit the experimental data better than the first order model showing that the adsorption system was better described by the pseudo second order model; indicating that the mechanism for the adsorption is chemisorption involving force through sharing or exchange of electrons between adsorbent and adsorbate (Ho and McKay, 1998; Kannan and Sundaram 2001).

The rate parameter (k) for the intra particle diffusion by Morris and Weber is calculated from Equation 4

$$q_t = k_{id} t^{1/2} + C \qquad 4$$

Where: q_t (mg/g) represent the amount of indigo blue dyeadsorbedat any time t, k_{id} is the intraparticle diffusion rate constant (mg/g/min$^{1/2}$), C isthe intercept related to the boundary layer effect (mg/g), andt is the contact time (min).

The intra particle diffusion model for the adsorption of Congo Red dye unto *Luffa* fibers is illustrated in Fig. 6 and its kinetic parameters are shown Table 1. From all the values obtained for each of the model tested, it could be concluded that the pseudo second order kinetic model provided the best fit for the experimental data.

Intra-particle diffusion has a nature with two or more steps that might be involved in adsorption. From the graph, there are sections of straight lines which are indications that intra-particle diffusion contributed to the adsorption process.

The first linear part can be attributed tofilm diffusion effects, which implied that for a short period of time indigo blue dye are transported to the external surface of *Luffa cylindrica* through film diffusion. Once the surface is saturated the dye molecules are transported inside the adsorbent by intra-particle diffusion through the pores and internal surface diffusion is continued in the adsorbent pores until equilibrium is reached; the second phase is represented by the second straight line section in the Fig. 6 (Fatombi *et al.,* 2019; Babalola *et al.*, 2019b).

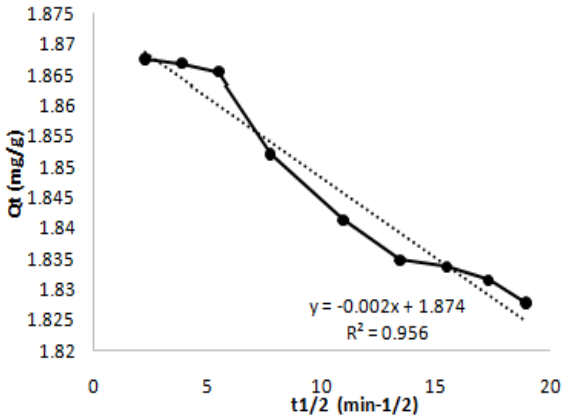


Fig. 6: Intra-particle diffusion model for the adsorption of Congo Red dye on *Luffa cylindrica*

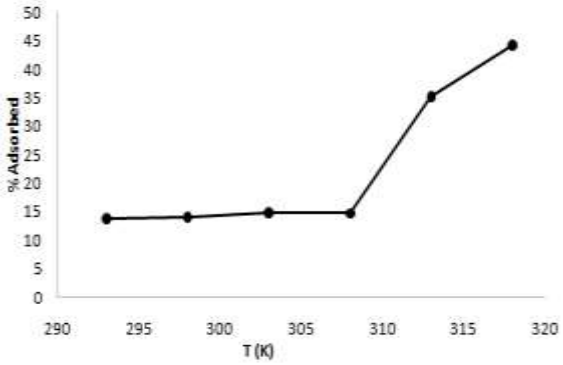


Fig. 7: Effect of temperature on the adsorption of Congo Red dye

Effects of temperature on the adsorption of Congo Red dye

Temperature is well known to play an important role in adsorption processes (Boudechiche *et al.,* 2016). The biosorption of Congo red on *Luffa cylindrica* powder was investigated over the range (20 – 45^{0}C).

The temperature is well known to play an important role in adsorption processes (Boudechiche *et al.,* 2016). The adsorption of Congo red on *Luffa cylindrica powder* was investigated over the range (20 – 45^{0}C). Fig. 7 showed that when temperature was increased from 20 to 25^{0}C, the uptake of Congo red dye was increased from 13.8 to 14%; further increase in temperature to 35^{0}C slightly increase the percentage dye removal to approximately 15%. The percentage adsorbed increased to about 44.5% as the temperature increase to 45^{0}C. An increase in dye adsorption with raising temperature was observed from Fig. 7 suggesting the reaction to be endothermic. It is due to the increase in surface activity as temperature increases and also because at elevated temperature, the mobility of the Congo Red dye increases. Similar result was also recorded by Raval *et al.* (2016) and Salleh *et al.* (2011) that used teak leaf powder and different agricultural adsorbents respectively. The positive enthalpy (ΔH°) confirm that the adsorption is an endothermic process (Nadaroglu *et al*., 2018). The positive value of entropy **(**ΔS°**)** highlights increased randomness at the solid-solution interface during the adsorption (ElHadaad *et al.*, 2014; Xiyili e*t al*., 2017) and also signifies an increase in the degree of freedom of the adsorbed species, thus favouring adsorption of Congo red dye. By applying the Van't Hoff equation presented in Equation 5, the change in enthalpy (ΔH°) = 13201.04 KJ/mol and change in entropy (Δ**S**°) = 26.3032 J/K/mol of the adsorption system were obtained from the slope and intercept of the plot of $ln\, Kd$against $\frac{1}{T}$ shown in Fig. 8.

$$ln\, k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad 5$$

Where k is the distribution co-efficient of the adsorbate (Lg^{-1}), which represents the ratio between C_{eq} and Q_e, ΔH° is the enthalpy change of the reaction (kJ/mol), Δ**S**° is the entropy of the system (J/mol), R is the Molar gas constant (8.313

J/K/mol), andT is the temperature in Kelvin. It is possible to calculate the Gibb's free energy (ΔG°) of the system (Equation 6) at various temperature used in this work since the value of ΔH and ΔS have been determined.

$$\Delta G = \Delta H - T\Delta S \qquad 6$$

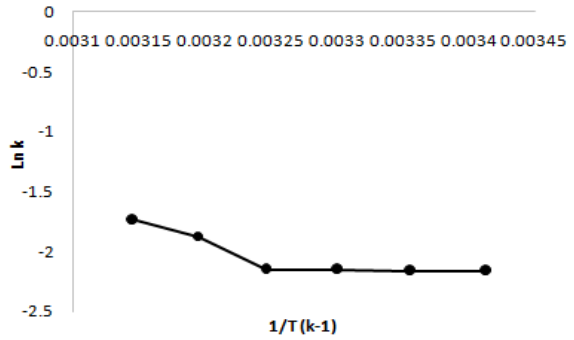


Fig. 8: The Vant's Hoff plot

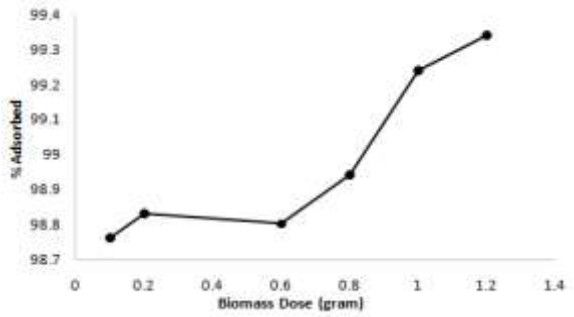
Table 2: Thermodynamic parameters for the adsorption of Congo red dye onto Luffa cylindrica

T (K)	293	298	303	308	313	318
ΔG° (KJ/mol)	13193.33	13193.20	13193.07	13192.94	13192.81	13192.68

Effect of Luffa cylindrica dose on adsorption of Congo Red dye

The biosorbent dosage is an important parameter because it determines the capacity of biosorbent for a given concentration of adsorbate (Boudechiche *et al*., 2016). The effect of the biomass dosage on the Congo Red adsorption was studied in 50 mL Congo Red dye solution (20 ppm) under the conditions of pH and contact time used in this study. The percentage dye removal decreases from 99.37 to 98.63% for adsorbent dosage of 0.1 and 1.2 g/L, respectively. The absorbent dosage effect on the removal of Congo Red dye is shown in Fig. 9.

Figure 9 reveals that the removal of Congo Red dye increases within the range tested in this study. The observed result is due to the addition of more binding sites as the dose of adsorbent increases. This will consequently lead to a high number of active sites for sorbent interaction during the sorption process (Gedam *et al.*, 2019; Hameed, 2009).



Effects of particle size on the adsorption of Congo Red dye

The particle size of the adsorbent can greatly influence the external surface of the adsorbent, thus impacting on its interaction with the solution. A variation in the adsorbent particle size modifies the accessibility and availability of reactive groups present on its surface (Boudechiche *et al*., 2016). The adsorption of Congo Red dye was studied using four different sizes (150, 425, 600, and 1180 µm) of the *Luffa cylindrica*. It is seen that the smaller the particle size used in the adsorption, the higher the observed adsorption of Congo Red dye. For the smaller particle sizes, the available binding sites are more and are also more exposed to the adsorbate in comparison to the large particle size.

The value of ΔG°shows anincreasing tendency in the feasibility and spontaneity of Congo red dye adsorption (Nadaroglu *et al*., 2018). However, for a reaction with positive Gibb's free energy (ΔG°)and endothermic in nature, the reaction will not be spontaneous but such a reaction, however, will be spontaneous if the resultant of the two opposing influence; the enthalpy (ΔH°) and the entropy (ΔS°)of the system, leads to a net decrease in free energy, from Table 2, the decrease in free energy (ΔG°) is insignificant; therefore we could confirm that the reaction will not be or moderately spontaneous.

Conclusion

Luffa cylindrica fibers were used for the adsorptive removal of Congo Red dye from aqueous solution by batch adsorption procedure. The FTIR spectra showed *Luffa cylindrica* to be a lignocellulosic agricultural material. Kinetic and thermodynamic studies carried out revealed that the adsorption kinetic data were best described by pseudo second order kinetic model while the thermodynamic study showed the adsorption to be endothermic and non-spontaneous in nature. The adsorption of Congo Red dye is highly dependent on pH and contact time. The optimum pH and time at which adsorption occurred was pH 7 and 180 min, respectively. The result showed that particle size and adsorbent dose could affect the percentage adsorption recorded.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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