Equilibrium, Kinetics, and Thermoynamics of anionic Dye Congo Red Absorption by Pine Tree Leaves

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ABSTRACT

The The implementation of low cost adsorbents which is Pine Leaves obtained from an agricultural by product was used to remove Congo Red Dye from wastewater. Congo red dye comes from many industry processes and the common industry produces the Congo red dye is textile industries during the processes of rinsing and dyeing. Congo red dye affects negatively on the environment because it is a carcinogenic. The effect of various operating parameters has been studied like pH, dye initial concentration, adsorbent does, temperature, ionic strength, speed, and contact time. The kinetic experimental data were fitted to pseudo second order model and the maximum adsorption capacity of CR was found to be 25.84 mg/g (77.53%) at 303 K and pH 3.03. The Congo red adsorption data were fitted to various isotherm Models. They were analysed by Freundlich and Langmuir Isotherms. Freundlich isotherm was fitted with high correlation coefficients. . This adsorbent was found to be both effective and economically viable.

Keywords: Congo red - Pine leaves powder - Kinetic model

1. Introduction

A worldwide problem these days is the introduction of waste produces in the environment where many environmentalist groups warn from this issue that has many serious impacts on the environment (Kaur, Mahajan and Rani, 2012). Papers starts with introduction. It contains the brief idea of work, requirement for this research work, The main industries are used dyes are textiles, plastics, rubber, cosmetics and paper (Janveja & sharma, 2008). The main leftover in these industries is dyes because of the "chemical constructions" of dyes which could not regeneration to the process again. The main properties of dyes are resistant to fading on water and exposure to light. Dyes are very difficult to decolorize when release into the aquatic environment (Shu and Chang, 2005) (Das and Kumar, 2010). Therefore, the serious impacts of organic dyes are on the marine life and agriculture (sheikh et al, 2009). Furthermore, the dye is a carcinogenic, so it is harmful to humans (Pinheiro, Touraud and Thomas, 2004) (Das and Kumar, 2010). The release of Congo dyes to aquatic environment from tanneries and other industries can produce tremendous chemico-azo that could cause the stress on aquatic life such fishes and sometimes could cause mass mortality (Das and Kumar, 2010). Thus, the treatment of dyes in industries before disposing them to the aquatic environment is essential for environmental protection and health. There are many technologies to treat textile dye wastewaters that could comprise of "chemical, physical and biological processes". Good examples are: adsorption, nanofiltration, electrochemical oxidation, liquid-liquid extraction, electro coagulation and supported liquid membrance (Kaur, Mahajan and Rani, 2012). Natural materials and waste products from agricultural processes are available in abundance to use as sorbents. Natural materials have great potential to use as sorbents, because of low cost, expending materials and the disposed without high cost (Dakiky et al, 2002) (Das and Kumar, 2010). The common technical used to removal colour is an adsorption process. Adsorption is a one of the most method used to remove the dyes and also used wide in wastewater treatment. The adsorption process is being the simple technique and low cost method which will use in this study (Dakiky et al, 2002) (Das and Kumar, 2010). Adsorption is the one of the most methods of separation processes used in chemical industries (Dutta, 2007). It occupies an important position in processing of water and wastewater treatment. Nowadays, agricultural and forestry products are used widely as new adsorbent in absorption processes (Ulmanu et al, 2003) (Kaur, Mahajan and Rani, 2012). The purpose of this study is to investigate the feasibility and efficiency of choosing pine leaves (natural material) to remove Congo red dye from wastewater.

2.Materials

2.1 Adsorbent

Pine leaves was used as an adsorbent, was collectively and washed with tap water and lastly with double distilled water to remove the suspended impurities, dust, and soil and then dried in oven. After that, the dried pine leaves were crushed in a mortar to obtain powder and then passed through "British Standard Sieves (BSS) of 150 µm. Finally, put the powdered of pine leaves in an airtight plastic container for storage.

2.2 Adsorbate

The dye Congo red (C32H22N6O6S2Na2, Formula weight = 696.65) is supplied by Curtin University (Department of Chemical Engineering). Prepare "a stock solution" of 1000 mg/l by dissolving (1000 mg) of dye Congo in a one liter of distilled water in 1000 ml glass bottle this solution using as an adsorbate.

2.3 Adsorption experiments

Adsorption experiments were conducted by agitating 15 mg of Pine leaves powder (adsorbent) in a series of 250 ml conical flasks with 50 mL of CR solution (10 PPM) in a thermostat shaker with a shaking of 150 rpm at 303 K. The samples were reserved from "the shaker" at prearranged time intervals (150 min) and dye solutions were separated from the adsorbent using Centrifuges. The absorbance of supernatant solution was measured spectrophotometrically by monitoring the absorbance at 500 nm using a “UV-vis spectrophotometer” (1800, Shimadzu, Japan) at different conditions of the desired concentration.

3.Theory

The amount of dye adsorbed onto pine lives powder biomass at time t, qt (mg/g) was calculated by the following mass balance relationship:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

And dye removal efficiency i.e. % of adsorption was calculated as

$$\%\ \text{adsorptiom} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

Where: Co and Ct (mg L−1) are the concentrations of dye before and after adsorption, V is the amount of Congo dye (50 ml), m is the weight of Pine leaves (15 mg). All measurements are, in general, reproducible within ±10%.

3.1 Adsorption isotherm

The Freundlich (1906) and Langmuir (1918) have used to simulate the adsorption isotherm to explicate dye-pine leaves interaction.,

3.1.1 Freundlich isotherm.

Freundlich isotherm is assumption that absorption takes place on heterogeneous surfaces which can be expressed as (Arias and Sen, 2009):

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (3)$$

Where: qe is the amount of dye adsorbed per unit of adsorbent at equilibrium time (mg/g), Ce is equilibrium concentration of dye in solution (mg/L), Kf and n is isotherm constants which indicate the capacity and the intensity of the adsorption respectively

3.1.2 Langmuir isotherm.

Langmuir isotherm can be calculated by (Bhattacharya et al., 2006):

$$\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m} \tag{4}$$

Where: qm is maximum adsorption capacity (mg/g), Ka is values for Langmuir constant related to the energy of adsorption (L/mg).

3.2. Adsorption kinetics:

the pseudo-first-order, pseudo-second-order have used to investigate the mechanism of adsorption which include potential rate-controlling step and the transient behaviour of the dye adsorption process.

3.2.1 Pseudo-first-order model:

The pseudo-first-order model can be expressed as (Mohammad et al., 2010) (Vimonses et al., 2009) (Rengaraj et al., 2004)

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{5}$$

Where: qt is the amount of dye adsorbed (mg/g) at any time t, qe is the amount of dye adsorbed (mg/g) at equilibrium time, k1 is the adsorption first-order rate constant (min-1), K1 has calculated from plot of $\log(q_e - q_t)$ VS t, t is the contact time (min).

3.2.2 Pseudo-second-order model:

The pseudo-second-order mechanism can be determined by (Mohammad et al., 2010) (Vimonses et al., 2009) (Rengaraj et al., 2004)

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{6}$$

Where: k2 is the pseudo-second-order rate constant (g/mg min), which can be calculated from plot between t/qt VS t from flowing equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

The Constant k2 also is used to calculate the initial sorption rate h, at t → 0, as follows:

$$h = k_2 q_e^2 \tag{8}$$

So, equation (9) can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

Thus, equation (9) can be calculated the rate constant k2, initial adsorption rate h and predicted qe from the plot of t/qt VS time t.

3.3 Adsorption mechanism

The common method used for identifying the adsorption mechanism is Intra-particle diffusion model. Adsorption process usually uses t1/2 rather than contact time for identifying the adsorption mechanism which is shown in following equation:

$$q_t = K_{id} = t^{0.5} + 1 \quad (10)$$

Where: qt is the amount adsorbed (mg/g) at time t, Kid is the rate constant of intra-particle diffusion (mg/g min0.5), t0.5 is the square root of the time.

3.3.1 Thermodynamic study

The main thermodynamic parameters have determined for the adsorption of dye on pine leaves are enthalpy change (ΔHo), change in entropy (ΔSo) and Gibb's free energy (ΔGo). The following equations show how can be calculated (Arias and Sen, 2009):

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (11)$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^o}{2.303R} + \frac{-\Delta H^o}{2.303RT} \quad (12)$$

Where: qe is the amount of dye adsorbed per unit mass of pine leaves (mg/g), Ce is equilibrium concentration (mg/L), T is temperature in K, R is the gas constant (8.314 J/mol K).

Thermodynamic properties of change in entropy (ΔSo) and enthalpy change (ΔHo) can be calculated from the intercept and slope of the plot of log (qe/Ce) vs. 1/T. From those values, Gibb's free energy (ΔGo) can be found using the equation (11).

4.Results and Discussion

4.1 Factors Effecting on adsorption

4.1. 1. Effect of pH solution

The effect of pH was analysed for adsorption of CR by pine leaves powder in the range of 3.03 to 10.9 which is presented in figure 1. The investigation was found that the amount of dye adsorbed increased from 9.31 mg/g (27.94 % removal efficiency) at pH 10.9 to 25.84 mg/g (77.53% removal efficiency) at pH 3.03 for a fixed initial dye concentration of 10 ppm at equilibrium as illustration in figure 3. The maximum adsorption of dye was occurred at acidic pH. The maximum adsorption onto pine leaves at lower pH could be due to the greater positive charge on the adsorbent surface (Yu et al, 2003). The increasing of adsorption in low pH (acidic pH) is because of there are worthy active sites of Pine leaves that mean wide internal surface of pine leaves which can adsorption an essential amount of Congo red (Blázquez et al, 2011).
Moreover, The more efficiently of adsorption occurred at low pH by reason of the larger positive charge on the adsorbent surface (pine leaves) and the negative charge on the adsorbate CR (Ahmad and Kumar, 2010).

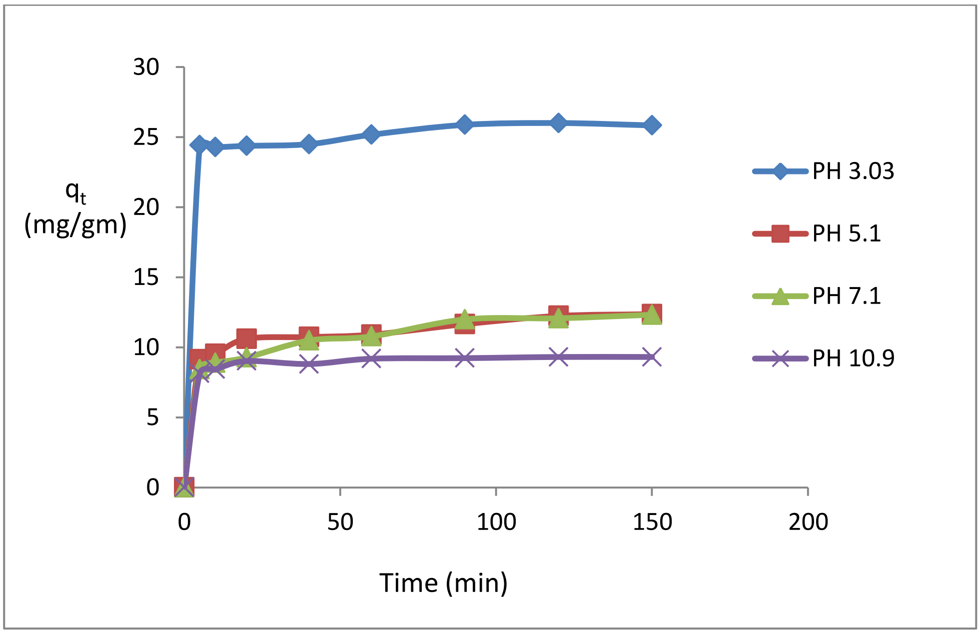

Figure 1: Effect of initial solution pH on the adsorption of CR onto pine leaves; adsorbent 15 mg, volume of dye solution 50 ml, initial dye concentration 10 ppm, temperature 30 °C, shaker speed 150 rpm.

4.1.2. Effect of adsorbent dosage

The purpose of study the effect of adsorbent dosage is to find the minimum dosage that can be adsorbed efficient amount of dye. This might play important role to identify the economical side (Salleh et al., 2011). Figure.2 shows that the increase in adsorbent dosage from 0.015 g to 0.03 g caused in decrease of amount of adsorbed dye from 9.314 mg/g to 6.435 mg/g. It was also found that at equilibrium the percentage dye removal was increased from 27.95 % to 38.61 % with the increase of adsorbent mass from 0.015 g to 0.03 g.

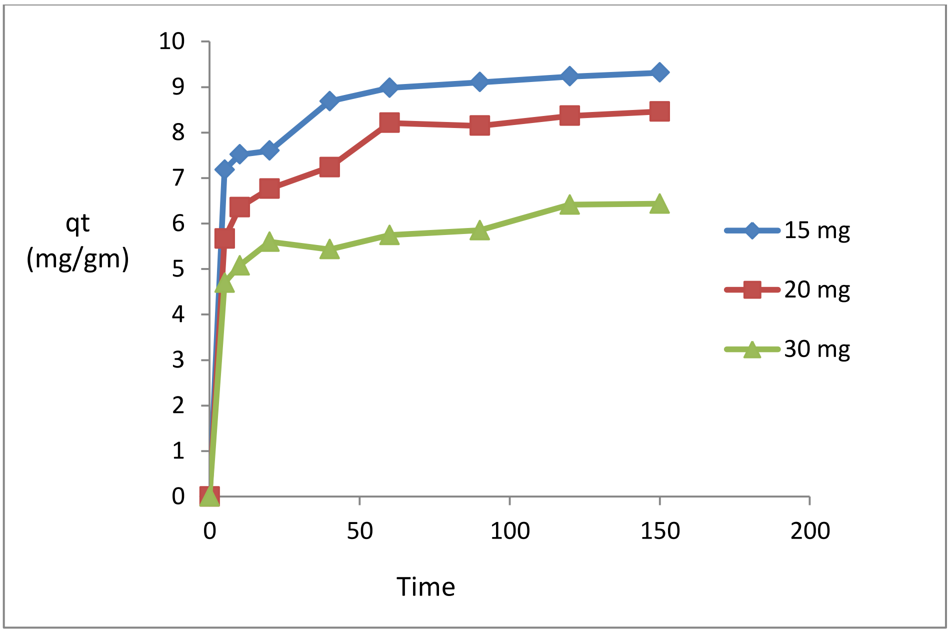

Figure 2 Effect of adsorbent dosages on the amount of CR adsorption by raw pine leaves biomass. Volume of CR Solution 50ml; Initial CR Concentration 10 ppm; pH 6.25; Temperature30 oC; Shaker Speed 150 rpm.

4.1.3. Effect of temperature

To observe the effect of temperature on the adsorption capacity, experiments are carried out for 10 ppm CR at three different temperatures (30, 50 and 60 ◦C) using 0.015 g of pine leaves and 50 mL of the 10 ppm CR solution. It has been observed that with increase in temperature, adsorption capacity increases as shown in Figure 3. That is means high temperature favours for removal the CR from wastewater. This happens according to decrease of the solubility of dye that occurs due to increase in the temperature hence adsorption increases (Bilal, 2004). Furthermore, it could be as a result of increasing the mobility of dye with temperature (Kaur, Mahajan and Rani, 2012).

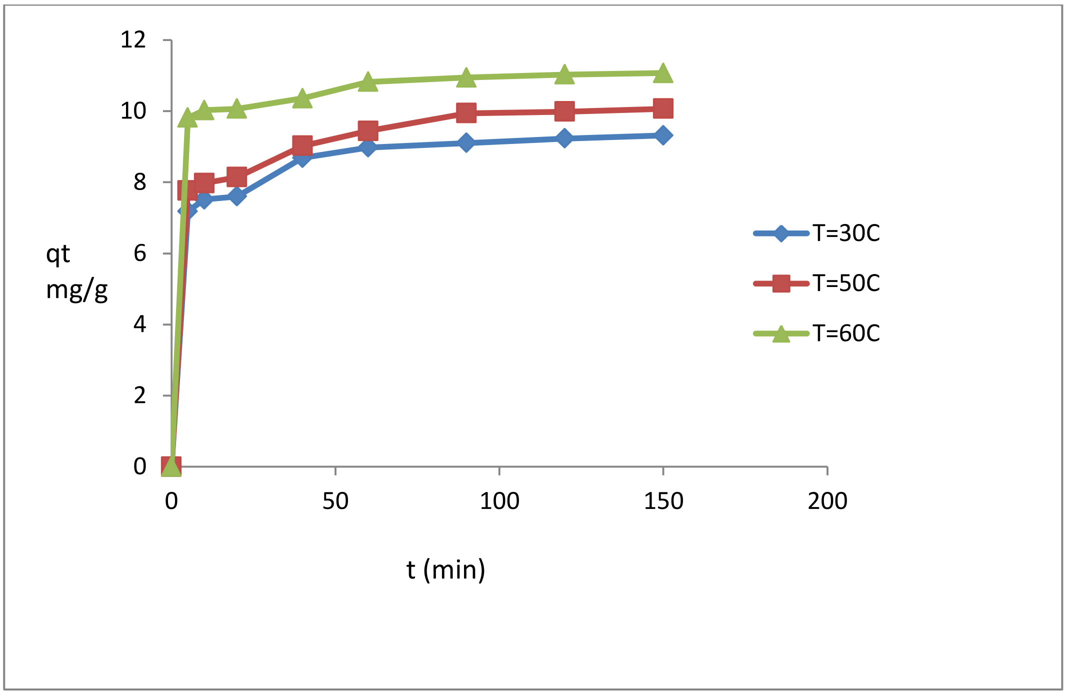

Figure. 3 Effect of temperature and time contact on the adsorption of CR onto raw pine leaves powder: Mass of Adsorbent 15 mg; Volume of CR Solution 50 ml; Initial CR Concentration 10 ppm; pH 6.25; Shaker Speed 150 rpm.

4.1.4. Effect of Ionic Strength

The ionic strength of NaCl could be affected on the removal of dyes from wastewater (Hu, Chen, and Yuan, 2010). The effect of NaCl on removal of dye CR was studied at different concentrations of NaCl that are 100, and 200 mg L^{-1} at fixed adsorbent dose of 15 mg. Figure 4 illustrations that the amount of dye adsorption by pine leaves increased with increase of inorganic salt. The anionic exchange capacity was increased, possibly by reason of a decrease in the repulsive forces (Hu, Chen, and Yuan, 2010). Hence, pine leaves can be used to remove CR from aqueous solutions with a higher salt concentration.

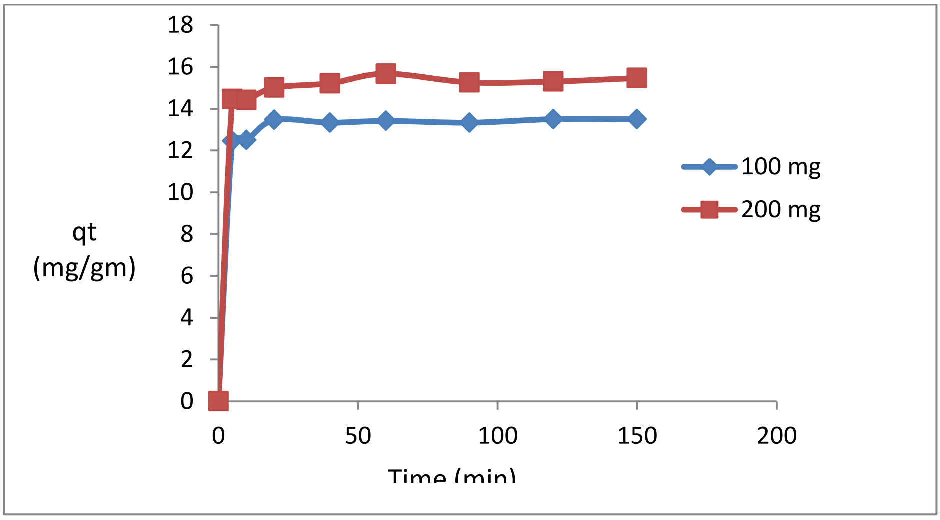

Figure. 4 Effect of salt concentration on the adsorption of CR onto pine leaves; volume of dye solution 50 ml, temperature 30 °C, pine leaves dosage 15 mg, PH 6.5, agitation speed 150 rpm, and initial dye concentration 10 mg L−1

4.1.5. Effect of contact time

Figure 5 explain the effect of contact time on the adsorption of CR dye at different temperatures. It is indicated that uptake of CR is rapid in the beginning and then becomes constant. It can see that the curves are single and continue. It could be because of monolayer coverage on the surface of adsorbents (pine leaves) by the CR molecules (Kaur, Mahajan and Rani, 2012). The equilibrium time of CR could be at 90 minutes due to the results.

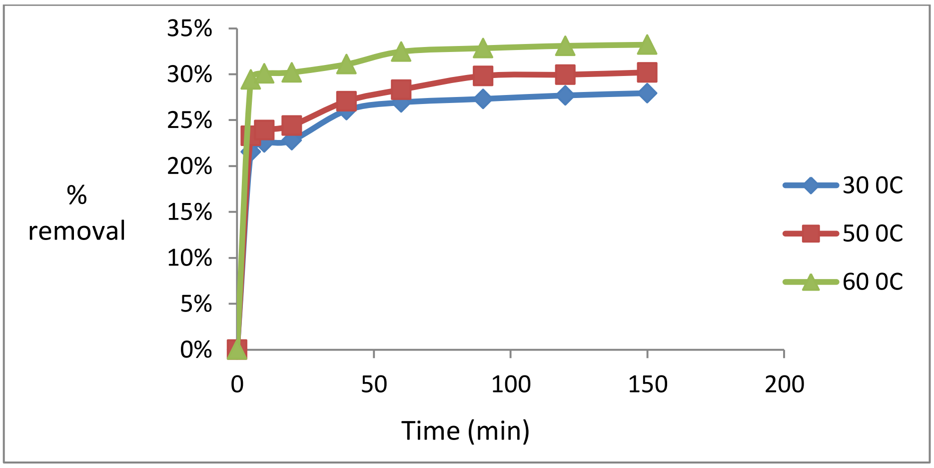

Figure 5 Effect of temperature and time contact on the adsorption of CR onto raw pine leaves powder: Mass of Adsorbent 15 mg; Volume of CR Solution 50 ml; Initial CR Concentration 10 ppm; pH 6.25; Shaker Speed 150 rpm.

4.1.6. Effect of initial dye concentration

The effect of initial concentration on the removal of CR by pine leaves is indicated in figure 6. Experiment was done at initial concentrations of 10, 30, 50 and 70 ppm, 0.015 gm of adsorbent dosages (pine leaves), temperature is 30 ^{o}C and pH is 6.25. It evident from the figure that the amount of CR adsorbed (qt) is increased with increasing the initial concentration of CR. This is as a result of increasing of surface area of CR (Kaur, Mahajan and Rani, 2012). Likewise, the percentage of CR removal increased with increase the initial concentration of CR except at 70 ppm where the percentage of CR removal decreased with increase in CR concentration with time. Where the percentage of CR removal of 70 ppm was 50.8% at 5 minutes compared with 41.84% at 150 minutes. This may due to the active sites of pine leaves (adsorbent) were saturated (Kaur, Mahajan and Rani, 2012).

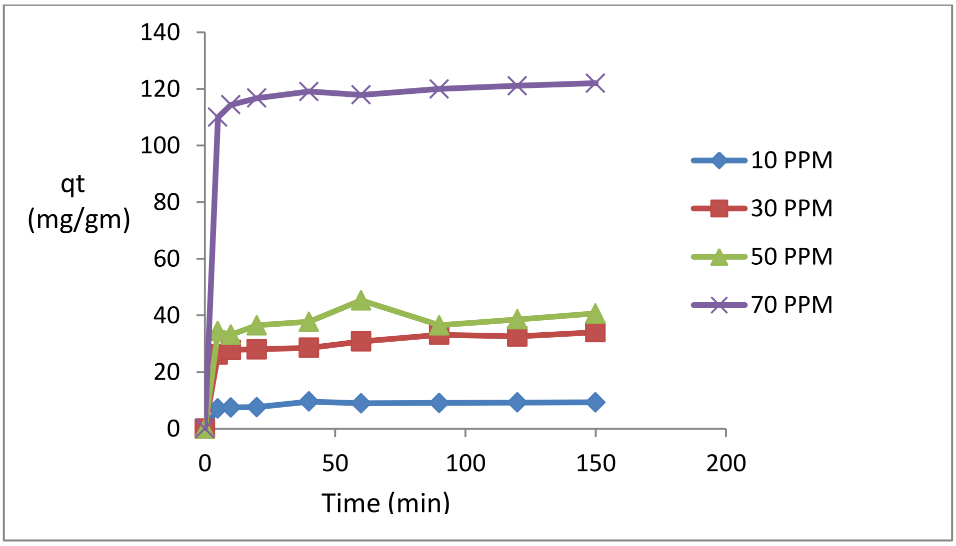

Figure. 6 Effect of initial CR concentration on the amount of adsorption (removal) of CR onto raw pine leaves powder: Mass of Adsorbent: 15 mg; Volume of CR Solution: 50 ml; pH: 6.25; Temperature: 30 C; Shaker Speed: 150 rpm.

4.1.7. Effect of Agitation Speed

Figure 7 illustrates the effect of agitation speed on the adsorption of CR on pine leaves. Experiment was conducted at different speed of 120, 150 and 180 rpm. It is indicated that there was slight increase of adsorption with increase the speed. The percentage removal of CR at 120 rpm was 27.57% and 28.57% for 180 rpm. The slight increase may due to turbulence increased and the decrease of the thickness of boundary layer around the adsorbent particles.

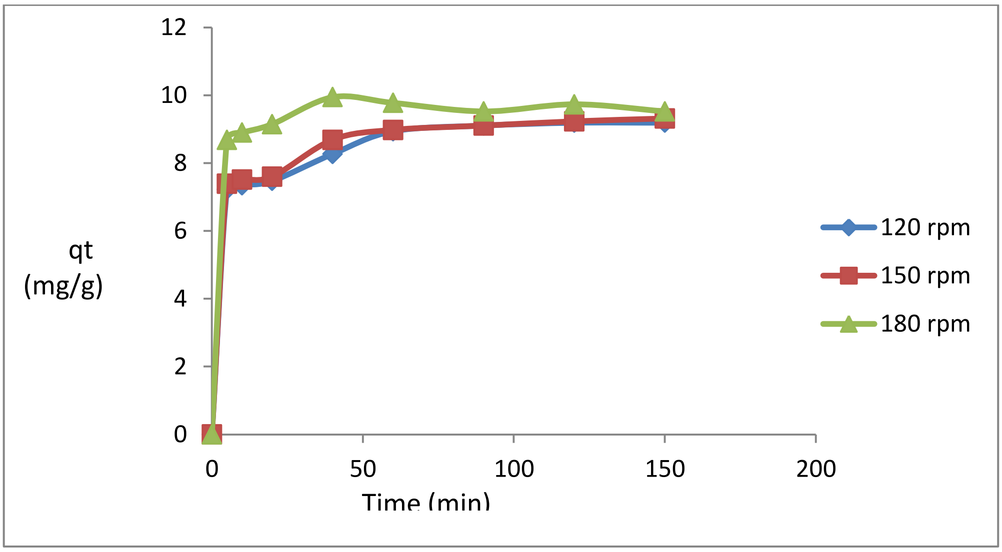

Figure. 7 Effect of agitation speed on the adsorption of CR onto pine leaves; volume of dye solution: 50 ml, initial dye concentration: 10 ppm, temperature: 30 °C, pine leaves dosage: 15 mg, pH: 6.25

4.2. Adsorption kinetic modeling

The pseudo-second order equation is shown in equation (6). Figure 8 is represented an example of plot between t versus t/qt. The equilibrium capacity qe is estimated from the slope and K2 is obtained from the intercept of linear plots. The values of qe calculated of different effects were very close to the value of qe experimental. Also, the correlation coefficients R2 were close to 1. The sorption could be approached more fittingly by pseudo-second order kinetic model than the first-order kinetic model for adsorption CR by pine leaves.

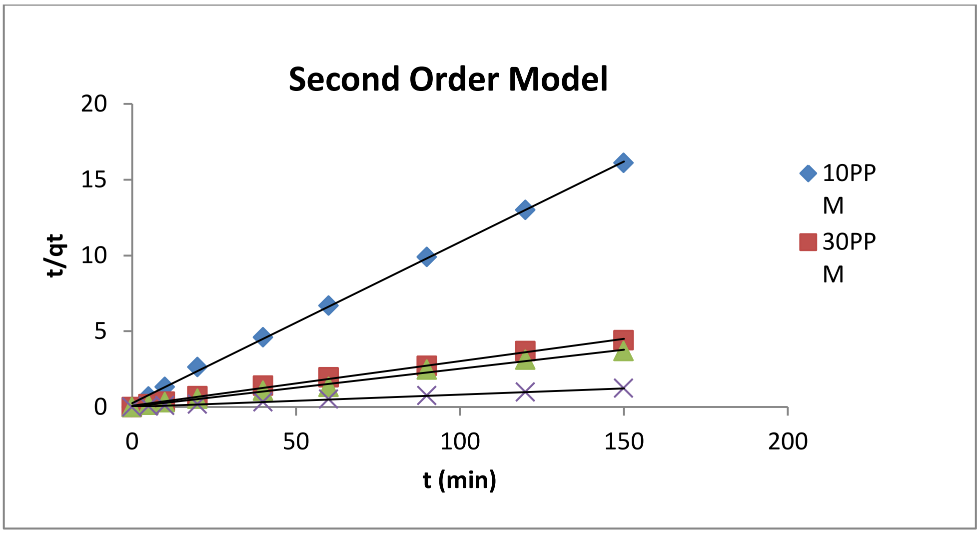

Figure 8: Pseudo-second-order kinetic model for CR adsorption at different initial solution concentration: Mass of Adsorbent = 15 mg; Volume of Dye Solution = 50 ml; pH = 6.25; Temperature = 30°C; Shaker Speed = 150 rpm

4.3. Adsorption equilibrium isotherm

The analysis of adsorption isotherm is used for describing how the adsorbent surface interacts with the adsorbate molecules as well to determine the capacity of the adsorbent at the best conditions of experiment that found (Sampranpiboon and Charnkeitkong, 2010). Two equilibrium isotherms including Langmuir and Freundlich within the CR concentrations range of 10 – 70 ppm have been tested. The correlation coefficients (R2) for all adsorbents of Freundlich isotherm are greater than Langmuir isotherm demonstrating that the Freundlich isotherm fits the experimental data splendidly.

4.3.1. Freundlich Isotherm

Figure 9 is shown adsorption equilibrium data of the Freundlich Isotherm that were fitted for pine leaves with linear correlation coefficient (R2) of 0.904. The slope was 1/n and the intercept is lnKf that found from plotting LnCe against Lnqe as represented in equation 3. The value of n was 1.11 and the adsorption capacity was 14.89 mg/g. Freundlich constant n is used to verify types of adsorption. The value of n when is equal to one the adsorption is linear.. The results display that the value of n above one that indicates the favourable nature of adsorption and a physical process. Freundlich isotherm described the adsorption on heterogeneous surface through a multilayer adsorption mechanism (Sampranpiboon and Charnkeitkong, 2010) (Teoh, Khan and Choong, 2012) (Yaneva, and Georgieva, 2012).

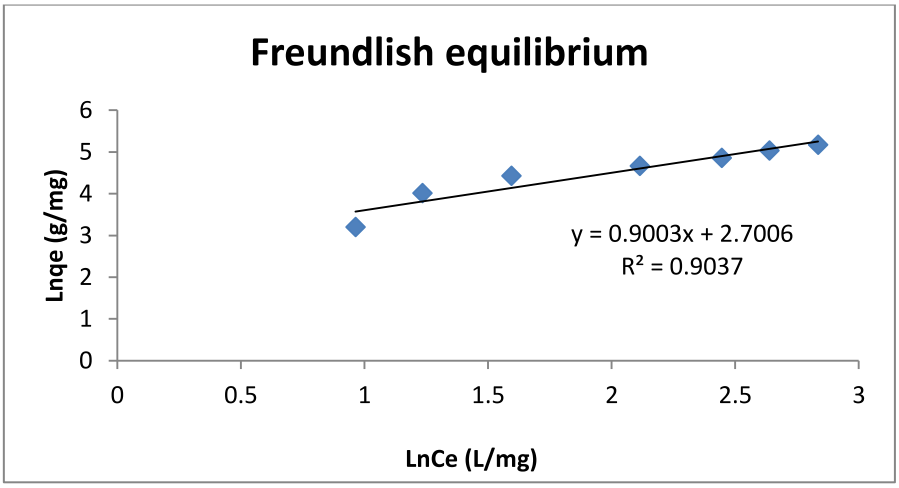

Figure 9: Freundlich plot: Amount of adsorbent (pine leaves) added 10 mg; Initial CR Concentration 10, 20, 30, 40, 50, 60, 70 ppm; pH 3.03 Temperature 30 oC; Shaker Speed 150 rpm.

4.3.2. Langmuir Isotherms

Langmuir isotherm model was an experiential isotherm. The model proposed a clear theory of adsorption onto a flat surface based on a kinetic viewpoint where there was a frequent process of offensive of molecules onto the surface (Teoh, Khan and Choong, 2012). The data showed correlation coefficient R2 is 0.1577 as presented in figure 10. This showed that the Langmuir has poor correlation coefficient in this case. However, Langmuir equation could give satisfactory approximation only in the high concentration range started at 40 ppm and the correlation coefficient was 0.909.

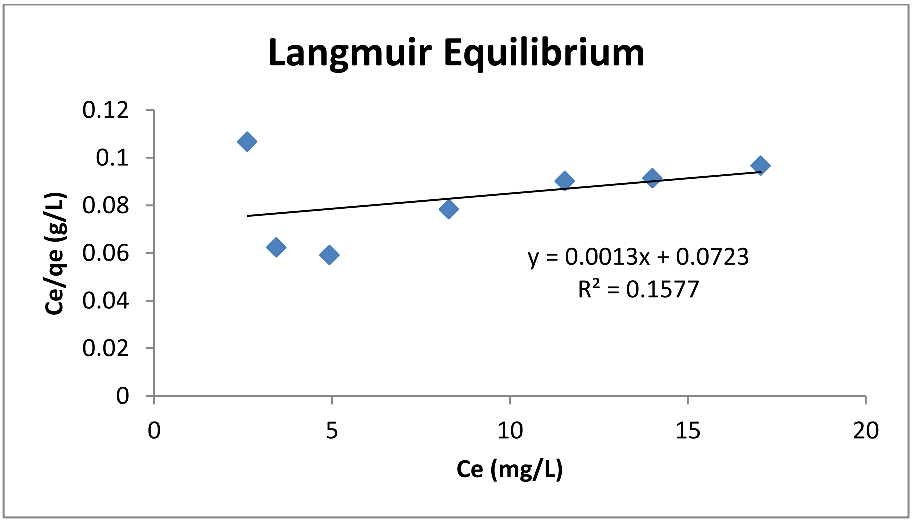

Figure 10 Langmuir plot: Amount of adsorbent (pine leaves) added 10 mg; Initial CR Concentration 10, 20, 30, 40, 50, 60, 70 ppm; pH 3.03 Temperature 30 oC; Shaker Speed 150 rpm.

4.4. Thermodynamic Studies

The study of the basic thermodynamic parameters of enthalpy of adsorption (ΔHo), entropy of adsorption (ΔSo) and Gibb's free energy of adsorption (ΔGo) is important as it allows to estimate if the process favours from thermodynamic or not and to identify the spontaneity of the system, as well to ascertain the type of nature of the process the endothermic or exothermic (Yaneva, and Georgieva, 2012). Additionally, thermodynamic study can identify types of adsorption which are chemisorption and physisorption (Houston, 2001) (Yaneva, and Georgieva, 2012). Physical adsorption occurs if ΔHo < 84 kJ mol–1 and as chemical when ΔHo lies between 84 and 420 kJ mol–1 (Ahmad and Kumar, 2010). The negative value of ΔHo reveals that the adsorption process is exothermic (Saha et al, 2012) (Vimonses, Jin and Chow, 2010). The negative ΔSo indicates a decrease in randomness at the solid/solution interface (Zhang et al, 2011). The calculation of thermodynamic parameters is estimated from plot Log (qe/Ce) vs. 1/T which is found to be linear as shown in Fig. 11. Change in enthalpy of adsorption, ΔH° and entropy change of adsorption, ΔS° values were calculated from the slope and the intercept of the plot using equation (12). Then the values of Gibb's free energy (ΔG°) have been calculated from equation (11). All these thermodynamic parameters are presented in Table 1. The results found that an increase of temperature with increasing of adsorption amount. When the temperature increased the rate of diffusion of the molecules adsorbate could increase across of the external boundary layer as well the internal pores of the adsorbent particle. This might lead to increase surface activity and decrease the viscosity of the solution (Ahmed and Kumar, 2010). The negative ΔGo values were estimated of: -18.02, -19.64 and -20.45 J mol–1 at 30, 50 and 60oC, respectively, indicated that the spontaneous nature of CR adsorption on pine leaves. The linear relation was found from plotting Gibb's free energy change versus temperature. The positive ΔHo value is found of 6.55 kJ mol-1 pointed out that the reaction was endothermic and physical nature of CR adsorption, whereas the positive value is calculated of ΔSo: 81.08 J mol-1 K-1 expressed that the affinity of CR towards pine leaves. Consequently, CR adsorption on pine leaves was thermodynamically favourable.

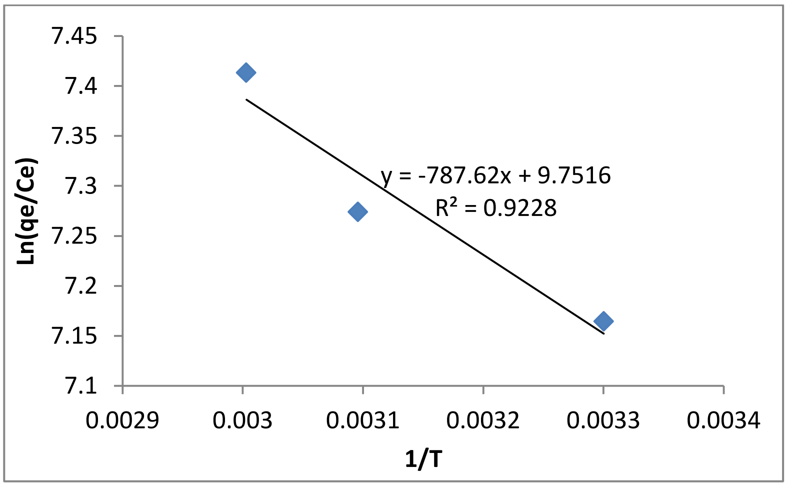

Figure 11: Study of Thermodynamic Properties for Adsorption

Table 1: *Thermodynamic Properties*

T (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol.k)
303	-18,018.97	6,548.27	81.08
323	-19,640.57		
333	-20,451.37		

5. Conclusions

The present project highlighted the effect of some major parameters on CR adsorption by pine leaves and visualized the following general findings. From the results, it is probable to conclude that:

i. Pine leaves powder has very good potential for utilization as an adsorbent for Congo Red dye (CR) from aqueous medium. The maximum adsorption capacity of CR was found to be 25.84 mg/g (77.53%) at 303 K and pH 3.03.

ii. The amount of CR removed increased with increasing temperature, time of contact, initial concentration, agnation speed and ionic strength and decreased with increase in pH and adsorbent dosage.

iii. The kinetics of adsorption of CR on pine leaves is presented and the results were tested with models based on pseudo first and second order. The adsorption data presented good agreement with the pseudo-second-order kinetic model (R2=0.99).

iv. Freundlich isotherm model gave excellent fittings with experimental data. The maximum adsorption capacity of pine leaves from Freundlich model was found to be 14.89 mg/g. Freundlich constant, n, give an indication of favourable adsorption which was physical adsorption.

v. The thermodynamic studies revealed the spontaneous, endothermic and physical nature of CR adsorption which observed from the negative values of Gibb’s free energy and positive values of enthalpy and entropy of adsorption.

The present research work established that pine leaves were excellent low cost adsorbent for removal of CR dye. the kinetic and thermodynamic data can be further explored for the design to promote large scale use of pine leaves as an adsorbent for industrial effluents treatment.

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