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Equilibrium and Kinetics Studies of Adsorption of Congo Red by Activated Carbon

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Abstract: Thevetia peruvianna seed shell could be effectively employed as raw material for the production of activated carbon which was utilized as biosorbent for treating synthetic waste water containing congo red. Thus the adsorption of Congo red (CR), a typical dye from synthetic waste water using *thevetia peruvianna* shell activated carbon was studied as a function of pH, adsorbate dosage, initial dye concentration and contact time. The residual CR in solution was determined using uv-visible spectrophotometer. All batch experiment was carried out at constant temperature of 30°C (± 2°C) using mechanical shaker that operates at 100 rpm. The result showed that dye adsorption increased with increase in amount of adsorbent. Optimum pH for the dye adsorption is 7.0. The biosorption is time dependent. The result of the kinetics study showed that the pseudo-second order rate equation better described the adsorption process. Adsorption isotherm obtained fitted well into both Freundlich and Langmuir equation but match Freundlich models better. Maximum CR removed at pH 7 from 50ml of 50 mg/L CR solution was 85.0% for adsorbent dose of 0.2g/50ml.

Key words: Biosorption · Thevetia peruvianna · Waste water · Congo red · Kinetics · Equilibrium and activated carbon

INTRODUCTION

Removal of dyes from a waste water has become a major concern. The discharge of dyes into water courses is a problem which may affect the quality of water supply[1]. This, undesirable increasing accumulation of dyes in the aqueous environment has a severe health hazard. Untreated disposal of this coloured water into the receiving water body can cause damage to aquatic life or human being by their mutagenic and carcinogenic effect [2].

The nature of dyes also necessitates proper treatment of waste water containing dyes before discharging to the environment, because even when released in small concentration, it will impact colour that as a result reduce the aesthetical value of the receiving water [2].

Dyes contamination exist in aqueous waste streams from many industries, interest not only in textile but polymer, paint, printing, cosmetics, food and many others. There are over 100,000, commercially available dyes and more than $7x10^5$ tonnes annually [3]. The dye effluents are highly coloured with a large amount of suspended organic solids [3].

Conventional waste water technologies for removing dyes from industrial effluents include; chemicals, biological and physiochemical treatments such as coagulation and flocculation [4], ozonation [5], electrochemical processes [6], nano filtration[7] and adsorption [8]. Amongst all, adsorption process has gained favours recently as one of the most efficient technique in the removal of pollutants from effluents. An adsorbent such as activated carbon has been widely investigated for the adsorption of dyes [9] but drawback such as its high cost limits its large scale application. There are thus extensive research towards finding inexpensive and effective alternatives to carbon. These materials include rice husk chitin, saw dust, egg shells, barley husk, corn cobs, coconut shells, lemon peel and date palm are not expensive and readily available [10-13].

Thevetia plant is a dicotyledon which belongs to Aponaceae family and is a tropical evergreen shrub. It grows in the wild and remains ornamental, despite the abundance of the plant around our homes, schools and other building, the plant s grown as hedgers and kept for its bright and attractive flowers. Thevetia plant thrives well in all climates and vegetation belt. The fruit when

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unripe is hard and green but gradually turns black as it ripens. The seed contain 60-64% oil on dry matter bases. [14] The plant is found useful in applications in many areas, Latex is analgesic and insecticides, the seed also provide protein in animal feed, the oil from the seed is used in livestock feed formulation, paint industries and some other potential applications. [15] The shells from the seeds are feely available, hence the objectives of this study was to evaluate the possibility of using the dried shell as bioadsorbent activated carbon. The parameters such as pH, adsorbent dose, initial concentration and time are systematically studied.

MATERIALS AND METHODS

All the reagents used were of A.R grade, Methylene Blue and Congo Red of BDH were used.

Preparation of Activated Carbon: Production of activated carbon from thevetia seed followed the literature methods of production from related materials [16, 17]. The raw material was prepared by impregnation into phosphoric acid (85% by weight) by using the weight ratio of raw material and phosphoric acid at 1:1. The mixture was carbonized in a muffle furnance at 500°C for 1hr. The product was washed with hot distilled water until it attained neutral pH and dried in an oven at 105°C for 4hr. The dry biomass was crushed sieved in the size managed between mesh number 325 (0.045mm) and 100 (0.150mm) and stored in a desiccators.

Characterization of Activated Carbon:

- The ash content of the carbon was determined according to a standard method [18]. The sample was pre-dried at 150°C, followed by burning in a muffle furnace at 650°c for 4hrs in the presence of air. The ash content was calculated from the combustion residue. The ash content was obtained from constant value resulting from repeated tests.
- The yield of activated carbon is the ratio of the weight of the activated carbon product to that of the original thevetia seed shell i.e

% Yield = wc/ws x 100 [18]

Where ws = the original mass of the dry shell and
wc = the mass of the charred product

- Bulk density of all samples was determined by calculating the ratio between weight and volume of packed dry material.
- Surface area was calculated on Methylene blue adsorption isotherm [18, 19]
- Percentage fixed carbon was determined in relation to Ash content as described in the literature [18].
- Iodine number was determined according to the method and Procedure given by Suteliffe Speakmen Carbon Ltd as described in the literature [20].
- Methylene blue value was determined according to standard testing method of Methylene blue on activated carbon [20].

Adsorption Procedure: Synthetic dye solution of congo red (CR) with concentration 500mg/l was prepared as standard stock solution. This was carried out by dissolving the appropriate amount of CR in 100ml and made to 1000ml with distilled water. Different concentrations of CR were subsequently prepared by dilution when necessary. The initial pH was adjusted with 0.1M HCl or 0.1M NaOH. All the sorption experiments were carried out at room temperature (30±1°C)

Equilibrum Studies: Time course experiments were investigated by shaking the sorption mixture of (adsorbent and adsorbate) at various predetermined interval and conditions. The mixtures left were filtered and the filtrate analysed for the adsorbate concentration, blank solutions without adsorbent were also shaken and the concentrations determined. This was used as initial concentration. The dye concentrations in this work were analyzed using uv-visible spectrophotometer.All measurements were made at the wavelength corresponding to maximum adsorption, for CR λ_{max} = 498nm.

The experiment were carried out in duplicate and the results obtained from the means (with relative standard deviation RSD of less than 10%)

In the determination of adsorption capacity of solute intake per unit mass of activated carbon (q_c mg/g) was calculated using adsorption system mass balance

$$qc = \frac{v(ci - cf)}{w}$$

Where v = volume of solution (ml)
w = amount of dry adsorbent (g)
ci = initial concentration (mg/l) and
cf = final concentration (g)

The percentage of dye uptake (% uptake) was also calculated in some cases using the following equation;

$$\%uptake = \frac{ci - cf}{ci} \times 100$$

Effect of pH on Cr Adsorption Studies: The effect of pH on the equilibrium sorption of dyes was investigated by employing an initial concentration of CR of 100mg/L and 0.2g of thevetia shell activated carbon (TSC) in 50ml of CR solution. The suspensions were shaken for 100min and the amount of CR adsorbed determined.

Time Dependency Studies: The effect of contact time on the adsorption of CR from aqueous solution. on TSC. The batch studies was carried in 250ml shaking flask.

The TSC (0.5g) together with 100cm^3 of 100mg/l of CR were shaken in mechanical shaker between 10-80 mins. The clear solution were analysed for the residual CR concentration.

Effect of Adsorption Dosage on Cr Adsorption: The effect of TSC dose on the equilibrium uptake of CR was investigated with various qualities of TSC 0.2-0.8g in 50ml 0f 100mg/L of CR solution. The shaken time was 100min.

Construction of Adsorption Isotherm: The batch adsorption experiment was carried out by adding fixed amount of TSC 0.2 g into 250 ml shaking flask container, 50 ml of CR solution of varying initial concentrations

RESULT AND DISCUSSION

Characterisation of Activated Carbon: Table 1 summarizes the characteristics of the activated carbon from the technique employed. The activated from this work has a relatively high Methylene blue adsorbative surface area when compared with those prepared from other agricultural by-product such as cashew nut 801m^2/g, Coconut shell 998m^2/g, Corn cob 659 m^2/g, Guinea-corn stem 519 m^2/g.

This might be connected to the removal of considerable organic by-products and minerals presented in the activated carbon surface with the phosphoric acid during the activation process.

Effect of pH on Cr Adsorption: The pH of the system plays an important role on the whole adsorption process of adsorbate molecule, presumably due to its influenced on the surface properties of the adsorbent and on the ionization/ dissociation of the adsorbate molecules [19]. In this study, the adsorption of the dye is highly pH dependence as shown in figure 1. The maximum removal of CR colour was observed at pH 7.

Similar influence of pH was observed on dyes adsorption on activated carbon such as adsorption of malachite green [20] and acid yellow 36[21].

Table 1: Characteristics of the activated carbon

Parameters,	Value
Yield of charred product	67.7%
Ash content	26.5%
Bulk density	0.37g/cm^3
Percentage fixed carbon	73.5%
Iodine number	918.6
Methylenes blue value	425
Methylene blue Langmuir Xm	0.44mol/g

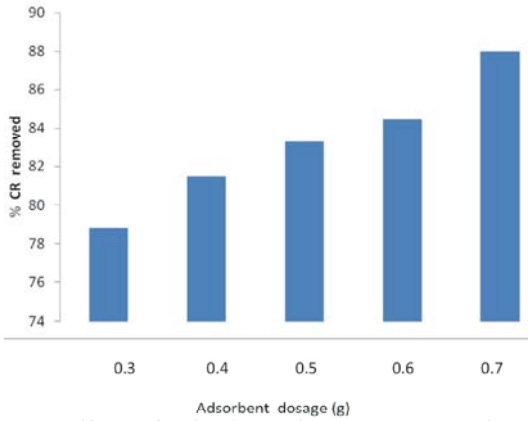

Fig. 1: Effect of adsorbent dosage on CR adsorption capacity (%) in 50ml of initial concentration 100mg/L, pH 7,agitation speed 100rpm for 2hrs,temperature 30±2°C

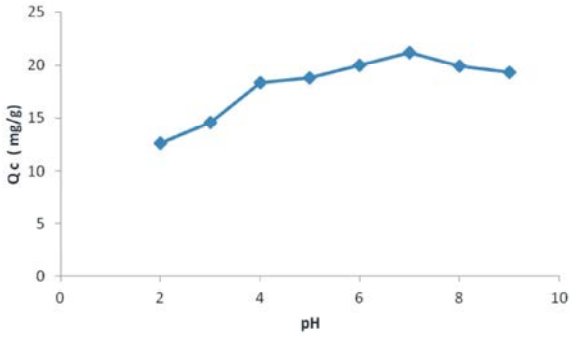

Fig. 2: Effect of pH on CR adsorption capacity (%) in 50ml of initial concentration of100mg

Effect of TSC Mass on Cr Adsorption: The adsorption of CR on TSC was carried out by varying of TSC (0.3, 0.4, 0.5, 0.6 and 0.7g) added to the CR solution keeping the initial CR concentration, pH and temperature constant at contact time of 100 min. The result in figure 2 shows an increase in the adsorption with an increase in TSC dose. This can be attributed to the increase in adsorptive surface area and hence availability of more adsorption sites [10, 22].

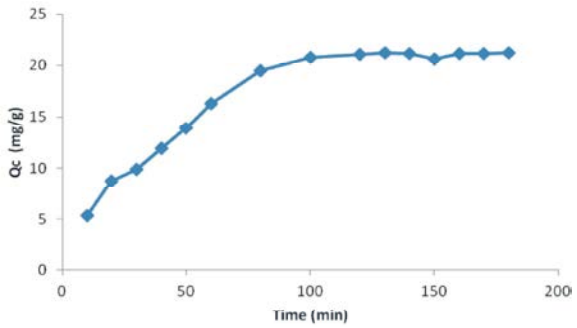

Fig. 3: Effect of agitation time on CR adsorption capacity Qc (mg/g) in 50ml of initial concentration 100mg/L, pH 7,agitation speed 100 rpm for 2hrs, temperature 30 ± 2 °C ; amount of adsorbent 0.2 g

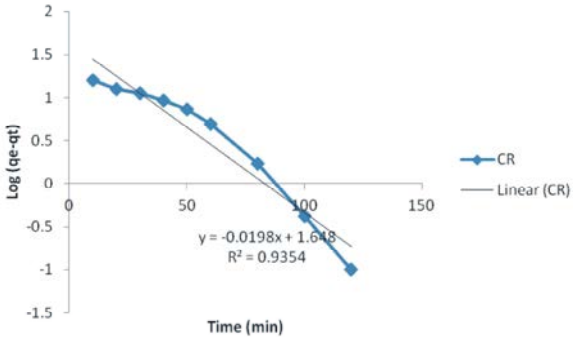

Fig. 4: Pseudo-first order kinetic model for CR adsorption

Effect of Initial Cr Concentration on Adsorption: The effect of initial concentration of CR in the solution on the adsorption capacity on TSC was shown in fig 3. The experiments were carried out at fixed dose of TSC (0.2g), temperature, pH and different initial concentration of CR 25-250 mg/L. The amount of CR adsorbed per unit mass of adsorbent Q_e increased with increase in CR concentration in the solution, the percentage was greater at lower initial concentration and smaller at higher initial concentration. At lower concentration, the ratio of amount of CR available and the number of adsorption dyes was low, hence comparatively, a higher percentage of adsorption resulted. With subsequently higher concentrations, this ratio progressively increased due to number of adsorption sites becoming fewer compared to the amount of CR available and therefore, a decreasing trend in percentage adsorption from a lower concentration to a higher concentration [22, 24].

Adsorption Equilibrum Modelling: The capacity of the adsorption isotherm is fundamental and plays an important role in the determination of the maximum capacity of the adsorption. It has been observed to produce a panorama of the course taken by the system under study in a concise form indicating how efficiently a carbon will adsorb and allows an estimate of the economic viability of the carbon's commercial application for the specified solute. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of equilibrium data of each system. The most widely accepted surface adsorption models for single-solute system (i.e. adequate model that can reproduce the experimental results obtained) are the Langmuir and Freundlich models [24].

Frendlich and Langmuir Isotherm were used, the linearized form of Freuundlich isotherm is given as

$$Log\, qe = Log\, k + \frac{1}{n} Log\, Ce$$

- Where qe is the dye adsorbed at equilibrium onto carbon.
- Ce is the final concentration of dye mg/L in the solution.
- K is the empirical constant that provide an indication of the overall adsorption capacity (mg/g).

1/n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity (dimensionless). The value of 1/n ranges from 0-1 and the closer the value to zero, the more heterogeneous the adsorbent surface. The Freundlich isotherm equation is an empirical equation based on the sorption on a heterogeneous surface which is an indication that the binding site are not equivalent or independent. The model that assumes a monolayer adsorption, Langmuir isotherm model in linearized form is given as

$$\frac{1}{qe} = \frac{1}{q\max} + \frac{1}{q\max KL}\frac{1}{Ce}$$

Where qe is also dye adsorbed mg/g at equilibrium, q_{max} maximum sorption or dye uptake from solution mg/g and K_L is Langmuir equilibrium constant related to overall solute adsorptivity (L/mg).

The experimental data were fitted with the selected isotherm. Figure 4 and 5 shows the isotherm models plot for adsorption of CR on TSC. The values of parameters and correlation coefficient for each isotherm model are shown in Table 2.

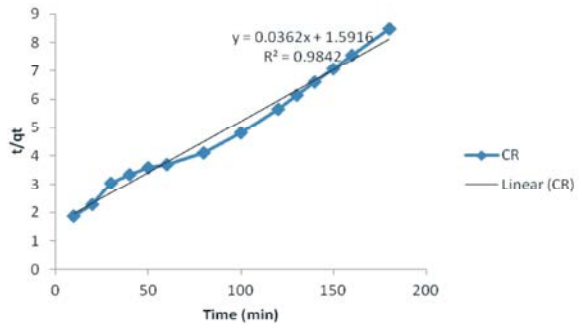

Fig. 5: Pseudo – second- order kinetic s model for CR adsorption

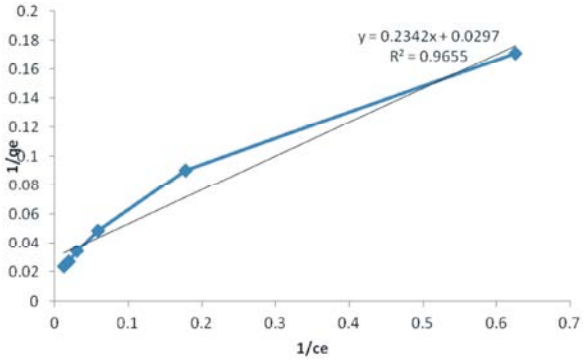

Fig. 6: Langmuir Isotherm for CR adsorption Process

Table 2: shows the values of Parameters and correlation coefficient for each isotherm model

Isotherm Model	Value
Langmuir	
q_m (mg/g)	34.5
K_L (L/mg)	0.1240
R^2	0.965
Freundlich	
1/n	0.524
K_f(mg/g)	4.507
R^2	0.997

Langmuir isotherm for the removal of CR on TSC shows that the correlation coefficients obtained indicates a strong positive evidence on the adsorption of CR on to TSC follows the Langmuir isotherm. The maximum monolayer capacity q_{max} from Langmuir model is 34.5mg/g.The applicability of the linear form of Langmuir model TSC was also proved by this high correlation coefficient 0.965. This suggests a good model of the sorption system. Data were also fitted to Freundlich equation. The correlation coefficients of 0.997 shows that the data fitted more to Freundlich model than Langmuir. The 1/n is below 1.0 indicating that CR is fairly adsorbed by TSC. [24, 26, 27,].

Kinetics Modellings: The process of adsorption is time dependence, thus the kinetics parameters which are helpful for the production of adsorption rate gives important information for designing and modeling the adsorption processes [28]. The kinetics of CR onto TSC were carried out. The batch adsorption data was analysed using pseudo-first order and second kinetic models.

Pseudo-First Order Model: The linearised form of pseudo-first order equation is given by the following expression [29].

$$Log\, qe - qt = \log qe - \frac{k1t}{2.303t}$$

Where qe and qt adsorption capacity of equilibrium and at time t_1 respectively (mg/g). K_1 is the rate constant of pseudo-first order (L/min).

Pseudo-Second Order Model: The expression for linearised form of pseudo-second order kinetics is given as

$$\frac{t}{qt} = \frac{1}{k2q2e} + \frac{1}{qe}t \quad [30].$$

Where K_2 (mg min)$^{-1}$) is the second order rate constant for the adsorption.

In order to obtain the rate constants, the values of Log (qe-qt) against t.

The kinetic constants and equilibrium adsorption qe values are given in table 3.

Table 4: Kinetics parameters of the pseudo-first order and pseudo-second order for CR adsorption.

Pseudo first order parameter			Pseudo second order parameter		
qe (mg/g)	K_1 (Lmin^{-1})	R^2	qe (mg/g)	K_2 gm^2/g min^{-1}	R^2
44.46	0.044	0.935	27.78	0.001	0.984

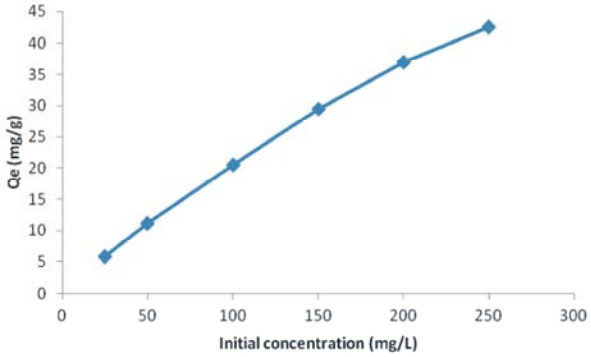

Fig. 7: Effect of Initial concentration on CR adsorption Capacity, Qe

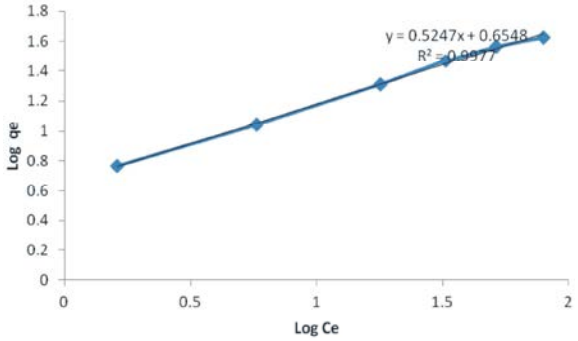

Fig. 7: Freundlich Isotherm for CR adsorption Process

The plot of second kinetics drawn for 1/qt against time are shown in fig 4.

The value of rate constants, equilibrium uptake and correlation coefficients of the two kinetic models are shown in Table 4. It was observed that the experimental data showed a better compliance with pseudo second order model, than the pseudo first order model as the correlation co-efficients are close to unity for pseudo first order kinetic model. Similar results was reported for the adsorption of CR from aqueous solutions on surfactant modified Montmorillonite [31] and CR on ethylenediamne modified rice husks [32].

CONCLUSION

The study indicates that carbon prepared from the shell of *thevetian peruvinian* seed has a suitable adsorption capacity to remove congo red a typical dye from aqeous solution. This further strengthen the call for the use of conventional and expensive methods in the treatment of industrial effluents.The biosorption was found to depend on pH, adsorbate dosage, initial dye concentration and contact time.The adsorption equilibrium is practically achieved in 100 mins. The adsorption process follows the Freudlich and Langmuir isotherm but better fitted to Freudlich. The determination.The results of kinetics data was appropriately fitted with pseudo- second order kinetics

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