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Removal of congo red from aqueous solutions using plant biomass: equilibrium & kinetic studies

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ABSTRACT

Biosorption is potentially an attractive technology for the treatment of waste water for retaining dyes from dilute solutions. Studies carried through environmental biotechnology have shown that many biosorbents present in the nature have great capacity for removal of dyes. Biosorption of Congo red on *bauhinia purpurea* leaves had been studied and compared by using batch techniques. The biosorption experiments were performed under various conditions such as different initial concentrations, pH, bio sorbent dosage and biosorbent particle size. About 0.1g of *bauhinia purpurea* leaves was found to be enough to remove 84% of Congo red at concentration of 20 mg/L from 50 ml aqueous solution in 40 min. The optimum pH was found to be 6. The pseudo first order, pseudo second order and Elovich kinetic models were used to describe the kinetic data. The dynamic data was fitted with the pseudo second order kinetic model. The experimental equilibrium data were tested by the biosorption isotherms like Langmuir, Freundlich and Temkin and their equilibrium parameters were determined. The best fitted model to the experimental data for *bauhinia purpurea* leaves was Langmuir model.

KEYWORDS

Congo red;
Biosorption;
Isotherms;
Kinetics;
Waste water treatment.

INTRODUCTION

Dyeing industry is one of the oldest industries known to the mankind. Large amount of dyes are annually produced and used in textile, cosmetics, paper, leather, pharmaceutical, food and other industries. There are almost 10,000 various dyes are present and almost 2/3rd of dyes are used in textile industry[1]. Colour is a visible pollutant and presence of a minute amount of colouring substance makes it undesirable. Wastewater from the dyeing industries having dye content is one of the major problems due to its toxic nature and thus causing pollution[2]. Therefore, many researchers worked to eliminate these dye contaminated water before discharging into the water bodies. The removal of colour from dye bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. The most commonly used methods for the dye removal are biological oxidation and chemical precipitation. However these methods can be employed only when the concentration of the dye is relatively high[3]. The majority of the technologies employed for the colour removal are based on the physiochemical process such as chemical precipitation, coagulation and flocculation[4], ultra filtration[5], oxidation, reverse osmosis, ion exchange, dilution, adsorption[6] and ozonation[7]. Of among the above techniques coming to the efficiency and cost factor adsorption is the most preferable one. Adsorption is carried out mostly by using activated carbon because of having high adsorptive capacities. But the production of activated carbon is expensive and its regeneration is very difficult[8]. Recent research has been directed towards the looking alternatives to investigate a low cost method, which is both economical and effective which can be used on an industrial scale. Among the treatment technologies biosorption is getting prominence because it is economically favourable, effective and technically feasible[9].

Recent research has been concentrated on the low cost adsorbents such as agricultural solid waste, orange peel[10], sand[11], harsh wood[12],cellulose based wastes, palm kernel fibre, saw dust[13] dead fungal biomass like Funalia trogii, pith[14], fly ash[15-16], caulerpa recemosa etc. Biosorption using dead cells have many advantages over the other live cells. Because dead organisms are not affected by toxic wastes and don't require a continuous supply of nutrients, that can be regenerated and reused for many cycles. Presently the study is carried on the feasibility of removal of Congo red using *bauhinia purpurea* leaves on the lines of biosorption process.

Congo red is benzadene based dye shown in Figure 1. Congo red causes allergic reaction and metabolized to Benzedrine. Further it decomposes into cancer causing carcinogenic products. It is a gastrointestinal irritant which acts on skin and eyes. It induces drowsiness and creates respiratory problems and also has impacts on, blood factors such as clotting[17-18].

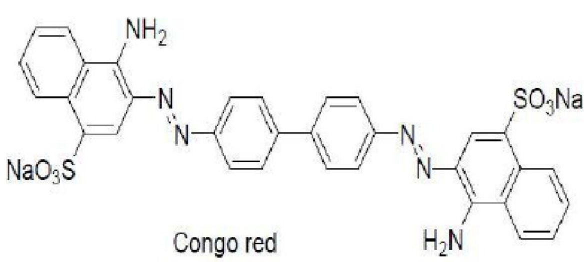

Figure 1 : Molecular formula of congo red

EXPERIMENTAL

Material

The *bauhinia purpurea* leaves used in the present study were collected in GMR Institute of Technolo and washed with deionised water. The washing process was continued till the wash water contains no dirt. The washing leaves are then completely dried in sunlight for 30 days. The resulting product was used directly as Biosorbent.

Particle size

In the present study, the powdered materials i.e., Biosorbent is powdered in the range of 81-162.3μm. average size were then directly used as Biosorbent without any pre treatment.

Dye solution

Stock solution of Congo red, concentration 1gm/L was prepared by dissolving 1gm of Congo red in 1000 ml of distilled water. The range of concentration of prepared solutions varied between 20 and 100ppm.

Contact time

Optimum contact time was determined by shaking 0.1gm of Biosorbent in 50 ml of synthetic solution of initial dye concentration 20mg/L with a pH of 6. Shaking was provided for different intervals like 1min, 2min, etc up to 55min at constant agitation speed.

Initial dye concentration

To study the effect of initial dye concentration, 0.1g of Biosorbent is taken and 50ml of synthetic solution of dye concentration of 20mh/L is mixed it and kept it for shaking for optimum time. The same procedure is repeated with 50ml of stock solution, but with different initial concentrations like 40mg/L, 60mg/L etc. keeping the remaining conditions like agitation speed and room temperature constant. Then the samples are analysed for dye concentration.

Biosorbent dosage

Taking 50ml of 20mh/L Congo red stock solution with a known amount of Biosorbent dosage 0.1g of 81μm (average size) is shaken with constant agitation speed for optimum time at constant temperature. This is repeated for different dosages ranging from 0.1g to 0.5g of same Biosorbent size. The concentration of the dye for each individual sample is determined by UV visible spectrometer.

Initial pH

The effect of initial solution pH was determined by agitating 0.1g of Biosorbent and 50ml of synthetic Congo red solution of initial dye concentration of 20mg/L at different pH values of solution ranging from 2 to 9 by adding 0.1N NaOH. Shaking was provided for optimum contact time at constant agitation speed and at room temperature. The concentration for each dye is determined for each case.

Analysis

The total dye concentration in solution was analysed by UV- visible Spectrometer (systronics power 230volts Model Number 117 made in Hyderabad) at a wavelength of 497 nm for Congo red.

RESULTS AND DISCUSSION

The experimental data on biosorption were obtained batch wise to study the effect of parameters on the removal of dye from the synthetic solutions prepared in the laboratory by *bauhinia purpurea* powder. All the experimental runs were taken at a room temperature (30± 1^0C).

Biosorption studies

Effect of contact time

The experimental results reveal that the uptake of dye is faster at initial stages of contact and it becomes slower at equilibrium. This is due to the availability of a large number of vacant sites are difficult to be occupied at later stages of adsorption, and most likely to the repulsive forces between the solute molecules on the adsorbent and aqueous solution.

Figure 2 shows the contact time for adsorption of Congo red from aqueous solutions containing 20mg/L of Congo red. The percentage adsorption increased from 19.34 to 84.0% for Congo red for 1min to optimum contact time 40min with 20mg/L of aqueous solution. The boundary layer resistance will be affected by the rate of adsorption; increase in optimum time decreases the resistance which facilitates the increase in mobility of dye to the biosorbent[19].

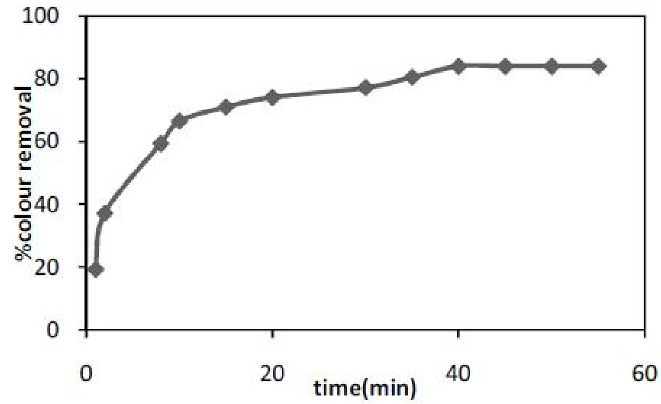

Figure 2 : Effect of contact time on %biosorption of Congo red on *bauhinia purpurea* leaves powder for 20mg/l of dye and 0.1g/50ml biomass sol

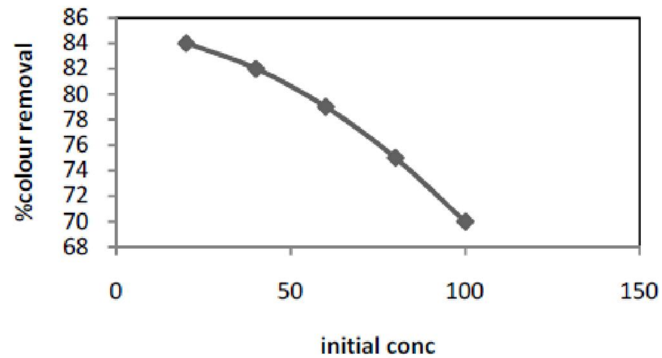

Figure 3 : Effect of initial dye conc on % Biosorption of Congo red by *bauhinia purpurea* powder for 20mg/L of dye at 0.1g/50ml of biomass conc

Effect of initial concentration of dye

In order to study the effect of initial concentration of Congo red in the solutions on the rate of adsorption on dye, the experiments were carried out at a fixed biosorbent dosage (0.1g) and at different initial dye concentrations of Congo red (20,40,60,80,100mg/L) for optimum time contact (40min) at 30^0C. Figure shows the effect of initial dye concentration on the adsorption. It is due to the effect of concentration gradient which is the main driving force for adsorption. Figure 3 shows the effect of initial dye concentration on the adsorption.

Effect of initial pH of the solution

The pH is an important factor on the biosorption of Congo red from aqueous solution since it is re-

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sponsible for the protonation of dye binding sites, calcium carbonate solubility and metal specification in the solution. The effect of pH studied at room temperature (30±1^{0}C) at an initial dye ion concentration 20 mg/L.

The removal of Congo red as function of hydrogen ion concentration was examined at pH 2-9. The removal efficiency was found to be highly dependent on the hydrogen ion concentration of solution. The effect of pH on adsorption efficiency is shown in Figure 4 the high adsorption yield was obtained at pH 6. The maximum adsorption efficiency was 84% at pH 6 and this pH is selected as optimum pH for further studies. Generally net positive charge on the H^+ ions decreases with the increase in pH which results in decrease in repulsion between biosorbent surface and the dye[20].

Effect of biosorbent dosage

For studying the effect of biosorbent dosage on removal of dye, the biosorbent dosage is varied from 0.1 to 0.5g, fixing the other parameters like initial concentration at 20mg/L, pH 6 and particle size 81µm. The contact time was 40min for Congo red stated earlier. The biosorption plot of Figure 5 shows an increase in % biosorption with an increase in Biosorbent dosage. This is because of availability of more binding sites for complexation of dye ions.

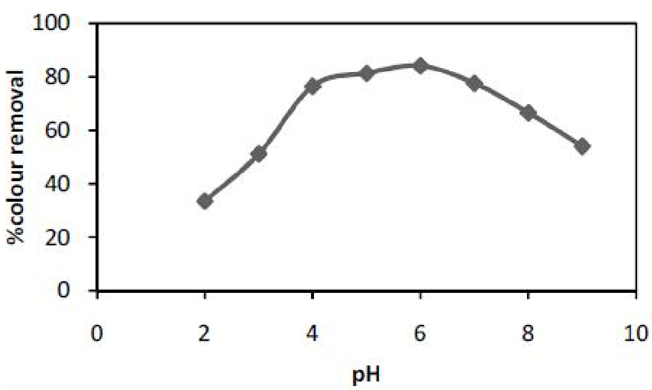

Figure 4 : Effect of pH on congo red dye Biosorption by *bauhinia purpurea* leaves powder for 20mg/L of dye and 0.1/50ml biomass conc sol

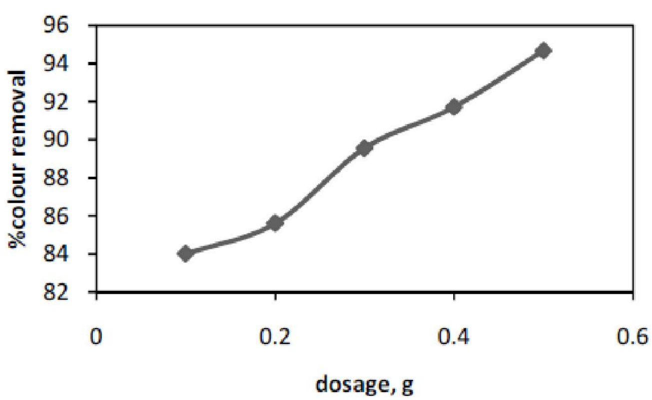

Figure 5 : Effect of dosage on Congo red dye Biosorption by *bauhinia purpurea* leaves powder for 20mg/L of dye and 0.1g/50ml biomass conc sol

Effect of biosorbent particle size

Fixing the initial concentration of solution at 20mg/L, pH6, and the fixed volume of 50ml solution is allowed for 40min for Congo red biosorption with 0.1g each of the varied size particles of biosorbent ranging from 81 to 162.3µm, the plot Figure 6 drawn for the variation of the percent biosorption against the particle size, shows that with increase in particle size biosorption decreases. This is due to the less surface area available with increased particle size, thus reducing the biosorption[21].

Adsorption isotherm constants

The biosorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of sorbent and can be also used to compare biosorptive capacity of biomass.

Langmuir isotherm

Langmuir isotherm is a basic assumption that biosorption takes places at homogenous sites within the adsorbent. The Langmuir isotherm model is represented by the following equation

$$q_e = \frac{k_L q_{\max} c_e}{1 + bC_e}$$

Where q_e (mg/g^{-1}) is the amount of dye biosorbed per unit mass of biosorbent, C_e (mg/L) is the equilibrium dye ion concentration in the solution, q_{max} (mg/g) is the Langmuir constant related to the maximum monolayer biosorption capacity and k_L (L/mg) is the constant related to the free energy or net enthalpy of biosorption. The Langmuir model in linear form is given as

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{\max}} + \frac{1}{q_{\max} c_e}$$

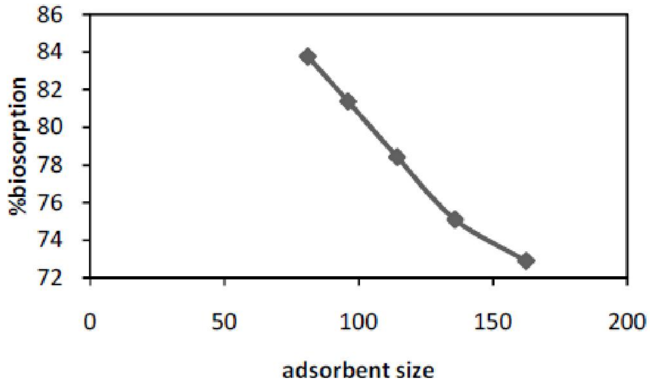

Figure 6 : Effect of particle size on Congo red dye biosorption by *bauhinia purpurea* leaves powder for 20mg/L of dye at 0.1mg/L biomass conc sol

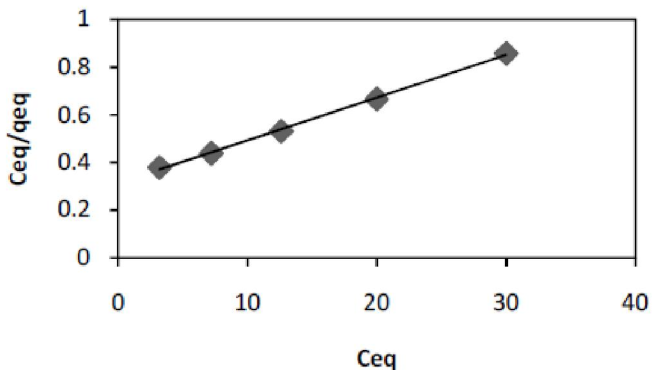

Figure 7 : Langmuir adsorption isotherm Congo red dye biosorption by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/50ml biomass conc sol

The Langmuir constants q_m and k_L are evaluated from the slope and intercept of the linear plot of C_e/q_e versus C_e.

From the Figure 7 the biosorption affinity constant (b), maximum capacity (q_{max}) and separation factor (R_L) of the Congo red to form a mono layer on the surface to the *bauhinia purpurea* leaves powder was estimated at 0.068 L/mg, 44.44mg/g and 0.4237 respectively. The correlation constant obtained was 0.997

Freundlich isotherm

Freundlich isotherm relates non ideal and reversible adsorption. Freundlich isotherm theory describes the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations. The Freundlich isotherm model was given by

$$q_e = K_f C_e^{1/n}$$

Where is the amount of dye biosorbed per unit mass

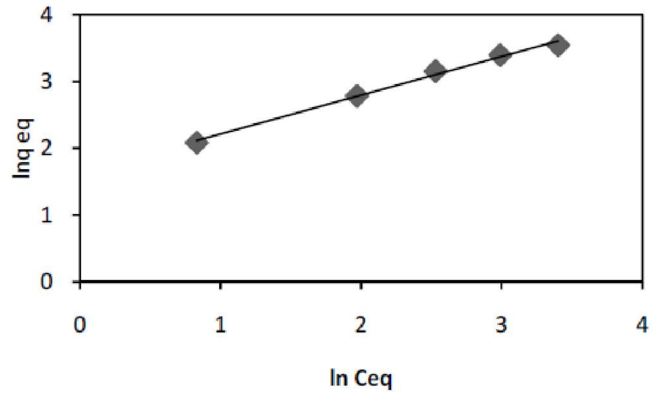

Figure 8 : Freundlich adsorption isotherm Congo red dye biosorption by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/50ml biomass conc sol

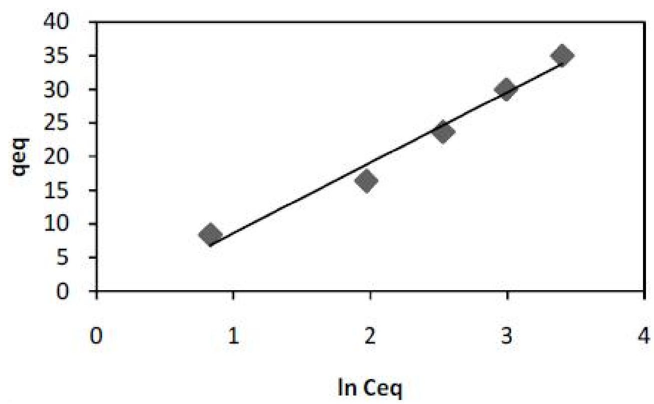

Figure 9 : Temkin adsorption isotherm Congo red dye biosorption by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/50ml biomass conc sol

of biosorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_f is the Freundlich adsorption constant related to the biosorption capacity of the biosorbent ((mg/g)/(L/g)^n) and 1/n, a dimensionless constant.

The linear form of Freundlich isotherm is

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

The values of K_f and n are calculated from the intercept and slope of the plot of ln q_e versus ln C_e.

From the Figure 8, the Freundlich isotherm the constant related to the biosorption coefficient (K_f) and intensity ($1/n_f$) were 1.45 and 0.69. The correlation co efficient obtained was 0.993

Temkin isotherm

Temkin model is applied to evaluate the adsorption potential of the adsorbent for adsorbate ions. The Temkin isotherm equation is expressed as

TABLE 1 : Comparison table

Biosorbent	pH	Biosorbent capacity (mg/g)	references
Baggasse fly ash	7.0	9.638	22
Activated carbon	7.0	0.477	23
Radish	10	0.49	24
Live biomass	6.0	23.81	25
Tamarind fruit shell	9.0	23.87	26
Sugarcane baggasse	5	38.2	27
Bauhinia purpurea	6.0	44.44	present

$$q_e = \frac{RT}{b} ln(A_T C_e)$$

The linear form of Temkin equation is

s$q_e = B_T \ln A_T + B_T \ln C_e$

Where, B_T = RT/b, R-universal gas constant (8.314 $Jmol^{-1}K^{-1}$), b- related to heat of adsorption (J mol^{-1}), T-absolute temperature (K) and A_T is the equilibrium binding constant (Lg^{-1}) and q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. A plot of q_e versus lnC_e enables the determination of the isotherm constants A_T and B_T.

From the Figure 9 Temkin isotherm constants were B_t and A_t were found to be 1.192 and 14.2 for Congo red aqueous solution. The correlation coefficient from Temkin model obtained was 0.995.

The biosorption capacities of different biosorbents on Congo red was given in TABLE 1.

Kinetic studies

In order to characterize the kinetics of reactions, three kinetic models were used to fit the experimental data. The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full scale batch process. The kinetics of biosorption data was analysed using three models, pseudo first order, and pseudo second order and Elovich model.

Pseudo first order model

The possibility of adsorption data following lagergren pseudo first order kinetic is given by

$$\frac{dq}{dt} = K_1(q_{eq} - q)$$

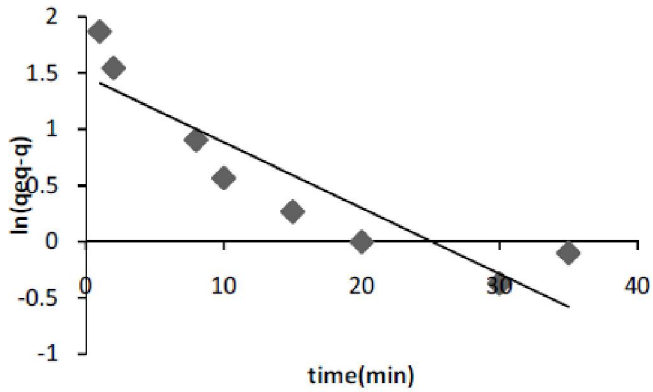

Figure 10 : Pseudo first order biosorption of Congo red dye by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/50ml biomass conc sol

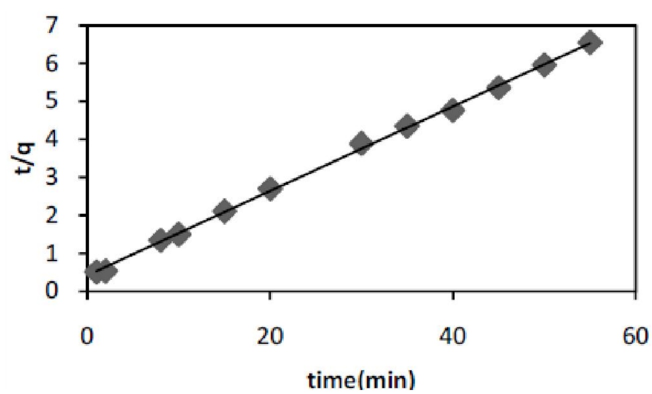

Figure 11 : Pseudo second order biosorption of Congo red dye by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/50ml biomass conc sol

Integrating the above equation with respect to integration conditions q=0 to q=q at t=0 to t=t, the kinetic rate expression becomes

$$\ln(q_{eq} - q) = lnq_{eq} - K_1 t$$

In order to obtain the rate constant, the straight line plot of Figure 10 of ln (q_{eq}-q) vs. time was made for *bauhinia purpurea* for initial dye concentration, 20mg/L. The intercept of above plot should be equal to log q_{eq}. However, if q_{eq} from intercept does not equal to equilibrium Congo red dye uptake then the

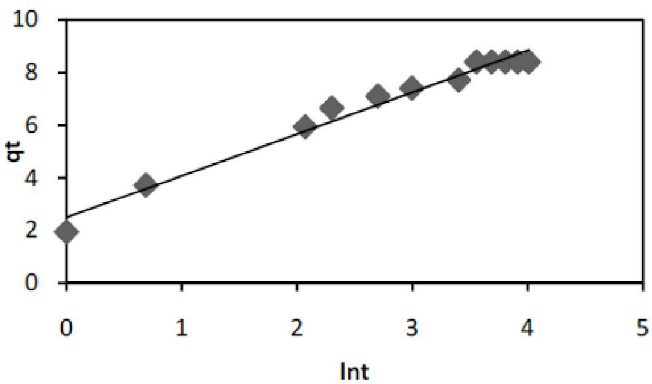

Figure 12 : Elovich model for Congo red dye biosorption by *bauhinia purpurea* leaves for 20mg/L of dye and 0.1g/ 50ml biomass conc sol

reaction is not likely to be first order, even if this plot has high correlation coefficient with the experimental data, correlation coefficients were found to 0.946 for Congo red, but the calculated q_e is not equal to experimental q_{eq}, suggesting the insufficiency of pseudo first order model to fit the kinetic data for the initial dye concentration examined.

Pseudo second order model

A pseudo second order model proposed by Ho and McKay was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorptions. The pseudo second order model can be expressed as

$$\frac{dq}{dt} = K_2(q_{eq} - q)^2$$

Integrating the above equation for boundary conditions q=0 to q=q at t=0 to t=t, simplifies to

$$\frac{t}{q} = \frac{1}{K_2\, q_{eq}^2} + \frac{1}{q_{eq}} t$$

Where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) is the amount of dye adsorbed at equilibrium and at any time, t. Correlation coefficients were found to be 0.998 for Congo red for initial concentration 20mg/L. If the second order kinetics is applicable, the plot Figure 11 of t/q vs. time of equation should give a linear relationship from which the constants q_{eq} and K_2 can be determined. The rate constants and the correlation coefficients of Congo red for both tested models have been calculated.

Elovich model

The Elovich model gives the information about type of adsorption mechanism (i.e physical and chemical). It is expressed as:

$$\frac{dq}{dt} = \alpha e^{-\gamma q}$$

Where α is initial rate and represents the extent of surface coverage and activation energy required for chemisorptions (g/mg). Integrating the above equation between the boundary conditions q=0 at t = 0 and q = q at t = t gives

$$q = \frac{\ln(t+t_0)}{\gamma} - \frac{1}{\gamma} l$$

Where $t_0 = 1/\alpha$. Simplifying the above equation under very large t over t_0, gives

$$q = \frac{1}{\gamma}\ln(\alpha\gamma) + \frac{1}{\gamma}\ln t$$

The γ is the desorption constant obtained from the slope and intercept of a straight line plot of q vs ln t shown in Figure 12 should yield a linear relationship with slope of $(1/\gamma)$ and an intercept of $(1/\gamma)\ln(a\gamma)$. The correlation coefficient was obtained at 0.977

Out of the above models pseudo second order model was found to best fit for the 20mg/L concentration of biosorbent

CONCLUSION

In this work, the biosorption capacity of *bauhinia purpurea* leaves for the removal of congored from aqueous solution was investigated. Effects of process variables such as contact time, pH, dosage, initial dye concentration, particle size, as well as kinetics and isotherms of the congored adsorption, were determined. Removal of congored using *bauhinia purpurea* leaves can be best fitted by the Langmuir model. The pseudo second order model best describes the biosorption of congo red onto *bauhinia purpurea* leaves.

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