Scientific Journal of Impact Factor (SJIF): 4.72

e-ISSN : 2348-4470
p-ISSN : 2348-6406

International Journal of Advance Engineering and Research Development

National Conference On Nanomaterials, (NCN-2017)

Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

ADSORPTION OF NAPHTHOL BLUE BLACK-B DYE FROM AQUEOUS SOLUTION BY LOW-COST AGRICULTURAL BYPRODUCT SAGO WASTE

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Abstract:- *Dyes are aromatic coloured compounds and they are commonly used in textile, paint, paper, plastic, cosmetics and food processing industries for colouring purpose. Every year, around 2,80,000tons of textile dyes are discharged as effluents from textile industries. Waste water containing dye effluents are difficult to degrade. When these textile effluents reach the environment, they cause mainly water pollution. In the present work, adsorption of Naphthol Blue Black-B dye from aqueous solution over sago waste has been investigated at batch mode experiments. Experimental observations are analysed using various isotherm & kinetic models and thermodynamic parameters are evaluated. It is concluded that the sago waste is an excellent adsorbent for removal of dye from textile waste water.*

Keywords*: Adsorption, Naphthol Blue Black-B, sago waste and dye removal.*

1.INTRODUCTION

Water pollution is one of the biggest issue in the world. Water is being polluted by various means of sources like textile industry, dye house, factory, poultry etc. Nearly 10,000 dyes and pigments are used in dyeing and printing industries. Globally about 7 x 10^5 tonnes of dyes are produced. About 10 to 15% of the dye consumed in the dyeing process is disposed into the environment as effluent[1]. Discharge of coloured effluent without proper treatment can degrade the environment such as water bodies, ground water and soil[2,5].

Various methods are used for the treatment of textile waste water. They are broadly fall into three categories-physical, biological and chemical methods[2]. The physio-chemical methods have many disadvantages such as high cost, low efficiency, limited versatility, toxic byproducts and handling of the waste generated.

Amongest all, adsorption is an efficient and low-cost treatment method and also it occupies a prominent place in dye removal Hence this paper suggests a low-cost method using the waste material as an adsorbent giving good results. If these wastes could be used as adsorbents, it will provide two advantages that first one is the volume of waste materials could be partly reduced and second thing is the low-cost of the adsorbent.

Literature survey shows that most of the low-cost agricultural byproducts are used to prepare activated carbon as adsorbent. In this work, the waste material has been used as adsorbent directly without any modification. It is an effective method interms of simplicity, ease of operation, high adsorption capacity, etc.

The aim of this study is to evaluate the adsorption process by sago waste, an agricultural byproduct for the removal of Naphthol Blue Black-B from the aqueous solution.

2.MATERIALS AND METHODS

2.1.Instruments

In the present experimental studies, MAPADA V-1100D Spectrophotometer was used for determination of dye

concentrations. Equip-Tronics digital pH meter model EQ-610 was used in pH measurements for adsorption experiments.

2.2.Materials

The sago waste was collected from sago industries, Rasipuram.

Naphthol Blue Black-B used in the adsorption studies was obtained from Loba Chemie Pvt. Ltd., Mumbai.

2.3.Methods

2.3.1.Preparation and Activation of sago waste

The Sago waste sample is an agricultural byproduct and it is obtained from sago industries. Impurities were removed from the samples after which they were washed and sun dried for 6hrs. The samples were crushed and heated in the oven for 24 hrs and used for all adsorption experiments.

2.3.2.Preparation of Stock dye solution

A stock solution of 500mgL^{-1} was prepared by dissolving the appropriate amount of Naphthol Blue Black-B in 100ml. The pH of the solution was adjusted using 0.1N of HCl and NaOH. All the adsorption experiments were carried out at room temperature.

2.3.3. Adsorption Studies

Solution of Naphthol Blue Black-B was standardized by measuring the optical densities of the various concentrations of the dye solution at 618nm by using MAPADA spectrophotometer. Batch adsorption experiments were carried out. 100ml of dye solution of required concentration was taken in a pyrex bottle which contains the required amount of sago waste at room temperature. The solutions were shaken at 250rpm in orbital shaker. At appropriate time intervals, 7ml of aliquot was centrifuged in ultra centrifuge machine at 2500rpm speed. Then the optical density of the clear supernatant dye solution was measured till the equilibrium was attained.

Percentage decolourisation(%) was calculated using the following equation

$$\text{Percentage decolourisation (\%)} = [(C_i - C_e)/C_i] \times 100$$

The adsorption capacity of dye adsorbed per gram of adsorbent was calculated by

$$q_e = (C_i - C_e)/M$$

Where C_i and C_e are the initial and equilibrium dye concentrations (mg/L)

M is the mass of the adsorbent (g/L)

Adsorption experiments permit convenient evaluation of influence of parameters such as contact time.(0-40min), initial dye concentration(7.5-17.5mg/L), dosage of sago(10-30g/L), temperature(34-40°c), pH(4-9pH), agitation speed(50-250rpm), activation time(0-2hour) and desorption studies (0.1-0.5N NaOH) have been investigated.

3.RESULTS AND DISCUSSION

Adsorption of Naphthol Blue Black-B from aqueous solution over sago waste has been investigated.

3.1. Variation of contact time

The Naphthol Blue Black-B dye solution (100ml, 12.5mgL^{-1}) was agitated with 2g of sago waste at 34°c for various intervals of time in an orbital shaker[3]. The percentage sorption exhibited an increasing trend as the agitation time increased and reached equilibrium after 40 minutes (Figure 1). It is known that % decolourisation increases with increase in contact time.

3.2.Variation of initial dye concentration

Naphthol Blue Black-B dye solution (100ml) of different initial concentrations (7.5,10,12.5,15,17.5mgL^{-1}) were agitated for 40 minutes with 2g of sago waste at 34°c (Figure 2). Increase in dye concentration increases the time required to reach equilibrium[3]. It was found that the % decolourisation decreases with increasing initial dye concentrations. It is attributed to the formation of monolayer of dyes on the surface of sago waste which hinders the further formation of layer of dyes.

3.3.Variation of sago waste dosage

Naphthol Blue Black-B dye solution (100ml, 12.5mgL^{-1}) was agitated with variable amounts of sago waste (10,15,20,25,30gL^{-1}) for 40 minutes at temperature of 34°c[2,3](Figure 3). It was found that % decolourisation increased with increase in sago waste dosage. Results of effect of sago dosage were quite logical on the basis of increase in sorption site.

3.4.Variation of temperature

Naphthol Blue Black-B dye solution (100ml,12.5mgL-1) was agitated with 2g of sago waste for 40minutes at different temperatures (34,37,40°c)[1,3] (Figure 4). It is known that % decolourisation increased with increasing temperatures.

3.5.Variation of pH

The pH of the medium plays a vital role on adsorption of dyes. Dye solutions were adjusted to pH(4,7,9) using 0.1N HCl and NaOH (Figure 5). The % decolourisation is increased with decrease of pH. The initial pH may affect the charge on the surface of the adsorbent altering its capacity to adsorb dye molecules [1,2,3]. The maximum adsorption shows that the favourability to anionic adsorption through an increase in acid medium (ie) reduction in OH^- concentration (or) production of H^+ ions on sorption sites and electrostatic attraction between anionic dye and adsorbent.

3.6.Variation of agitation speed

The effect of agitation speed[2] on the adsorption of dye by sago waste is shown in Figure 6. The significant decolourisation was observed in the speed range 50 to 250rpm. The results further revealed that the highest decolurisation of 79.2% was obtained. It is clear that the rate of adsorption increases with agitation speed. This is due to the fact that with the increased turbulence, there is a decrease in boundary layer thickness around the adsorbent particles.

3.7. Variation of activation time

The effect of activation time of sago waste on the rate of decolourisation was investigated by varying the time of activation (ordinary,1,2hour) (Figure 7). The rate of decolourisation is increased considerably with increase of activation time of sago waste.

3.2.8.Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent, dye and thereby make the treatment process more economical. Sodium Hydroxide of varying strengths 0.1,0.2,0.3,0.4 and 0.5N were used to regenerate the dye adsorbed on the sago waste. The % of desorption increases with increase in concentration of NaOH (Figure 8). If the desorption of dyes by mineral acids(HCl) and alkaline medium indicates that the dyes are adsorbed onto the sago waste by physisorption[3].

I.Adsorption isotherm studies

Adsorption isotherm is usually the ratio between the quantity adsorbed and remaining in solution at fixed temperature.

a) Freundlich isotherm

The Freundlich equation[2,4,5,6,7] is widely used in the environmental engineering practice to model adsorption of pollutants from an aqueous medium empirically. The linear form of Freundlich equation is given by the following expression

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

q_e is the amount of the dye adsorbed per unit mass of adsorbent (mg/g) at equilibrium which can be calculated as

$$q_e = x/m = (C_i - C_e)/ m$$

where

x = amount of dye adsorbed at equilibrium

m = amount of adsorbent (g/L)

C_e = equilibrium concentration of the dye in solution (mg/L)

C_i = initial dye concentration (mg/L)

K_f and n are Freundlich constants. Linear plot of $\ln q_e$ versus $\ln C_e$ shows that the adsorption follows Freundlich isotherm.

In the present study, the experimental data was fitted into Freundlich linearized equation and the plots of $\ln C_e$ versus $\ln q_e$ was found to be linear which indicates that the adsorption of Naphthol Blue Black-B over sago waste follows Freundlich isotherm (Figure.9). The value of n(1.0855) and K_f (10.9135) were calculated from the slope and intercept of the linear plots respectively.

b) Langmuir isotherm

Langmuir isotherm[2,4,5,6,7] is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and the linear equation is expressed by

$$C_e / q_e = (1/Q_0 b) + C_e/Q_0$$

Where Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively.

In the present study, the experimental data were fitted into the linearized equation by plotting C_e / q_e against C_e(Figure 10). The plot of C_e / q_e against C_e was found to be linear. Q_0(0.1303) & b(19.1865) values were calculated from the slope and intercept of the linear plot respectively.

Langmuir isotherm can be expressed by a separation factor called equilibrium parameter, R_L which is expressed as

$$R_L = 1 / (1+bC_i)$$

where b is Langmuir constant and C_i is the initial dye concentration. R_L value indicates the shape of the isotherm and nature of adsorption process.

In the present study, R_L value was obtained as 0.0400 for Naphthol Blue Black-B. This value indicates that the adsorption of Naphthol Blue Black-B dye using sago waste is a favourable process.

II.Adsorption Kinetics

The kinetics of decolourisation of Naphthol Blue Black-B dye solution over sago waste has been studied using mostly pseudo first and second order models. These kinetics models are used to examine the controlling mechanism of adsorption process.

a)Pseudo-first order model

The pseudo-first order rate equation[1,2,5] can be applied for the determination of the rate constant.

Pseudo-first order model is given by Lagergren as $dq_t/dt = k_1 (q_e-q_t)$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively

k_1 is the rate constant of the pseudo-first order adsorption.

After integration, the integrated form of the above equation becomes

$$\log(q_e-q_t) = \log q_e - k_1 t / 2.303$$

The graph is drawn by plotting $\log(q_e-q_t)$ against t (Figure 11). The present experimental data were modeled for pseudo-first order rate equation, but the rate equation was not obeyed.

b)Pseudo-second order model

Pseudo-second order kinetics[1,2,5] is expressed as $dq_t / dt = (q_e-q_t)^2$

Where k_2 is the rate constant of pseudo-second order adsorption.

After integration, the form of rearranged equation is $t/q_t = 1/k_2 q_e^2 + t/q_e$

The plot of t against t/q_t using the above equation should give a straight line (Figure 12). q_e and k_2 can be determined from the slope and intercept of the plot respectively. In the present study, the experimental data were modeled to linearized pseudo-second order plot. The linear plot shows that the reaction kinetics follows pseudo-second order model.

The rate constants k_2(2.1217) and q_e(0.2171) were determined from the intercept and slope of the plot respectively.

III.Diffusion Studies

a)Weber and Morris intra-particle diffusion model

The kinetic data were analysed by an intra-particle diffusion model to elucidate the diffusion mechanism. The Weber-Morris intra-particle diffusion rate equation[1,5] can be given as

$$q_t = K_d \sqrt{t} + C$$

Where, q_t is the amount of sorbate on the surface of the sorbent at time t

K_d is the intra-particle diffusion rate constant

C is a constant that gives idea about the thickness of the boundary layer.

The plot of $\sqrt{t}$ against q_t should be linear (Figure 13) if intra-particle diffusion is involved in the overall adsorption mechanism. The diffusion rate constants K_d (0.0450) and C (0.2140) were calculated from the slope and intercept of the plot respectively.

IV.Adsorption Thermodynamics Studies

The Gibbs free energy change of the adsorption process[2] is related to the equilibrium constant by the classic Van't Hoff equation

$$\Delta G^\circ = - RT \ln K_L$$

Where K_L (L/g) is an equilibrium constant obtained by multiplying the Langmuir constants Q_0 and b

T is the absolute temperature (Kelvin)

R is the gas constant (8.314J/mol/K)

The graph is plotted by taking ΔG°in y-axis against T in x-axis (Figure 14).

The relationship between the changes in the Gibbs free energy, entropy(ΔS°) and enthalpy (ΔH°) can be expressed as follows

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔS° and ΔH° could be calculated from the slope and intercept of the plot respectively. The negative value of ΔG°(-2.3387) and ΔH° (-2.316) indicate that the process is spontaneous & feasible process and exothermic nature of the adsorption. The negative value of ΔS° (-0.0192) suggests that the process is enthalpy driven.

4.Conclusion

In this study, sago waste was obtained by simple process and used for the adsorption of Naphthol Blue Black-B from aqueous solution. Adsorption efficiency of sago waste for Naphthol Blue Black-B at the equilibrium time of 40minute was found to be 79.2%. The rate of adsorption was found to increase with increase in contact time, dosage of sago, temperature, pH, activation time and decrease in initial dye concentration. In desorption studies, rate of colourisation was found to increase with increase in NaOH. The experimental results were analyzed using Freundlich and Langmuir adsorption isotherm models. Equilibrium parameter R_L value was calculated as 0.0400 for Naphthol Blue Black-B. This indicates that adsorption is a favourable process. The adsorption process was found to follow pseudo-second order kinetics and the experimental data

was found to fit into Weber-Morris intra-particle diffusion model. The correlation coefficient factor (R^2) was greater than 0.90 proving that the sorption data fitted well to all adsorption isotherm models. The thermodynamics parameters, as the negative value of ΔG° and ΔH° indicate that the adsorption process was spontaneous, feasible process and exothermic in nature. The negative value of ΔS° reveals that the process is enthalpy driven. The present study has proved that sago waste could be used as an efficient adsorbent for the removal of Naphthol Blue Black-B dye from aqueous solution.

Acknowledgment

We thank the Department of Chemistry, Seethalakshmi Ramaswami College, Trichy, for financial support providing facilities to carry out the study.

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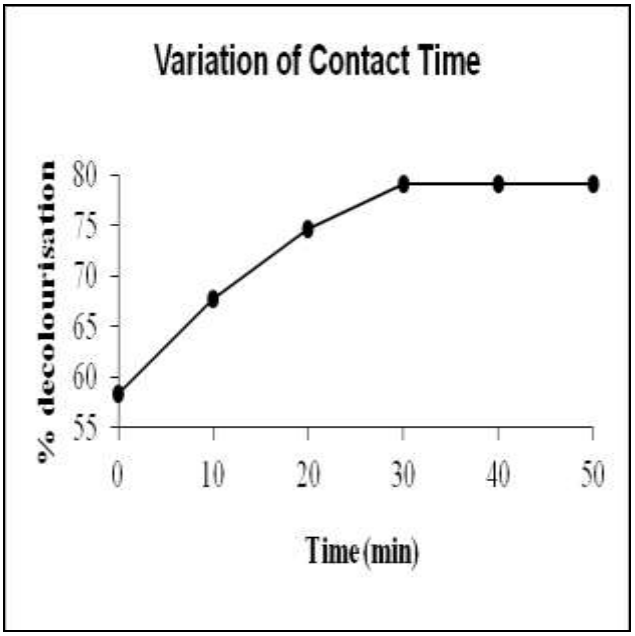

Figure 1 : Variation of contact time

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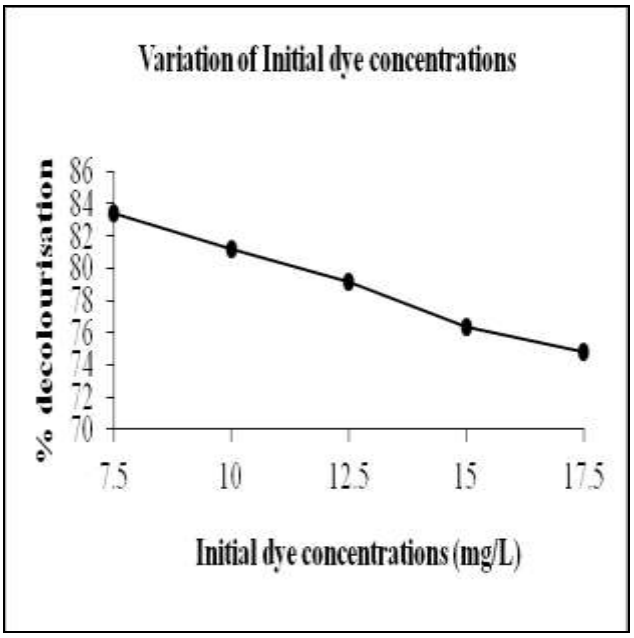

Figure 2: Variation of initial dye concentrations

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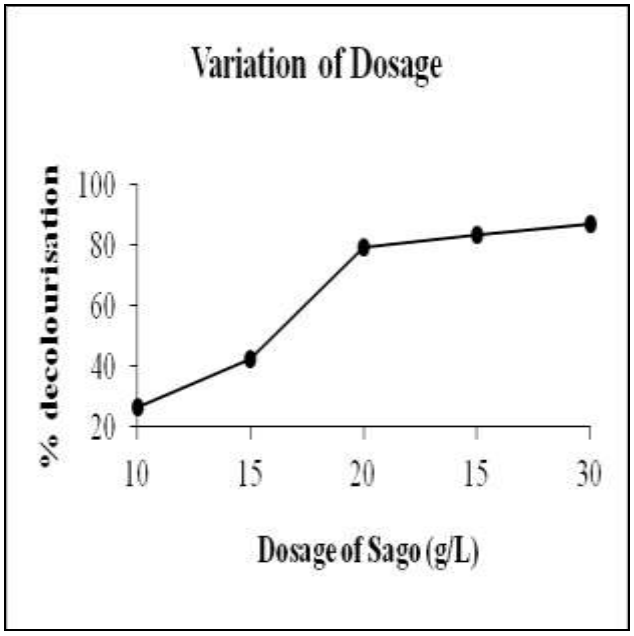

Figure 3 : Variation of Dosage of adsorbent

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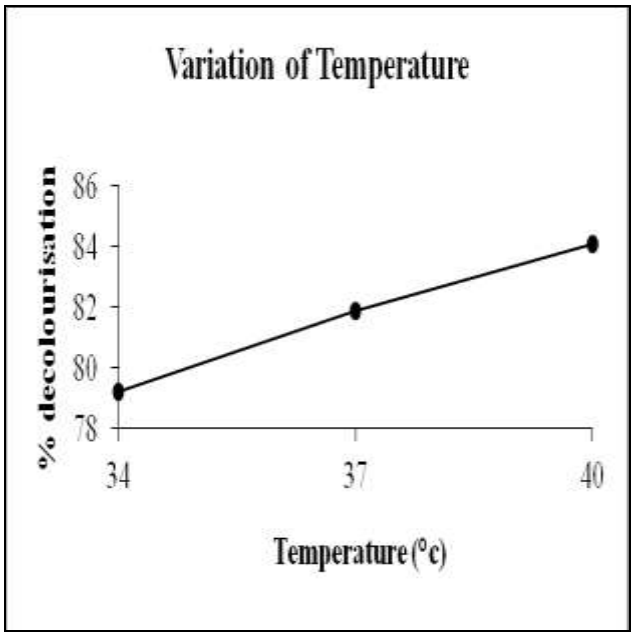

Figure 4 : Variation of Temperature

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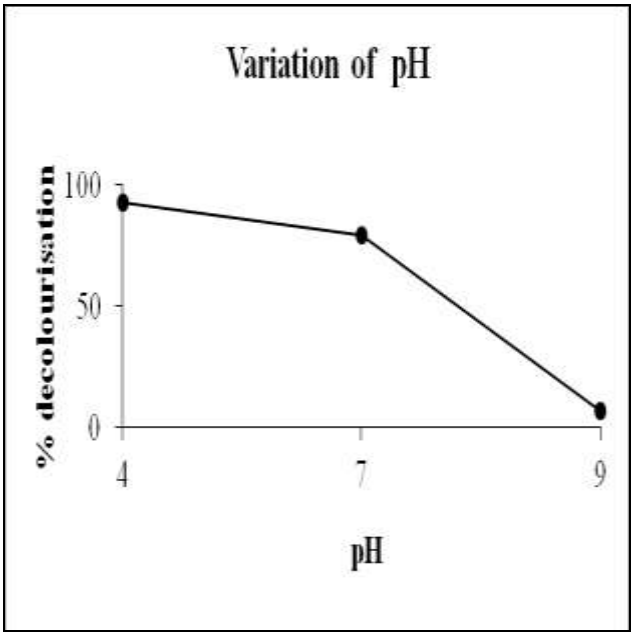

Figure 5 : Variation of pH

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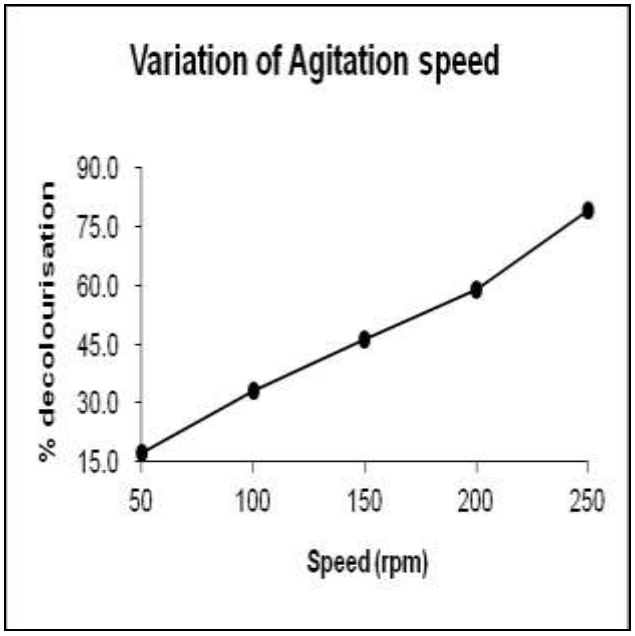

Figure 6 : Variation of agitation speed

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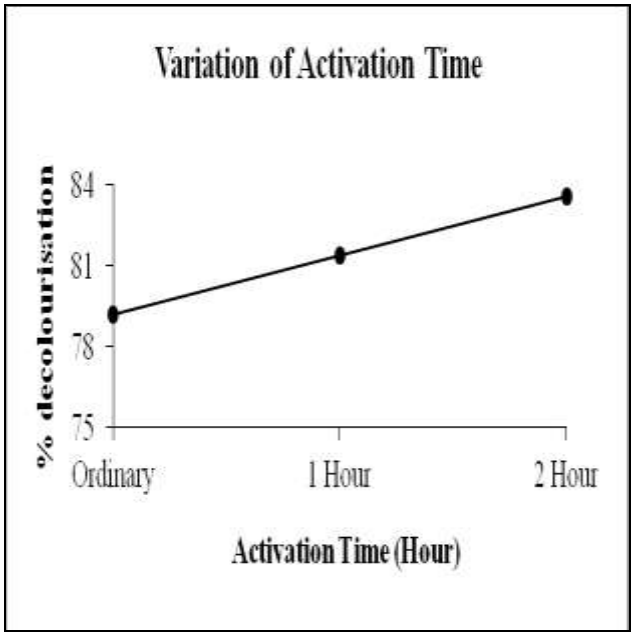

Figure 7 : Variation of activation time

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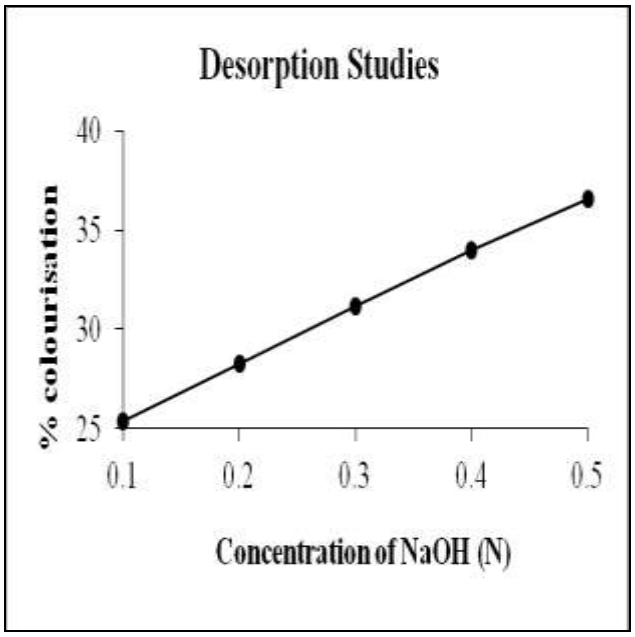

Figure 8 : Desorption studies

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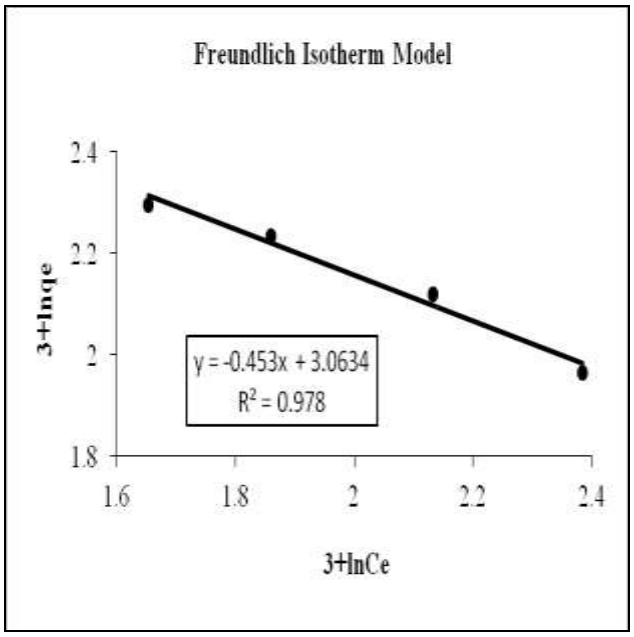

Figure 9 : Freundlich isotherm

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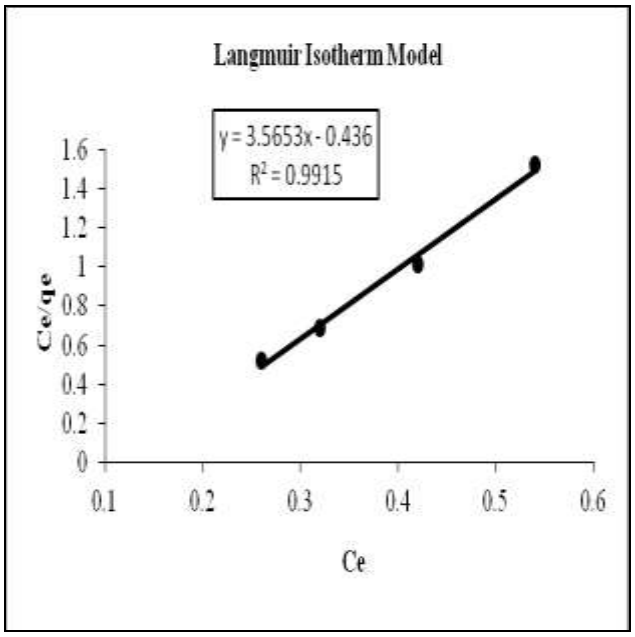

Figure 10 : Langmuir isotherm

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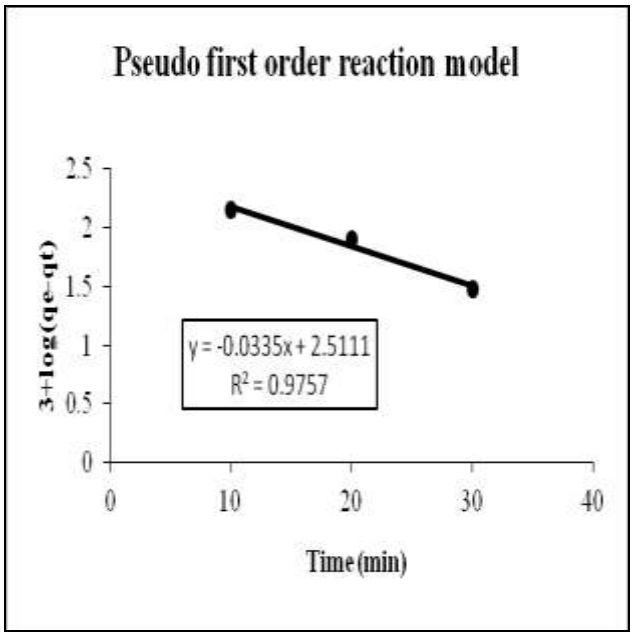

Figure 11: Pseudo-first order model

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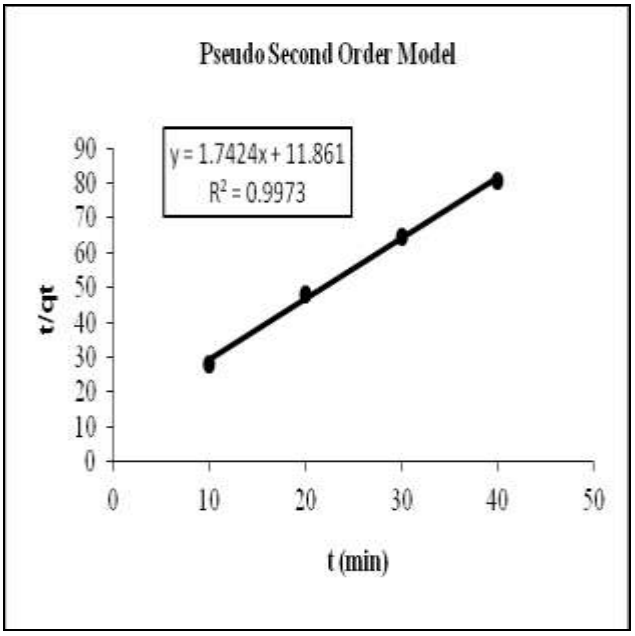

Figure 12 : Pseudo-second order model

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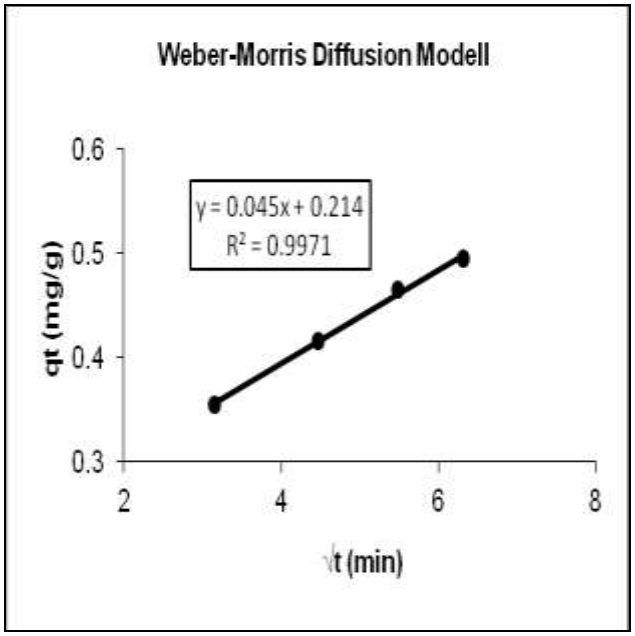

Figure 13 : Weber-Morris intra-particle diffusion model

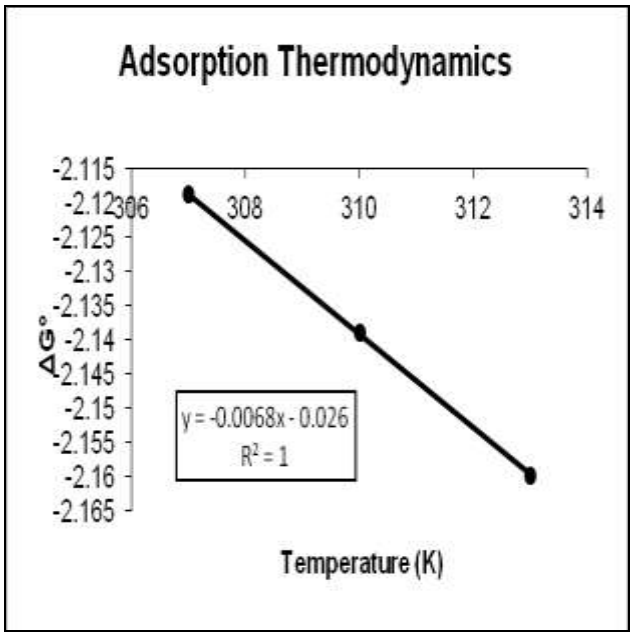

Figure 14 : Adsorption thermodynamics

