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Adsorption of Alizarine Red-S Dye from Aqueous Solution by Cane Sugar Bagasse: Resolution of Isotherm, Kinetic and Thermodynamics

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Abstract

Textile effluent contains huge quantities of toxic chemicals and high level chemical oxygen demands, which gets directly discharged into natural water bodies, thus contaminating the water quality. These effluents require prior treatment before being discharged into natural aqueous systems. In the present study, a novel low-cost, highly efficient, eco-friendly adsorbent cane sugar bagasse obtained from an industrial waste raw material is utilized for the removal of Alizarine Red-S from aqueous solution. Parameters that influence the adsorption process such as contact time, initial dye concentration, dosage of adsorbent, temperature, pH, agitation speed, activation time and desorption studies were studied in batch experiments. The experimental data were analysed using adsorption isotherm models like Freundlich, Langmuir, Dubinin-Radushkevich, Temkin, Jovanovic and Flory-Huggins. Kinetic studies showed that a pseudo-second order model was more suitable than the pseudo-first order model. Various thermodynamic parameters have also been calculated. It is concluded that cane sugar bagasse is a good adsorbent for removal of color from textile waste water.

Keywords: Adsorption, Alizarine Red-S, cane sugar bagasse and dye removal.

INTRODUCTION

Dyes are synthetic aromatic water-soluble organic substances having complex molecular structure and they are widely used for coloration in different industries like textile, paint, paper, plastic, food and cosmetics. Most of the dyes are toxic, carcinogenic and even mutagenic[1,2]. The removal of dyes from colored effluent is one of the major environmental concerns. Treatment of dye effluents is a difficult process because dyes have various synthetic origin and they contain complex aromatic molecular structure which make them more stable and more difficult to be degraded[3].

Interest in this area is proved by many publication of several reviews worldwide [4]. Among these reviews most considerable attention has been mainly devoted to the adsorption study of removal of dyes from wastewater using industrial byproducts [5]. Raw materials have been used as low-cost adsorbent, which are widely available with free of cost, ease of operation and eco-friendly [6]. The cane sugar bagasse is a segregated waste byproduct during production of sugar from sugar cane.

The present study deals with the adsorption efficiency of active cane sugar bagasse for the removal of alizarine red-s from aqueous solution. The modified raw material was characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR). The variation of different operating parameters like contact time, dye concentrations, etc have been investigated. Finally regeneration of the adsorbent has been tested by using various desorbing agents.

MATERIALS AND METHODS

MATERIALS

Stock solution of Alizarine Red-S (AR-S) was prepared using analytical grade obtained from Hi Media Laboratories Pvt. Ltd (Mumbai) in distilled water at room temperature.

INSTRUMENTATION

The dye concentrations were determined using Elico - UV-spectrophotometer. The IR absorption bands were taken by FT-IR (Jasco - 5300) spectrometer in the wave number range of 400 - 4000cm^{-1}. The surface morphological structure of sago waste was observed using SEM technique (ZEISS). The pH of the dye solution was measured in digital pH meter (EQ-610).

PREPARATION OF ACTIVATED CANE SUGAR BAGASSE (ACSB)

The cane sugar bagasse was obtained from sugar industries in Kattur (Tiruchirappalli District, Tamil Nadu). It was washed with distilled water, dried and powdered in a mixer grinder. The dry sample was sieved and then dried at 110°C for 6 hours. Finally, it was preserved in a desiccator.

ADSORPTION STUDIES

The objective of the current study was to understand the adsorbing and desorbing nature of cane sugar bagasse as reusable adsorbent. The batch experiments were carried out in 250ml pyrex bottle with 100ml of AR-S dye solution contains 0.25g of ACSB, shaken in an orbital shaker at 250rpm to investigate the effects of contact time, initial dye concentration, dosage of sago waste, temperature, pH, agitation speed and activation time on the adsorption process.

Before and after adsorption of the AR-S dye concentration is measured by using Elico UV-spectrophotometer at wave length of 503nm. The amount of AR-S dye adsorbed on the ACSB(mg/g) and percentage of adsorption of AR-S are calculated using Eq.1 and 2 respectively [7]

$$q_e = \frac{(C_i - C_e)V}{M} \quad \text{----------(1)}$$

and,

$$\%removal = \frac{(C_i - C_e)}{C_e} \times 100 \quad \text{----------(2)}$$

where q_e is the adsorption capacity (mg/g) of ACSB at equilibrium, C_i and C_e are initial and equilibrium concentration of AR-S (mg/L) respectively, V is the volume of AR-S dye solution and M is the weight of ACSB.

KINETIC AND THERMODYNAMIC STUDY

In order to find out the adsorption rate of AR-S dye solution by ACSB kinetic study was carried out. Adsorption kinetic study was carried out using 100ml of AR-S dye (8.5mg/L) solution having 0.25g of ACSB at 34°C. It was stirred in orbital shaker at 250rpm and concentration is measured at different time intervals (10-90min). Thermodynamic parameters were calculated by executing the experiment at different temperatures (34-40°C).

RESULTS AND DISCUSSION

CHARACTERIZATION

SEM is one of the most widely used surface diagnostic tools. SEM of adsorbent material was taken before and after dye adsorption on ACSB.

Fig.1(a) shows regular surface texture, porosity and heterogeneous surface of the ACSB. The SEM image of adsorbed sample (Fig.1(b)) show very distinguished dark spots which exhibit clearly the dye loaded on the adsorbent surface[8].

FT-IR spectrum of the active cane sugar bagasse showed (Figure.2(a)) peak at 3403.03cm^{-1} which can be assigned to the N-H stretching. The peak observed at 2976.95cm^{-1} denotes the presence of C-H stretching and peak observed at 1571.29cm^{-1} may be due to the presence of the C=C aromatic. The peak appeared at 1159.73cm^{-1} of the active cane sugar bagasse may be attributed to C-OH stretching[9].

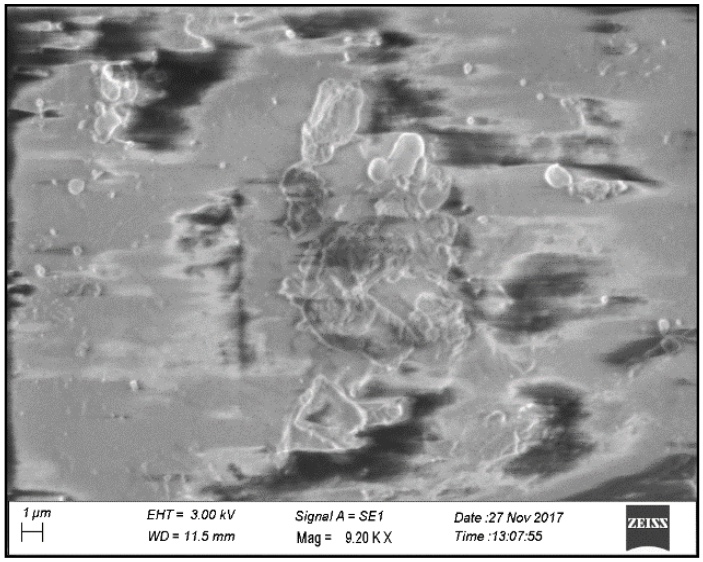


Figure 1(a): SEM of ACSB before adsorption

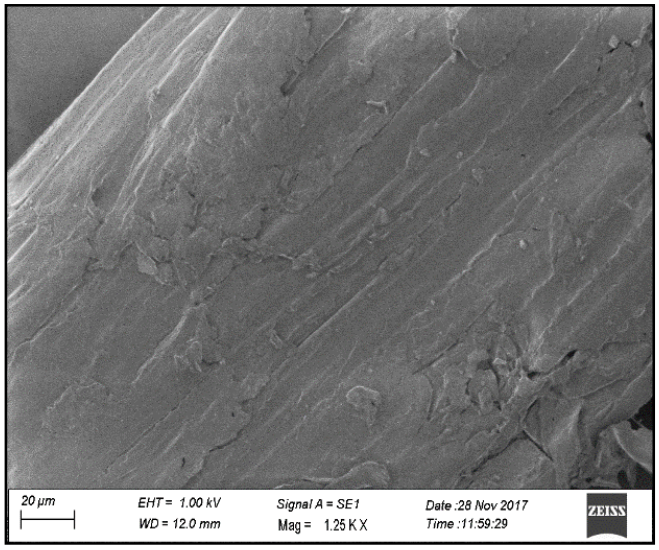


Figure 1(b): SEM of ACSB after adsorption

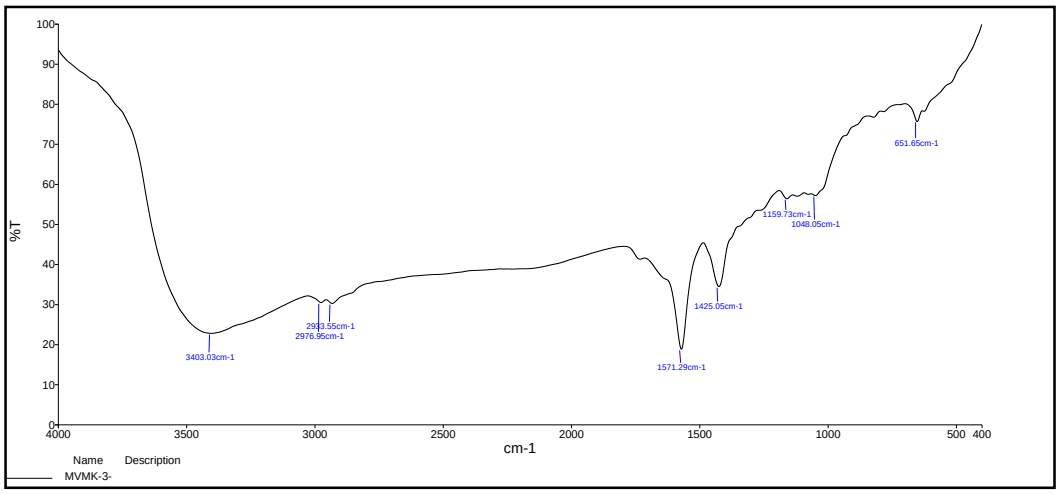


Figure 2(a): FT-IR spectrum of cane sugar bagasse before adsorption

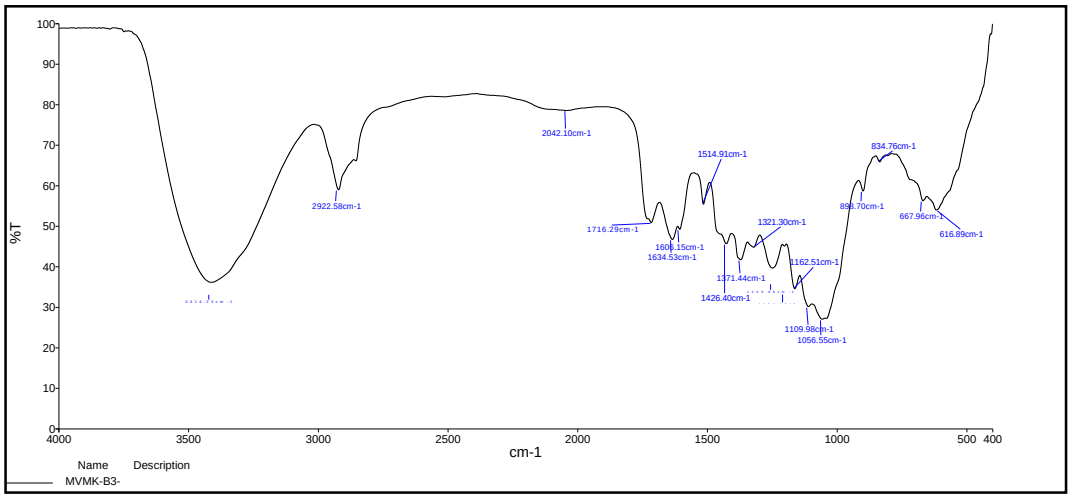


Figure 2(b): FT-IR spectrum of cane sugar bagasse after adsorption

Typical FT-IR spectra of dye adsorbed cane sugar bagasse shows (Figure.2(b)), a new peak appeared at 1716.29cm^{-1} indicates the presence of C=O ketone group at the surface of the cane sugar bagasse and it is due to the adsorption of the AR-S dye from the aqueous solution.

ADSORPTION STUDIES

Variation of contact time

Batch experiment was preformed at 34°C with initial dye concentration of 8.5mg/L using ACSB dose at 2.5g/L at pH 7 with agitation speed of 250rpm in an orbital shaker. The equilibrium data shows that the variation of contact time from 10 to 90 min on AR-S dye removal. It was observed that 96.1% of AR-S dye removed at 90min, thereafter it becomes constant. As all the adsorption sites were occupied, further adsorption was not possible and 90min was considered as optimum time for maximum adsorption.

Variation of initial dye concentration

The effect of different initial dye concentrations is studied by (7.5-9.5mg/L) maintaining the dose of ACSB at 2.5g/L, contact time to 90 min, temperature at 34°C, pH 7 and agitation speed at 250rpm. The adsorption data depicts that the % decolourisation follows decreasing trend with increasing initial dye concentration. This may be due to the formation of monolayer of dyes on the surface of ACSB which hinders the further layer.

Variation of ACSB dosage

The effect of ACSB dose was carried out by varying the ACSB mass from 1.5 to 3.5g/L keeping contact time to 90min, dye concentration to 8.5mg/L, temperature at 34°C, pH 7 and agitation speed at 250rpm. Fig.3(a) shows that the dye removal increased with increase in ACSB dosage due to increased amount of adsorption sites.

Variation of temperature

The effect of temperature was studied by varying the different temperatures (34, 37 and 40°C) maintaining contact time to 90min, dye concentration to 8.5mg/L, ACSB dose 2.5g/L, pH 7 and agitation speed at 250rpm. The equilibrium data evident that % decolourisation increased with increasing temperature due to the excitation of adsorbent particles.

Variation of pH

The effect of pH was studied by varying different pH (4, 7 and 9) keeping contact time to 90min, initial dye concentration 8.5mg/L, ACSB dose 2.5g/L, temperature at 34°C and agitation speed at 250rpm. Fig.3(b) depicts that the adsorption of AR-S increases with the decrease of pH of the solution [10]. The initial pH may affect the charge on the adsorbent surface, altering its adsorption capacity [11].

Variation of agitation speed

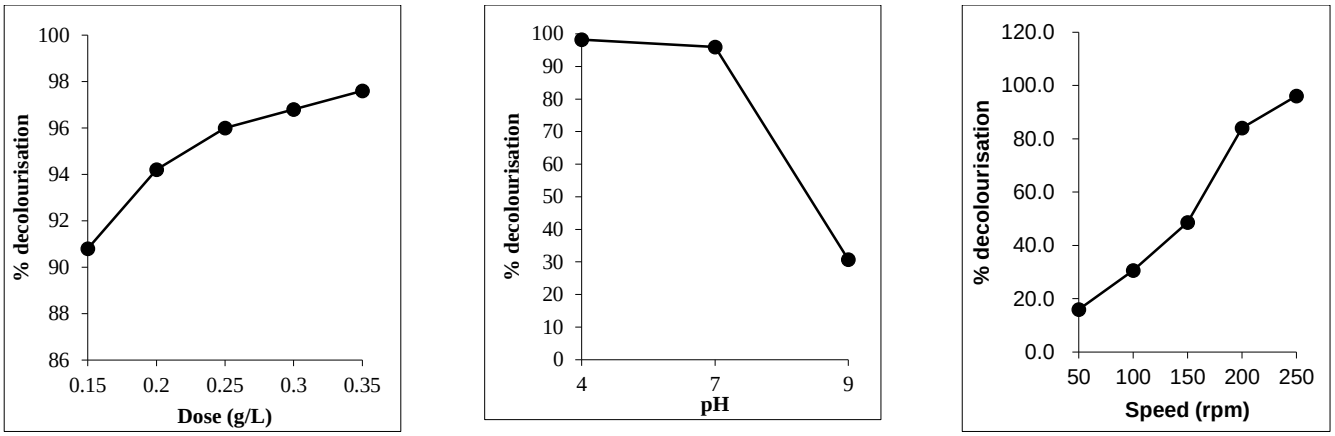
The effect of agitation speed of AR-S on ACSB was studied by varying the agitation speed from 50 to 250rpm, keeping the other parameters are constant. It is evident that the adsorption of AR-S is found to increase with increasing agitation speed due to the fact that with the increased turbulence, there is a decrease in boundary layer thickness around the adsorbent particles.

Variation of activation time

The effect of activation time of ACSB on the rate of adsorption was investigated by varying the time of activation (1, 2 hour) and other parameters are constant. The adsorption data illustrated that the activation time increases the amount of dye adsorbed also randomly increased.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling the spent adsorbent and dye is essential[12]. The desorption experiment was carried out with 0.1N NaOH. Fig.3(c) shows that the desorption efficiency increases with increase in strength of NaOH due to ion substitution.



(a) **(b)** **(c)**

Figure 3: Variation of (a) ACSB dose (b) pH and (c) desorption

ADSORPTION ISOTHERM STUDIES

The adsorption isotherm is widely used to elucidate the relationship between the amount of dye adsorbed at constant temperature and its concentration in equilibrium solution. It is an important tool of both theoretical and practical point of view. In order to optimize the adsorption design and also to predict its corresponding parameters. The parameters obtained from different isotherm models provide information about adsorption mechanism and the surface properties of the adsorbent. Linear regression coefficient is frequently used to determine the best fitting isotherm.

Freundlich isotherm

The Freundlich isotherm [13] is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact.

The linear form of Freundlich equation is given by the following expression

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

where q_e is the amount of the dye adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K_f and n are Freundlich constants. The slope 1/n indicates the favorable adsorption with the attractive force between adsorbed species [14].

Langmuir isotherm

Langmuir isotherm [15] is precise for the monolayer adsorption of a solute from a liquid on the adsorbent surface containing a definite number of identical active sites. The linear equation of Langmuir isotherm is expressed by

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \text{----------(4)}$$

where Q_0 and b are Langmuir constants. Langmuir isotherm can also be expressed in terms of separation factor, R_L which is referred as equilibrium parameter and expressed as

$$R_L = \frac{1}{(1 + bC_i)} \qquad \text{----------(5)}$$

R_L value indicates the shape of the isotherm and nature of adsorption process. When, the R_L value >1 adsorption is unfavorable, $0<R_L<1$ it is favorable, if $R_L = 0$ it is irreversible. In the present study, the R_L value was found to be 0.0149. This indicates that the adsorption of AR-S using ACSB is a favorable process.

Dubinin-Radushkevich model

The Dubinin-Radushkevich model [16,17] is used to estimate the characteristics porosity of the adsorbent and apparent energy of adsorption. The linear form of the equation is given by

$$\ln q_e = \ln q_D - 2B_D RT \ln\left(1 + \frac{1}{C_e}\right) \qquad \text{----------(6)}$$

where B_D is related to the free energy of sorption, q_D is the Dubinin – Radushkevich isotherm constant. The apparent energy of adsorption can be computed using the following equation

$$E = \frac{1}{\sqrt{2B_D}} \qquad \text{----------(7)}$$

The apparent energy (E) of the adsorption of AR-S using ACSB was obtained as 0.3333.

Temkin isotherm

Temkin isotherm [18] is assumed that the heat of adsorption decreases linearly with increasing coverage. The temkin isotherm is represented by the following linear equation

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad \text{----------(8)}$$

where K_T is the equilibrium binding constant(L/mg), B_T is the variation of adsorption energy (KJ/mol).

Jovanovic isotherm

Jovanovic model [19] is derived for describing the adsorption behaviour on heterogeneous surfaces. The linear form of Jovanovic isotherm equation is

$$\ln q_e = \ln q_m - K_J C_e \qquad \text{----------(9)}$$

where q_m and K_J are Jovanovic constants.

Scatchard analysis

Scatchard analysis [20] is employed to analyze the binding isotherm of dye molecules and adsorbent. The Scatchard equation can be expressed as

$$\frac{Q}{C} = \frac{Q_{\max}}{K_d} - \frac{Q}{K_d} \qquad \text{----------(10)}$$

where Q is the equilibrium adsorption amount at each concentration, Q_{max} is the maximum adsorption amount, K_d is the equilibrium dissociation constant at binding sites.

Flory-Huggins isotherm

Flory-Huggins isotherm [21] is the model describing the degree of surface coverage characteristics of adsorbate onto adsorbent. The linear plot of Flory-Huggins equation is expressed as

$$\log\left(\frac{\theta}{C_o}\right) = \log(K_{FH}) + n_{FH} \log(1 - \theta) \qquad \text{----------(11)}$$

where K_{FH} is the Flory-Huggins equilibrium constant, n_{FH} is the model exponent, θ is the degree of surface coverage.

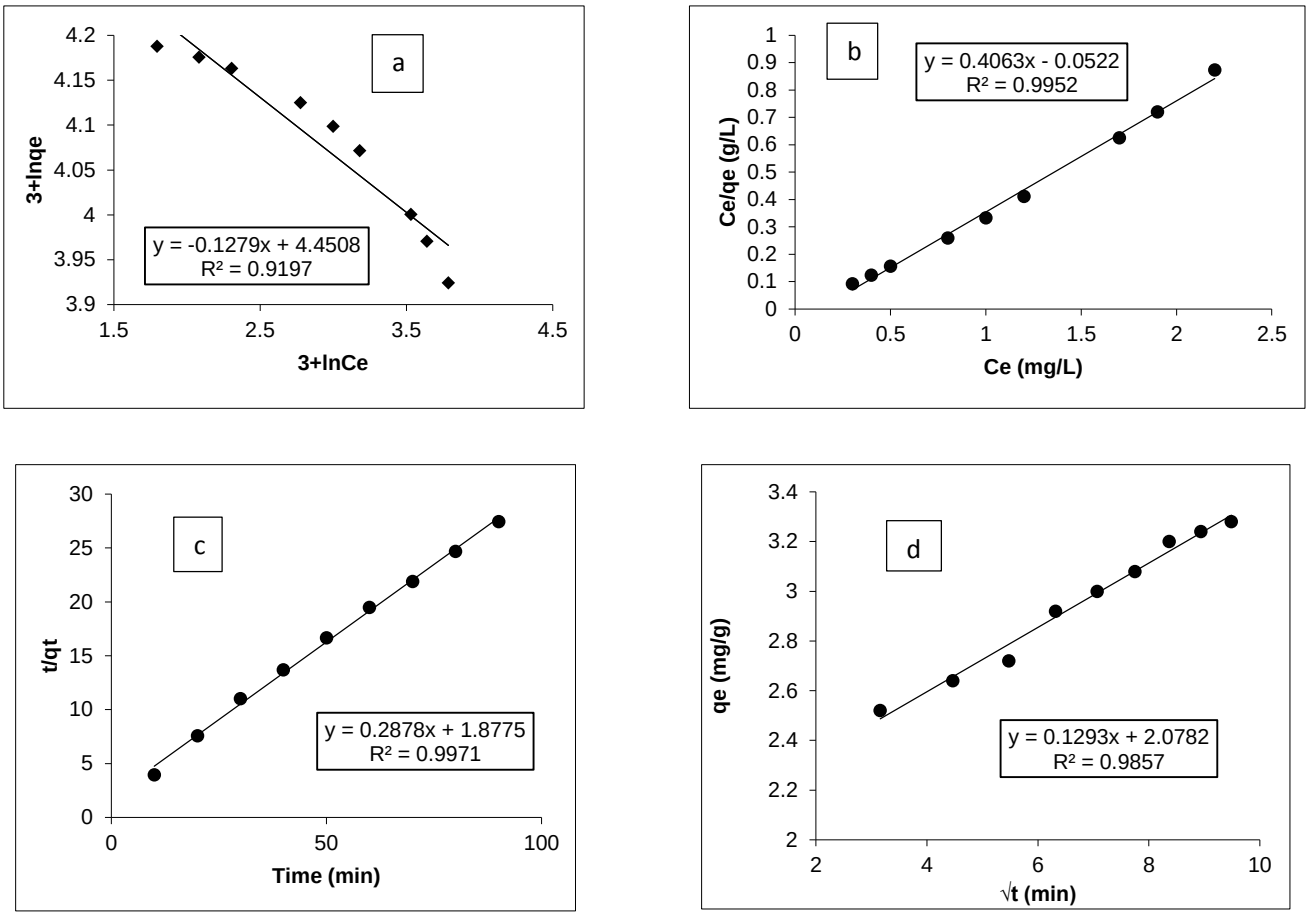


Figure 4: (a)Freundlich (b) Langmuir (c) Pseudo-second order kinetics (d) Weber-Morris model

The slope and intercept values for all adsorption isotherm models are listed as follows

Name of the isotherm	**Slope**	**Intercept**	**R^2 value**
Freundlich	n = 7.8186	K_f =12.0985	R^2 =0.9197
Langmuir	Q_0 =2.4612	b = 7.7821	R^2 = 0.9952
Dubinin-Radu.	B_D =4.5000	q_D =10.6035	R^2 =0.8466
Temkin	B = 6822.8	A =29.3596	R^2 =0.9366
Jovanovic	K_J =0.1380	q_{max} =11.5065	R^2 = 0.9988
Scatchard	K_d =0.3008	Q_{max} =0.0087	R^2 =0.9992
Flory-Huggins	n_{FH} =0.1279	K_{FH} = 13.0737	R^2 = 0.9196

ADSORPTION KINETICS

The kinetics of decolourisation of AR-S dye solution over ASW has been studied using pseudo-first and pseudo-second order kinetic models.

Pseudo-first order kinetic model

Pseudo-first order model [22] is given by Lagergren as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{----------(12)}$$

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

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad \text{----------(13)}$$

The equilibrium data shows that the adsorption of AR-S onto ASW cannot be applied and the reaction mechanism is not a first-order reaction.

Pseudo-second order kinetic model

Pseudo-second order kinetics [23] is expressed as

$$\frac{dq_t}{dt} = (q_e - q_t)^2 \qquad \text{----------(14)}$$

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

After integration, the form of rearranged equation is

$$\frac{t}{q_t} = \frac{1}{k_2}(q_e)^2 + \frac{t}{q_e} \qquad \text{----------(15)}$$

The plot was perfect linear shows that the reaction kinetics follows pseudo-second order model. The correlation coefficients (R^2) are also confirmed that the adsorption better fitted by the pseudo-second order kinetic model than pseudo-first order kinetics.

Weber and Morris intra particle diffusion model

Weber-Morris intra-particle diffusion model [24] is mainly used to elucidate the diffusion mechanism. The Weber-Morris intra-particle diffusion rate equation can be given as

$$q_t = K_d\sqrt{t} + C \qquad \text{----------(16)}$$

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 slope and intercept values are listed as follows

Name	**Rate constant**	**R^2 value**
Pseudo-first	k_1 = 0.0410	R^2 = 0.9216
Pseudo-second	k_2 = 3.4746	R^2 = 0.9971
Weber-Morris	K_d =0.1293	R^2 = 0.9857

THERMODYNAMIC STUDY

The Gibbs free energy change of the adsorption process [25] is related to the equilibrium constant by the Van't Hoff equation

$$\Delta G^\circ = -RT\ln K_L \qquad \text{----------(17)}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{----------(18)}$$

ΔS° and ΔH° could be calculated from the slope and intercept of the plot respectively. The negative value of ΔG°(-4.8887) and positive value of ΔH° (+0.5717) indicate that the process is spontaneous & feasible process and endothermic nature of the adsorption. The positive value of ΔS° (+0.0513) suggests that reflects the affinity of adsorbent for dye.

CONCLUSION

In this study, ACSB was prepared by simple process and used for the adsorption of AR-S from aqueous solution. Adsorption efficiency of ACSB for AR-S at equilibrium time of 90min was found to be 96.1%. The parameters influencing adsorption rate such as contact time, initial dye concentration, temperature, etc. were optimized. The equilibrium results were analyzed using several adsorption isotherm models. The equilibrium data were better fitted by the Langmuir model than other isotherm models. The adsorption process was found to follow pseudo-second order kinetics and the experimental data were found to fit into Weber-Morris intra particle diffusion model. In thermodynamic study, negative value of ΔG° and positive value of ΔH°indicate that the adsorption process is spontaneous, feasible process and endothermic in nature. The positive value of ΔS° reveals that reflects the affinity of adsorbent for dye. Thus, the present study has proved that ACSB could be used as an efficient adsorbent for the removal of AR-S dye from aqueous solution. Moreover, the use of ACSB as adsorbent not only to solve the environmental pollution but also to decrease the overall cost of waste water treatment and to reduce the amount of industrial byproducts.

ACKNOWLEDGMENT

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