

Adsorptive Removal of Synthetic Dye Effluent Using Sago Waste as Low-Cost Adsorbent

M Karthika* and M Vasuki

PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli, Tamil Nadu, India

Abstract

Agricultural waste (Sago waste) used as low-cost adsorbent for the removal of synthetic dye effluent from aqueous solution by batch adsorption technique. The various parameters that influence in this adsorption process such as contact time, initial dye concentration, adsorbent dosage, temperature, pH, agitation speed and desorption studies. The experimental data were analysed using Langmuir isotherm model. Kinetic data well fitted for pseudo-second order model. Thermodynamic parameters have also been calculated. The sago waste was characterized by SEM and FT-IR studies. The low-cost adsorbent was found to be efficient for the dye removal process.

Keywords: Sago waste; Synthetic dye effluent; Adsorption; Dye removal

Introduction

In recent years, discharge of waste products (mainly dye effluents) from difficult industries leading to aquatic and environmental pollution is a serious global problem of great concern [1,2]. Due to toxicity of dyes, it is necessary to remove them from wastewater before their discharge to the natural environment. Various physical-chemical and biological wastewater treatment methods such as anaerobic bioremediation, oxidative process, ozonation, electrochemical destruction, irradiation, ion-exchange, membrane filtration and adsorption have been used for the dye removal from effluents [3], as each method has some limitations.

Among all of these methods, the adsorption is one the most effective method for wastewater treatment [4]. The adsorption method is superior to other technique in terms of low-cost, high efficiency, simplicity of design, and ease of operation and insensitive to toxic substances [5]. The cost effectiveness, availability and adsorptive properties are the main criteria in selection of low-cost adsorbent to remove toxic compounds from wastewater [6].

Adsorption by agricultural by-products used recently as an economical and realistic method for removal of different pollutants, also application of bio-adsorbent especially based on non-toxic and eco-friendly with high surface area and active sites is a great demand [7]. The main objective of this work was to study the decolourization of synthetic dye effluent using activated sago waste by adsorption technique.

Experimental

In the experimental studies, Elico-UV-spectrophotometer was used for determination of dye concentrations. Equip-Tronics digital pH meter model EQ-610 was used in pH measurements for adsorption experiments.

Naphthol Blue Black-B (NBB-B) used in the adsorption studies was obtained from Loba Chemie Pvt. Ltd., Mumbai. Brilliant Green (BG) and Alizarine Red-S (AR-S) were procured from Hi Media Laboratory Pvt Ltd., Mumbai.

Preparation of stock dye solution

Stock solution of synthetic dye effluent (NBB-B, BG and AR-S) was prepared by dissolving 0.05 g of dyes in distilled water and making it up to 100 ml in a standard flask.

Preparation of activated sago waste (ASW)

The sago waste was obtained from sago industries in Rasipuram (Karur 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 experiment

The batch experiments were carried out in 250 ml pyrex bottle with 100 ml of Synthetic Dye Effluent (SDE) contains 2 g of ASW, shaken in an orbital shaker at 250 rpm to investigate the effects of contact time, initial dye concentration, dosage of sago waste, temperature, pH, agitation speed and desorption. Before and after adsorption of the (SDE) dye concentration is measured by using Elico UV-spectrophotometer at wave length of 618 nm. The amount of dye adsorbed on the ASW (mg/g) and percentage of adsorption of (SDE) dye are calculated using eqn. 1 and 2 respectively [8].

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

And,

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

Where, q_e is the adsorption capacity (mg/g) of ASW at equilibrium, C_i and C_e are initial and equilibrium concentration of SDE dye solution (mg/L) respectively, V is the volume of SDE dye solution and M is the weight of ASW.

Kinetic and thermodynamic study

In order to find out the adsorption rate of synthetic dye effluent by ASW kinetic study was determined by variation of contact time. Thermodynamic parameters were calculated by executing the experiment at different temperature (34°C-4°C).

*Corresponding author: M Karthika, PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620002, Tamil Nadu, India, E-mail: karthichemist1990@gmail.com

Received June 04, 2018; Accepted June 15, 2018; Published June 22, 2018

Citation: Karthika M, Vasuki M (2018) Adsorptive Removal of Synthetic Dye Effluent Using Sago Waste as Low-Cost Adsorbent. Int J Waste Resour 8: 344. doi: 10.4172/2252-5211.1000344

Copyright: © 2018 Karthika M, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Results and Discussion

Characterization

SEM is widely used to study the morphological features and surface characteristics of adsorbent materials. The surface morphology of the ASW was examined using Scanning Electron Microscopy (SEM) and the results are shown in Figure 1. SEM image in Figure 1 shows regular surface texture, porosity, holes and cave type openings on the surface of the ASW [9].

The FT-IR spectrum of the ASW in Figure 2 exhibits broad bands at 3345.55 cm^{-1} due to the -OH stretching frequency. The absorption band at 2929.37 cm^{-1} is due to contribution from C-H stretching. The stretching vibration obtained in the range $1250\text{-}1050\text{ cm}^{-1}$ is attributed to the presence of C-O-C bond. The strong band at 1026.76 cm^{-1} denotes the presence of C-OH stretching vibration [10].

Availability of more surface area due to typical holes and cave openings type of structure of the ASW surface was clearly witnessed in the SEM micrograph and FT-IR spectrum was confirmed that starch and cellulose moieties are present in the ASW sample.

Adsorption Studies

Variation of contact time

Batch experiment was performed at 34°C with initial dye concentration of 4 mg/L using ASW dose at 20 g/L at pH 7 with

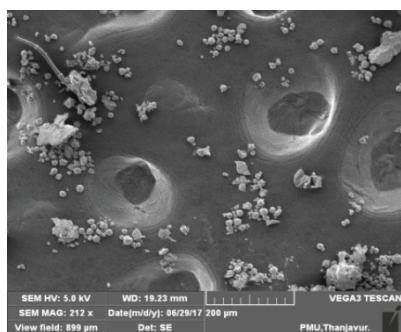


Figure 1: SEM image of activated sago waste.

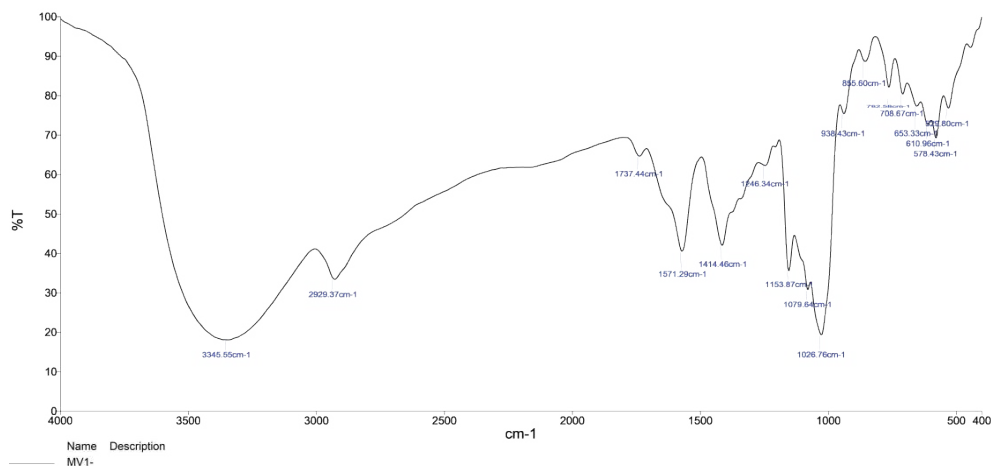


Figure 2: FT-IR spectrum of activated sago waste.

agitation speed of 250 rpm in an orbital shaker. The equilibrium data shows that the variation of contact time from 10 to 50 min on SDE dyes removal. It was observed that 78.3% of SDE dye removed at 50 min ; thereafter it becomes constant shown in Figure 3. As all the adsorption sites were occupied, further adsorption was not possible and 50 min was considered as optimum time for maximum adsorption.

Variation of initial dye concentration

The effect of different initial dye concentrations is studied by ($3\text{-}5\text{ mg/L}$) maintaining the dose of ASW at 20 g/L , contact time to 50 min , temperature at 34°C , pH 7 and agitation speed at 250 rpm . The adsorption data depicts that the % decolourisation follows decreasing trend with increasing initial dye concentration shown in Figure 4. This may be due to the formation of monolayer of dyes on the surface of ASW which hinders the further layer.

Variation of ASW dosage

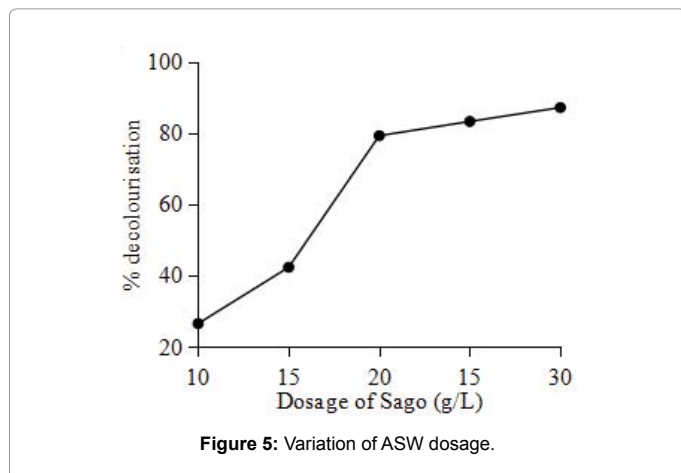
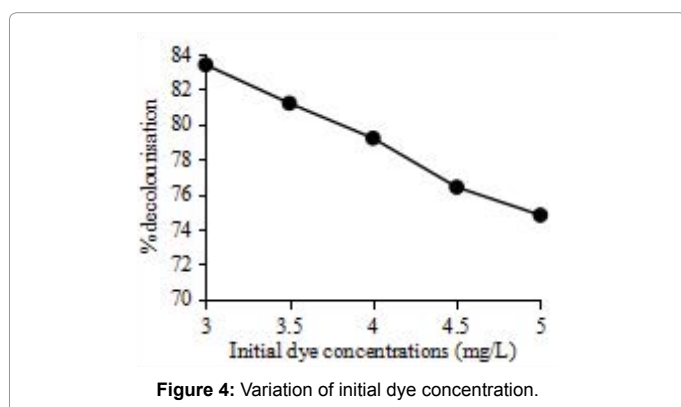
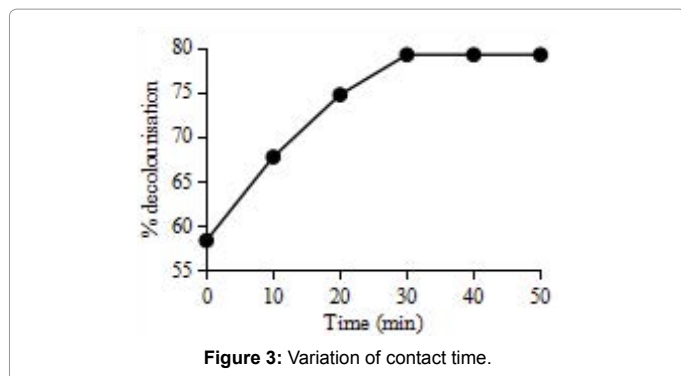
The effect of ASW dose was carried out by varying the ASW mass from 10 to 30 g/L keeping contact time to 50 min , dye concentration to 4 mg/L , temperature at 34°C , pH 7 and agitation speed at 250 rpm . Figure 5 shows that the dye removal increased with increase in ASW dosage due to increased amount of adsorption sites.

Variation of temperature

The effect of temperature (Figure 6) was studied by varying the different temperatures ($34, 37$ and 40°C) maintaining contact time to 50 min , dye concentration to 4 mg/L , ASW dose 20 g/L , pH 7 and agitation speed at 250 rpm . 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 50 min , initial dye concentration 4 mg/L , ASW dose 20 g/L , temperature at 34°C and agitation speed at 250 rpm . Figure 7 depicts that the adsorption of SDE increases with the decrease of pH of the solution [11]. The initial pH may affect the charge on the adsorbent surface, altering its adsorption capacity [12].



Variation of agitation speed

The effect of agitation speed of SDE on ASW was studied by varying the agitation speed from 50 to 250 rpm, keeping the other parameters is constant. It is evident from Figure 8 that the adsorption of SDE 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.

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling the spent adsorbent and dye is essential [13]. The desorption experiment was carried out with 0.1 N NaOH. Figure 9 shows that the desorption efficiency increases with increase in strength of NaOH due to ion substitution.

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.

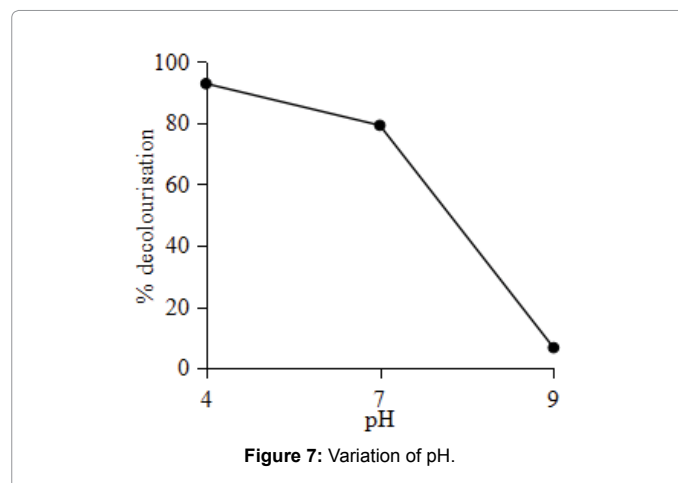
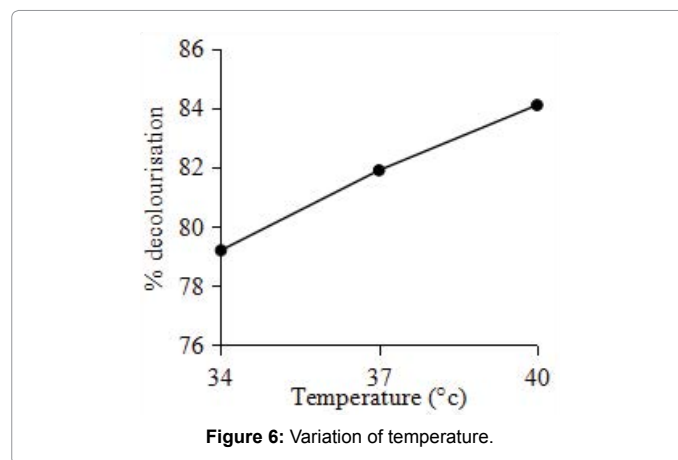
Freundlich isotherm

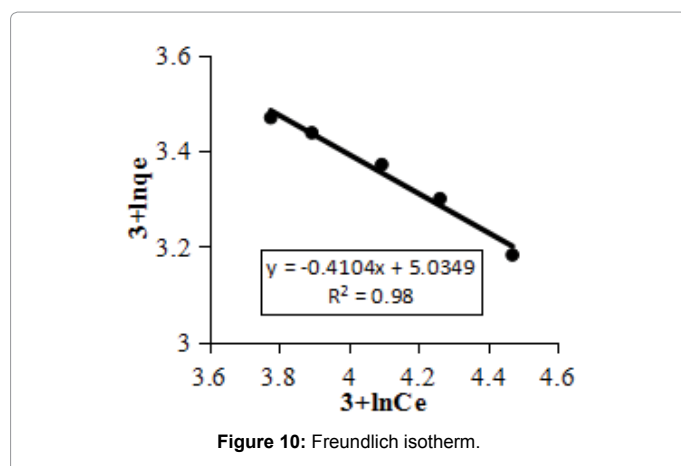
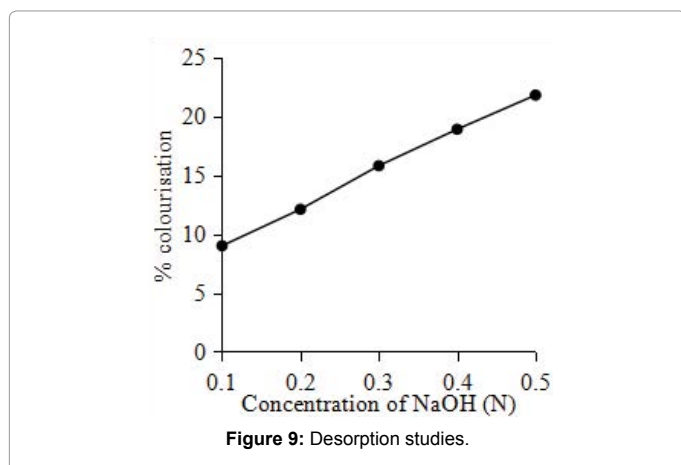
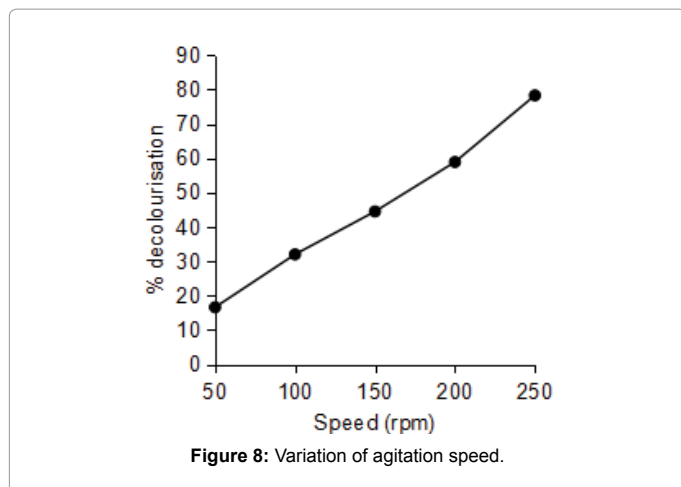
The Freundlich isotherm [14] is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact.

The linear form of Freundlich equation (Figure 10) is given by the following expression:

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

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 favourable adsorption with the attractive force between adsorbed species [15].





Langmuir isotherm

Langmuir isotherm [16] 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:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

Where, Q_0 and b are Langmuir constants. In the present study, the experimental data was fitted into Langmuir equation (eqn. 4) and the plot of C_e/q_e versus q_e was found to be linear which indicates that the adsorption of SDE dye on ASW follows Langmuir isotherm (Figure 11).

Langmuir isotherm can also be expressed in terms of separation factor, R_L which is referred as equilibrium parameter and expressed as:

$$R_L = \frac{1}{(1 + bC_i)} \quad (5)$$

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 0.4123. This indicates that the adsorption of SDE using ASW is a favorable process.

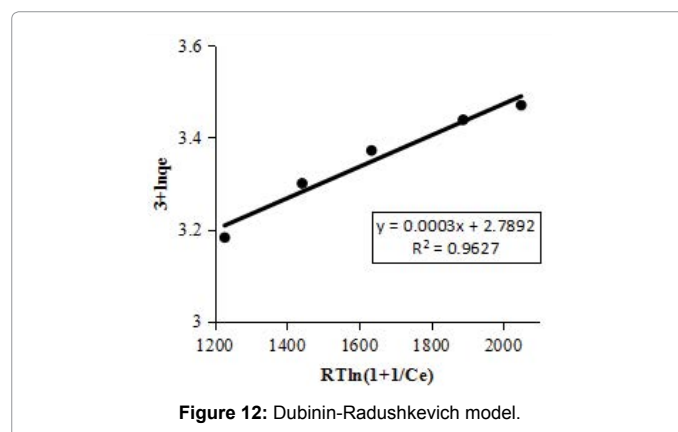
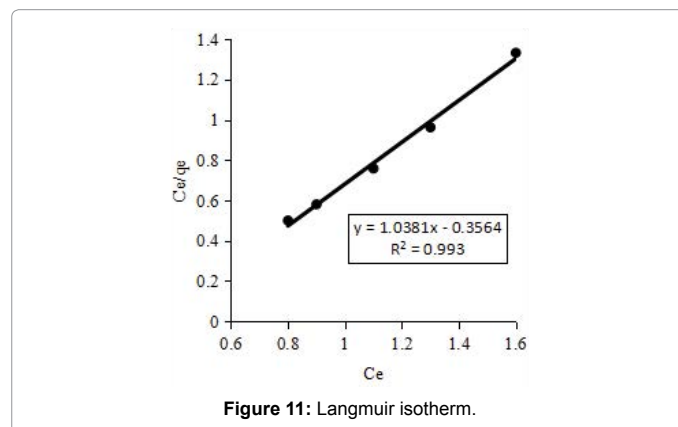
Dubinin-Radushkevich model

The Dubinin-Radushkevich model [17,18] is used to estimate the characteristics porosity of the adsorbent and apparent energy of adsorption. The linear form (Figure 12) of the equation is given by:

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

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:

$$E = \frac{1}{\sqrt{2B_D}} \quad (7)$$



The apparent energy (E) of the adsorption of SDE using ASW was obtained as 57.7350.

Temkin isotherm

Temkin isotherm [19] is assumed that the heat of adsorption decreases linearly with increasing coverage. The temkin isotherm (Figure 13) is represented by the following linear equation:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (8)$$

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

Jovanovic isotherm

Jovanovic model [20] is derived for describing the adsorption behaviour on heterogeneous surfaces. The linear form of Jovanovic isotherm (Figure 14) equation is,

$$\ln q_e = \ln q_m - K_J C_e \quad (9)$$

Where, q_m and K_J are Jovanovic constants.

Scatchard Analysis

Scatchard analysis [21] is employed to analyse the binding isotherm of dye molecules and adsorbent. The Scatchard (Figure 15) equation can be expressed as:

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

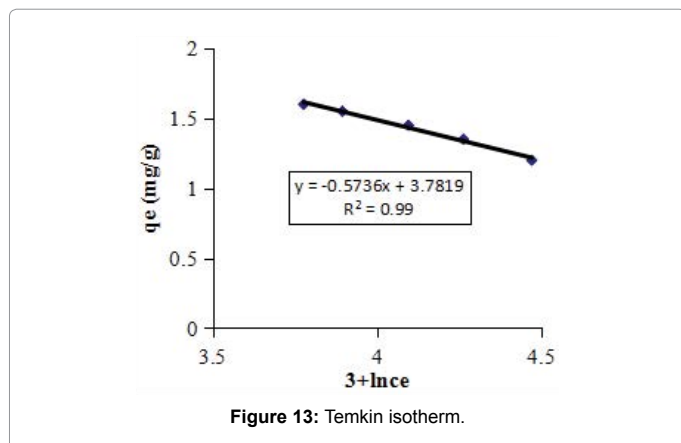


Figure 13: Temkin isotherm.

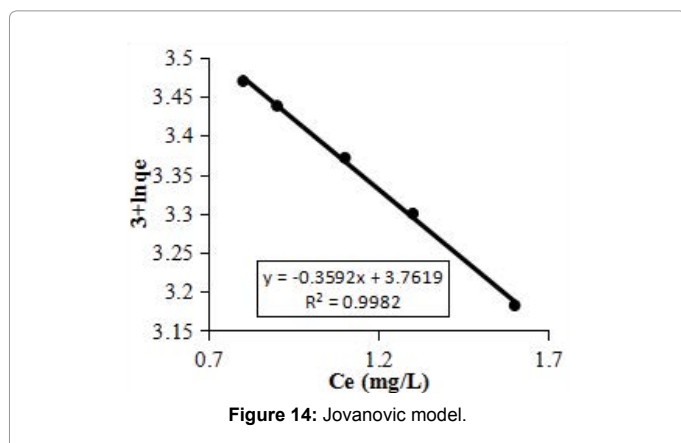


Figure 14: Jovanovic model.

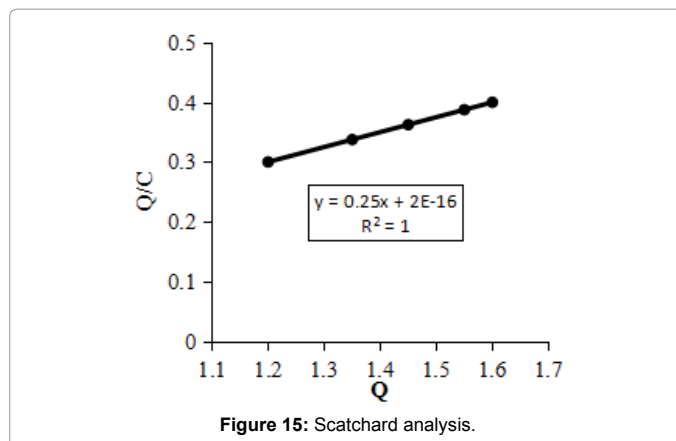


Figure 15: Scatchard analysis.

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 [22] is the model describing the degree of surface coverage characteristics of adsorbate onto adsorbent. The linear plot (Figure 16) of Flory-Huggins equation is expressed as:

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

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

Adsorption Kinetics

The kinetics of decolourisation of SDE dye solution over ASW has been studied using pseudo-second order kinetic model.

Pseudo-first order kinetic model

Pseudo-first order model [23] is given by Lagergren as:

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

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,

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

The equilibrium data shows (Figure 17) that the adsorption of SDE onto ASW cannot be applied and the reaction mechanism is not a first-order reaction.

Pseudo-second order kinetic model

Pseudo-second order kinetics [24] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2} (q_e)^2 + \frac{t}{q_e} \quad (14)$$

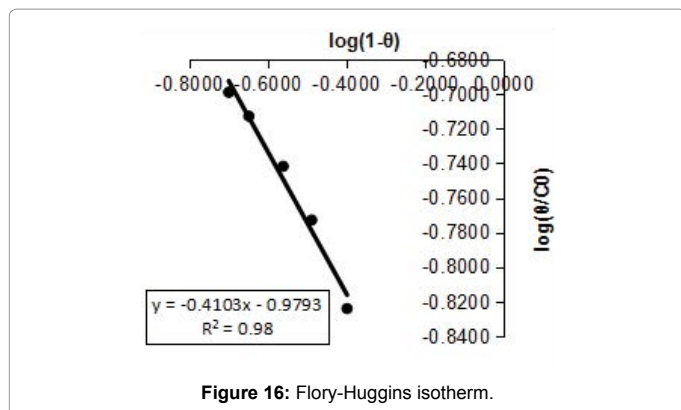


Figure 16: Flory-Huggins isotherm.

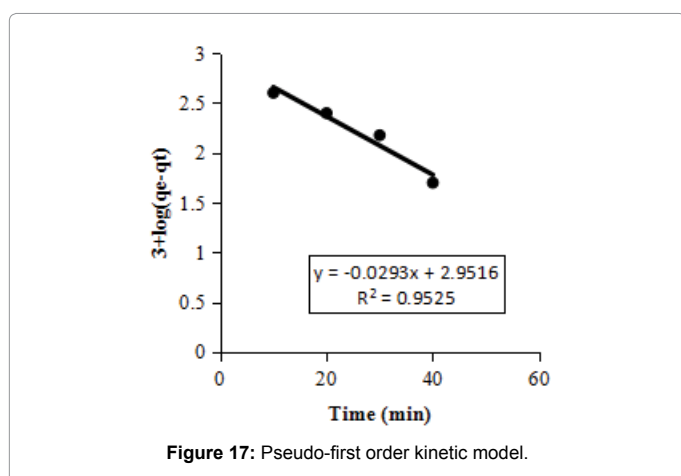


Figure 17: Pseudo-first order kinetic model.

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

After integration, the form of rearranged equation is,

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

The plot (Figure 18) 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.

Weber and Morris intra particle diffusion model

Weber-Morris intra-particle diffusion model [25] is mainly used to elucidate the diffusion mechanism. The Weber-Morris intra-particle diffusion rate equation can be given as:

$$q_t = K_d \sqrt{t} + C \quad (16)$$

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 plot of q_t versus \sqrt{t} is linear indicates occurrence of intra-particle diffusion (Figure 19).

Thermodynamic Study

The Gibbs free energy change of the adsorption process [26] is related to the equilibrium constant by the Van't Hoff equation,

$$\Delta G^\circ = -RT \ln K_L \quad (17)$$

Where, K_L (L/g) is equilibrium constant obtained by multiplying the Langmuir constants Q_0 and b , T is the absolute temperature (Kelvin), R is the gas constant (8.314 J/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:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

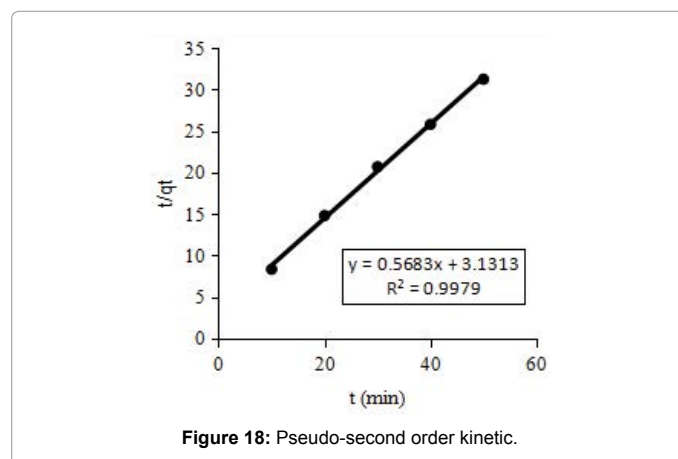


Figure 18: Pseudo-second order kinetic.

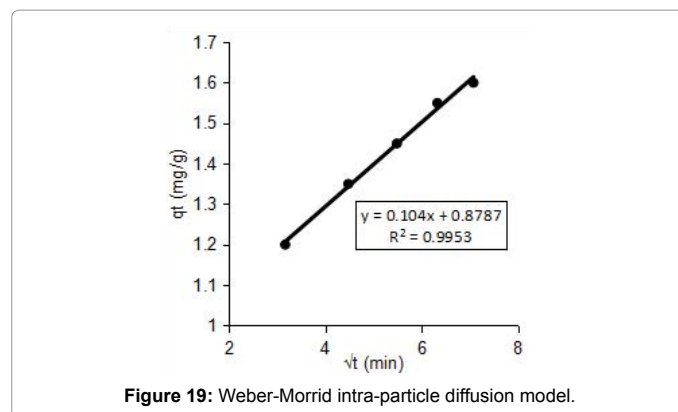


Figure 19: Weber-Morris intra-particle diffusion model.

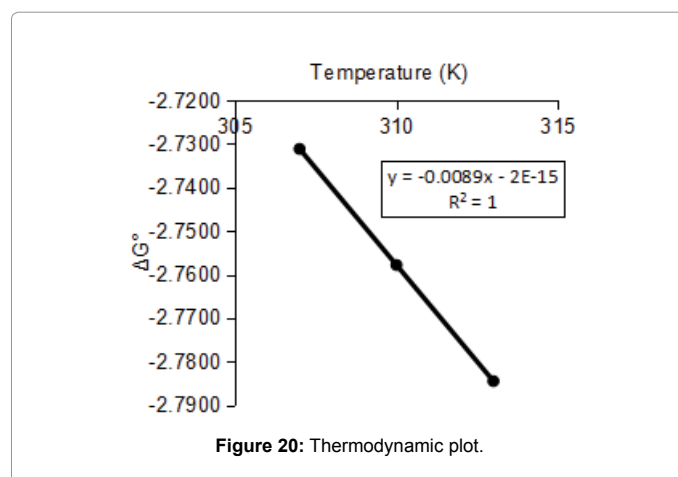


Figure 20: Thermodynamic plot.

The plot (Figure 20) of ΔG° versus T was perfect linear which helps ΔS° and ΔH° could be calculated from the slope and intercept of the plot respectively. The negative value of ΔG° (-2.7311) and ΔH° (-2×10^{-15}) indicate that the process is spontaneous and feasible process and exothermic nature of the adsorption. The negative value of ΔS° (-0.0089) suggests that decreased randomness at the solid/solution interface during the adsorption.

Conclusion

In this study, ASW was prepared by simple process and used for the adsorption of SDE from aqueous solution. Adsorption efficiency of ASW for SDE at equilibrium time of 50 min was found to be 78.3%. 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 ΔH° indicate that the adsorption process is spontaneous, feasible process and exothermic in nature. The negative value of ΔS° reveals that the process is enthalpy driven. Thus, the present study has proved that ASW could be used as an efficient adsorbent for the removal of SDE dye from aqueous solution. Moreover, the use of ASW 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 by-products.

Acknowledgment

We thank the Department of Chemistry, Seethalakshmi Ramaswami College, Trichy, for financial support.

References

- Gupta VK, Gupta B, Rastogi A, Agarwal S, Nayak A (2011) A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113. *J Hazard Mater* 186: 891-901.
- Arunarani A, Chandran P, Ranganathan BV, Vasanthi NS, Sudheer Khan S (2013) Bioremoval of basic violet 3 and acid blue 93 by *Pseudomonas putida* and its adsorption isotherms and kinetics. *Colloids Surf B Biointerfaces* 102: 379-384.
- Salleh MAM, Mahmoud DK, Karim WA, Idris A (2011) Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination* 208: 1-13.
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour Technol* 97: 1061-1085.
- Kismir Y, Aroguz AZ (2011) Adsorption characteristics of the hazardous dye brilliant green on saklikent mud. *Chem Eng J* 172: 199-206.
- Ghaedi M, Sadeghian B, Pebdani AA, Sahraei R, Daneshfar A, et al. (2012) Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removals by adsorption onto silver nano particles loaded activated carbon. *Chem Eng J* 187: 133-141.
- Chiou M, Chuang G (2006) Competitive adsorption of dyes metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads. *Chemosphere* 62: 731-740.
- Vanderborcht BM, Van Grieken RE (1977) Enrichment of trace metals in water by adsorption on activated carbon. *Anal Chem* 49: 311-316.
- Khattri SD, Singh MK (1999) Adsorption of basic dyes from aqueous solution by natural adsorbent. *Indian J Chem Technol* 6: 112-116.
- EI Hendawy ANA (2006) Variation in the FTIR spectra of the biomass under impregnation, carbonization and oxidation condition. *J Appl Anal Pyroly* 75: 159-166.
- Mckay G, Otterburn MS, Sweeney AG (1980) The removal of colour from effluent using various adsorbents IV Silica: Equilibria and column studies. *Water Res* 14: 21-27.
- Annadurai G, Juang RS, Lee DJ (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J Hazard Mater* 92: 263-274.
- Zhao Y, Chen H, Li J, Chen C (2015) Hierarchical MWCNTs/Fe₃O₄/PANI magnetic composite as adsorbent for methyl orange removal. *J Colloid Interface Sci* 450: 189-195.
- Freunlich HMF (1906) Over the adsorption in solution. *J Phys Chem* 57: 385-470.
- Renugadevi N, Sreeja M, Laliitha P (2010) Adsorption of chromium (VI) from aqueous solution using activated carbon from the pods of wood apple. *Ind J Env Prot* 30: 67-73.
- Langmuir I (1916) The constitution and fundamental properties of solids and liquids. Part I. Solids. *J Am Chem Soc* 38: 2221-2295.
- Dubinin MM (1965) Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents. *Zh Fiz Khim* 39: 1305-1317.
- Radushkevich LV (1949) Potential theory of sorption and structure of carbons. *Zh Fiz Khim* 23: 1410-1420.
- Temkin VPMJ (1940) Recent modifications to langmuir isotherms. *Acta Physiochim* 12: 217-222.
- Shahbeig H, Bagheri N, Ghorbaman SA, Hallajisani A, Poorkarimi S (2013) A new adsorption isotherm model of aqueous solution of granular activated carbon. *W J Mod Sim* 9: 243-254.
- Panahi HA, Shakerin N, Zolriasatain F, Panahyab A, Moniri E (2013) Adsorption of brilliant green by poly (ethylene terephthalate) grafted acrylic acid/acrylamide fiber-isotherm study. *Eur J Exp Bio* 3: 215-224.
- Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 156: 2-10.
- Lagergren S (1898) About the theory of so-called adsorption of soluble substances. *Handlingar* 24: 1-39.
- Ho YS, McKay G, Wase DAJ, Foster CF, Ho YS, et al. (2000) Study of the sorption of divalent metal ions on to peat. *Adsorp Sci Technol* 18: 639-650.
- Malik PK (2003) Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of Acid yellow 36. *Dyes Pig* 56: 239-249.
- Kul AR, Koyuncu H (2010) Adsorption of Pb (II) ions from aqueous solution by native and activated bentonite: Kinetic, equilibrium and thermodynamic study. *J Hazard Mater* 179: 332-339.