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Use of indian almond shell waste and groundnut shell waste for the removal of azure a dye from aqueous solution

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ABSTRACT

This study investigate the use of activated carbons prepared from groundnut shell (GSC) and Indian almond shell (IASC) which are agricultural waste for the removal of Azure A (AA) dye from the aqueous solution by batch mode experiments. The activated carbons GSC and IASC adsorb Azure A by varying dye concentration, dosage, contact time and pH. The amount of dye removal increased with decrease in initial concentration of the dye increase in contact time, increase in dosage and increase in pH. The adsorption data were fitted with Freundlich, Langmuir Isotherm models and various first order Kinetic equations such as Natarajan Khalaf, Lagergren and Venkobachar – Bhattacharya equations. The intra particle study reveal that the adsorption process follow first order kinetics. The result shown that the low cost adsorbents groundnut shell carbon (GSC) and Indian Almond Shell Carbon (IASC) can be used as an effective adsorbents alternative to Commercial Activated Carbon (CAC) for the removal of Azure A dye from aqueous solution.

Keyword: Adsorption, Azure A, Groundnut Shell Carbon (GSC), Indian Almond Shell Carbon (IASC), Kinetics of Adsorption.

INTRODUCTION

Water is directly associated with mankind. Hence the quality of water should be in pure form. Nowadays the water is polluted by domestic wastes and industrial wastes. Dyes are using as colouring agents in textile industries, rubber, paper, plastics and cosmetics. The water emerge out after used from these industries create bad taste, offensive odour and affect the eco system [1]. A special attention had been given by the scientists on this part and they suggested different methods like electro chemical [2], Oxidizing agents [3], Coagulants [4] and adsorption [5], commercial activated carbon (CAC) has been widely used to removecolour from the industrial effluent [6]. Even though different methods are suggested, adsorption has been found to superior than other methods. Due to high cost of CAC a low cost adsorbent have to be developed. The low cost adsorbents developed from agricultural wastes were wool fibre and cotton fibre [7], Banana pith [8], Chitosan [9], Neem husk [10], Tamarind fruit shell [11], Coconut tree sawdust [12], rice husk [13], Plum kernels [14], Palm tree cobs [15], Date Pits [16], fruit stones [17], cassava peel [18], sugarcane baggase [19], olive stones [20], Eucalyptus Globules Bark [21], Bentonite (clay) [22] etc., The motive of the present study is to develop an eco friendly low cost adsorbents for the removal of dyes from wastewater. In this study activated carbons Groundnut Shell Carbon (GSC) and Indian Almond Shell Carbon (IASC) were used as an adsorbents to remove Azure A from aqueous solution.

EXPERIMENTAL SECTION

The commercial activated carbon (CAC) was supplied by E.Merck, India. The raw material groundnut shell and Indian Almond Shell were collected locally and carbonised (at 400^{o}C). Then they were treated with acid, washed and thermally activated at 120^{o}C for 1 hour in an air oven. Finally they sieved to discrete particle sizes. Thus groundnut shell carbon (GSC) and Indian Almond Shell Carbon (IASC) were prepared. Azure A (AA) supplied by E.Merck, India was used as an adsorbate. The chemicals required for this study were reagent grade. Double distilled water was used for preparing all the solutions and reagents.

Adsorption Studies

A stock solution of AA (1000 mg/l) was prepared and exactly 50 ml of dye solutions of different initial concentrations were prepared in a standard measuring flask. The optical density of each solution was measured by using Elico UV – visible spectrophotometer (model : SL207) at λmax value 497 nm and thus a standard curve is drawn by plotting O.D. against concentration. From the standard curve the concentration of dye solution was calculated. Adsorption experiments were carried out at room temperature (30 $\pm$ 1°C) under batch mode. The percentage removal of dye was calculated using the relationship. [23]

$$\text{Percentage removal} = 100\,(C_i - C_f) / C_i$$

The amount adsorbed in (mg/g) was calculated using the following relationship.

$$\text{Amount adsorbed } (q_e) = (C_i - C_f) / m$$

C_i and C_f be the initial and final concentrations (in mg/l) of dye respectively and 'm' be the mass of activated carbon (in mg/l).

Exactly 50 ml of AA solution of known initial concentration (Ci = 50 mg/l) for IASC and 60 mg/l for GSC) was shaken at the constant agitation speed (200 rpm) with a required dose of activated carbon (100 mg) of a fixed particle size (range : 90 micron) for a specific period of contact time in a mechanical shaker (NEOLAB INDIA), after noting down the initial pH of the solution (pH = 7.2).

RESULTS AND DISCUSSION

The various experimental conditions for the adsorption studies are given in Table – 1 and the results obtained are discussed below.

Effect of Initial Concentration

The batch type adsorption studies on the extent of removal of dye AA on IASC and GSC were carried out at different initial concentrations (AA on IASC = 50 – 100 ppm and AA on GSC = 60 – 100 ppm) with a fixed dose of IASC and GSC (2 gL^{-1}) and 30 minutes of contact time at room temperature (28°C). The data obtained are tabulated in Table 1. The percentage removal of dye AA on IASC and GSC was found to decrease with the increase in the initial concentration (Fig. 1). This may be due to the reduction in the immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of AA. Similar results have been reported in literature on the extent of removal of dyes [24, 25] and metal ions [26].

Adsorption Isotherm

The data obtained from the study on the variation of initial concentrations of dye AA on IASC and GSC by batch adsorption were fitted with Freundlich and Langmuir isotherms respectively by plotting log (x/m) against log C_e (Figure 2) and (C_e/q_e) against C_e (Figure 3). These two isotherms plots for AA on IASC and GSC were found to be linear with correlation coefficient (r values) close to unity, which indicate the applicability of these two adsorption isotherms for the removal of AA on IASC and GSC.

Freundlich Isotherm

$$(\log x/m) = \log K + (1/n) \log Ce$$

Langmuir Isotherm

$$(C_e/q_e) = (1/Q_o b) + (Ce/Q_o)$$

q_e	-	Amount of dye adsorbed per unit mass of adsorbent (in mg g-1)
x	-	Weight of dye adsorbed
m	-	Weight of adsorbent
Q_o	-	Monolayer adsorption capacity (in mg g-1)
C_e	-	Equilibrium concentration (ppm)
b	-	Langmuir constant

The feasibility of the process is expressed in terms of separation factor R_L which is given by the equation.

R_L = $1 / (1+b\ C_i)$

b = Langmuir Constant
C_i = Initial concentration of dye

The separation factor R_L indicates the nature of isotherm and the feasibility of adsorption process as favourable. R_L value for AA on IASC is 0.0137 and AA on GSC is 0.0147 which indicate that the adsorption process is favourable. The R_L values are found to be in the range of 0 – 1, indicating that the adsorption process is favourable [27]. The values of monolayer adsorption capacity (Q_o) were found to be 55.55 for AA on IASC and 142.85 for AA on GSC. The data obtained are tabulated in Table 2.

Effect of Contact Time
To study the effect of contact time (range 5 - 60 minutes) on the extent of removal of AA on IASC and GSC, batch type adsorption experiments were carried out at constant dose of CAC, GSC (2 g L^{-1}) and optimum initial concentration of dye (C_i = 50 ppm for AA on IASC and C_i = 60 ppm for AA on GSC) at room temperature. The percentage removal of dye increases with increase in contact time and reaches a maximum value. (Figure 4)

Kinetics of Adsorption
The following equations were used to study the kinetics of adsorption under the conditions of first order kinetics (Table 3)

Natarajan and Khalaf Equation

$$K= (2.303 / t) \log (C_o / C_t)$$

Lagergren's Model

$$\text{Log } (q_e - q_t)= \text{Log } q_e - (K / 2.303)\ t$$

Bhattacharya and Venkobachar Model

$$\text{Log } [1 - u (T)] = - (K / 2.303)\ t$$
$$u (T) = [(C_o - C_t) / (C_o - C_e)]$$

C_o - Initial concentration of dye solution (in ppm)
C_t - Concentration of dye solution at various time (in ppm)
t - Contact time (in min)
K - First order rate constant for adsorption of dyes (in min^{-1})
q_e - Amount adsorbed per unit mass of adsorbent (mg g-1)

at equilibrium.
q_t - Amount adsorbed at any given time t (mg g-1)
C_e - Concentration at equilibrium contact time

The plots of log (C_o / C_t) ; log ($q_e - q_t$) ; Log (1 – u (T) against time were found to be linear and shown in figures 5, 6 and 7. These values are also linearly correlated and found to be close to unity. The result indicate the applicability of these kinetic equations and the first order nature of adsorption process.

Intra-particle Diffusion Model
The intra-particle diffusion process in the present adsorption system is tested by applying the intra-particle diffusion model.

$$q_t = K_p\ t^{1/2} + C$$

q_t is the amount of dye adsorbed at time t ;

C is the intercept and K_p is the intra-particle diffusion rate constant (in mg g^{-1} $min^{1/2}$). A graph was drawn by connecting q_t against $t^{1/2}$ ($min^{1/2}$) (Figure 13). The linear line obtained indicating the existence of intra-particle diffusion process. The correlation coefficient r value (for AA – IASC, r = 0.9996 and 0.9739 for AA – GSC) indicates the existence of intra-particle diffusion process. The extrapolation of the linear plots intercept (C) the Y – axis. These intercepts give an idea about boundary layer thickness. The larger the intercept greater the boundary layer effect [28]. The values of intra-particle diffusion rate constant (K_p) were calculated from the slope of the curve. The values of correlation coefficient (r), K_p and intercept are shown in Table 3. The intra-particle diffusion plots are given in figures 8 & 9.

Effect of Dose of Adsorbent

The effect of dose of adsorbents on the extent of removal of dye AA was studied. The percent removal of dye AA by IASC and GSC increases with increase in dose of adsorbents (Figure 10). This may be due to the increase in the availability of surface active sites resulting from the increased dose. The increase in the extent of removal of AA is found to be insignificant after a dose of 2 g/l for IASC and GSC which are fixed as the optimum dose of adsorbents.

Effect of initial pH

The effect of pH on adsorption process for dye AA on IASC and GSC were studied at different pH values (Range 2.7 to 11.4 and 2.7 to 11.3). The increase in pH increases the amount of dye adsorbed (Figure 11) which is due to the forces of attraction between the dye AA and surface charge of adsorbents (IASC, GSC). The results are in harmony with the literature reports.

Table : 1Experimental Condition for Batch Adsorption Studies of Azure A (AA) on IASC and GSC

Sl. No.	System	Variation	Initial Concentration (ppm)	Contact Time (Min)	Dose of Adsorbent (gL^{-1})	Initial pH	Particle Size
1.	AA on IASC	Initial Concentration	50 – 100	30	2	7.2	90
2.		Contact Time	50	5 – 60	2	7.2	90
3.		Dose of Adsorbent	50	30	1.4 – 2.6	7.2	90
4.		pH	50	30	2	2.7 – 11.4	90
5.		Particle Size (in micron)	50	30	2	7.2	90 - 250
1.	AA on GSC	Initial Concentration	60 – 100	30	2	7.2	90
2.		Contact Time	60	5 – 60	2	7.2	90
3.		Dose of Adsorbent	60	30	1.4 – 2.6	7.2	90
4.		pH	60	30	2	2.7 – 11.3	90
5.		Particle Size	60	30	2	7.2	90 - 250

Table – 2 Results of correlation analysis on testing the applicability of adsorption isotherm for the removal of Azure A (AA) dye by adsorption on IASC and GSC

Sl. No.	Parameter	AA – IASC	AA – GSC
I. Freundlich Isotherm			
1.	Slope (1/n)	0.4	0.1805
2.	Intercept (log K)	0.5	0.0425
3.	Correlation Coefficient (r)	0.9930	0.9056
II. Langmuir Isotherm			
4.	Slope ($1 / Q_o$)	0.0180	0.007
5.	Intercept ($1 / Q_o b$)	0.04	0.054
6.	Correlation Coefficient	1.02	1.01
7.	C_o ($mg\ g^{-1}$)	55.55	142.85
8.	b ($L\ mg^{-1}$)	0.4500	0.1296
9.	R_L	0.0137	0.0147

Table – 3: Kinetics and dynamics of adsorption of dye Azure A (AA) on IASC and GSC

Sl. No.	Parameter	AA – IASC	AA – GSC
I. Natarajan and Khalaf Equation			
1.	Correlation Coefficient (r)	1.003	0.9500
2.	K (min^{-1})	0.1443	0.0734
II. Lagergren Equation			
3.	Correlation Coefficient (r)	0.9965	0.9813
4.	K ($m\ m^{-1}$)	0.1900	0.1482
III. Bhattacharya and Venkobachar Equation			
5.	Correlation Coefficient (r)	0.9603	0.9809
6.	K (min^{-1})	0.2255	0.273
IV. Intra-Particle Diffusion Model			
7.	Kp	0.015	0.0104
8.	Correlation Coefficient (r)	0.9996	0.9739
9.	Intercept (C)	2.205	2.716
V. Log (% removal) VS Log (time)			
10.	Slope	0.015	2.335
11.	Intercept	1.9507	1.943
12.	Correlation Coefficient (r)	1.01	0.9957

Effect of Particle Size

The effect of particle size of GSC and IASC to remove AA dye by adsorption was studied by varying the particle size as 90, 125, 150, 212 and 250 micron. The amount of dye AA adsorbed increases with decrease in particle size of the adsorbent (Figure 12).

Relative Adsorption Capacity

The relative adsorption capacity was calculated from the Q_o values (Table 3) under optimum experimental conditions. GSC has the more adsorption capacity (Q_o = 142.85) than IASC (Q_o = 55.55). However the GSC and IASC are cost effective adsorbents and can be used to remove Azure A.

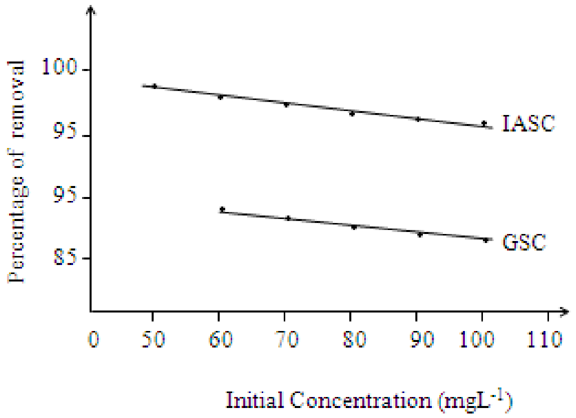

Figure 1. Effect of initial concentration

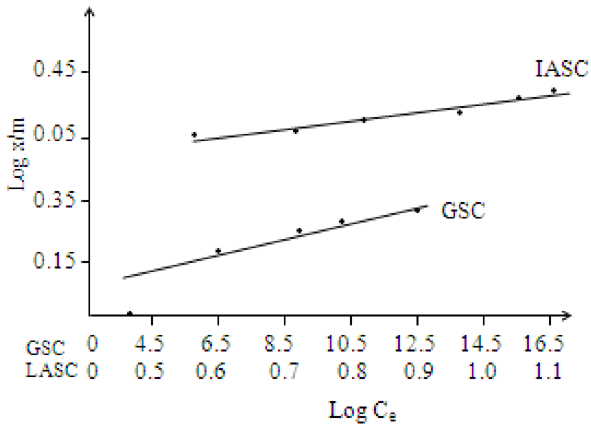

Figure 2. Effect of concentration variation: Freundlich Isotherm Model

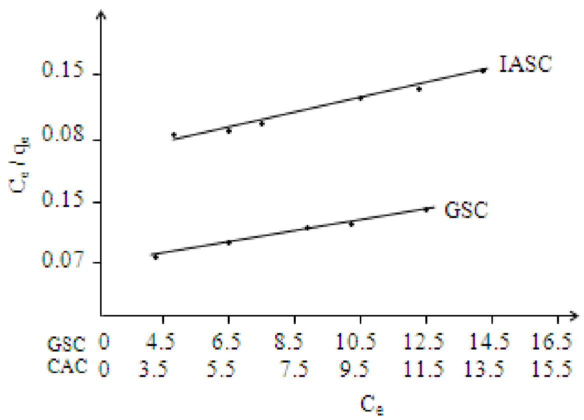

Figure 3. Effect of concentration variation: Langmuir Adsorption Isotherm Model

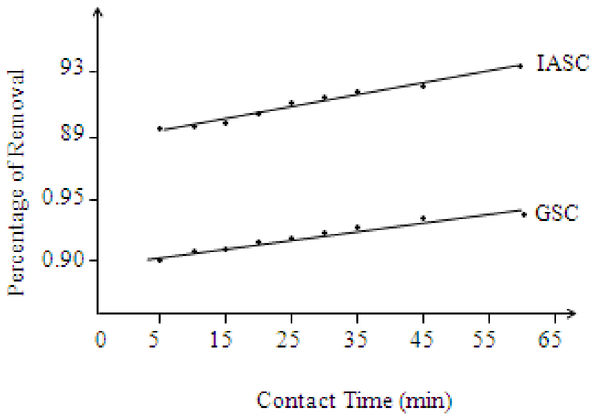

Figure 4 : Effect of contact time on the percentage removal of dye

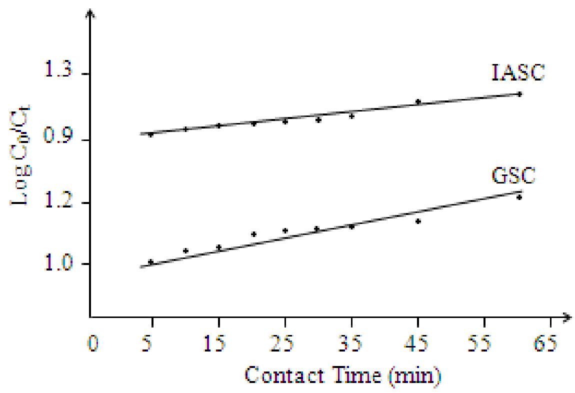

Figure 5. Effect of contact time variation: Natarajan and Khalaf Equation

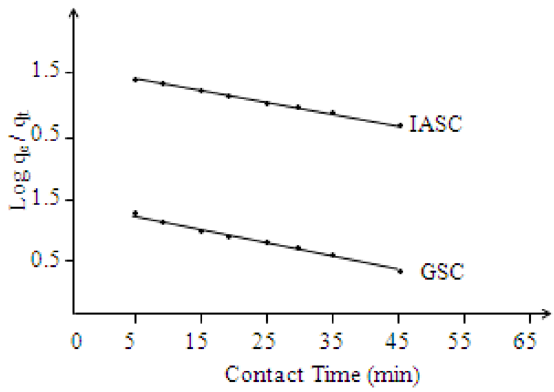

Figure 6. Effect of contact time variation: Lagergren Equation

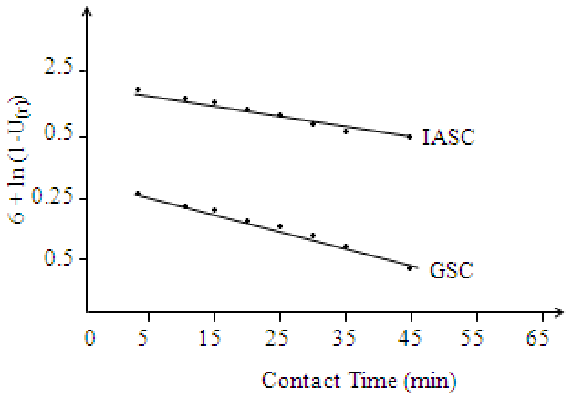

Figure 7. Effect of contact time variation: Bhattacharya and Venkobachar Equation

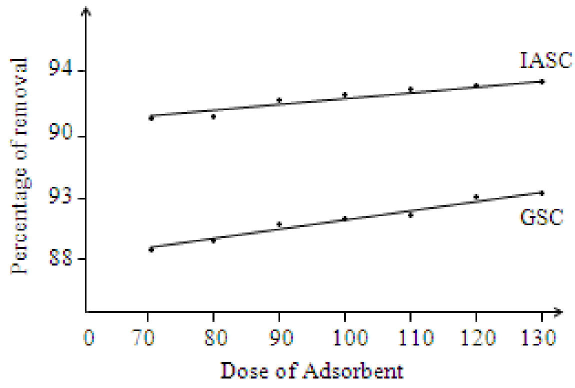

Figure 10. Effect of dose of adsorbents in percentage removal of dye

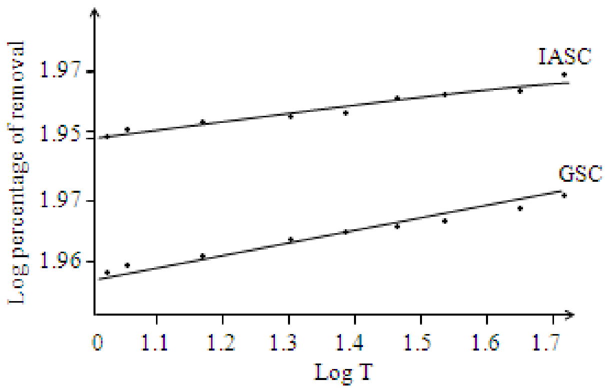

Figure 8. Effect of contact time variation: Intraparticle Diffusion Model

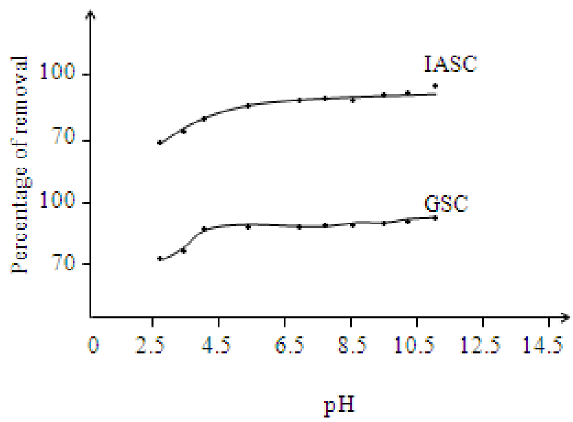

Figure 11. Effect of pH on the percentage of removal of dye

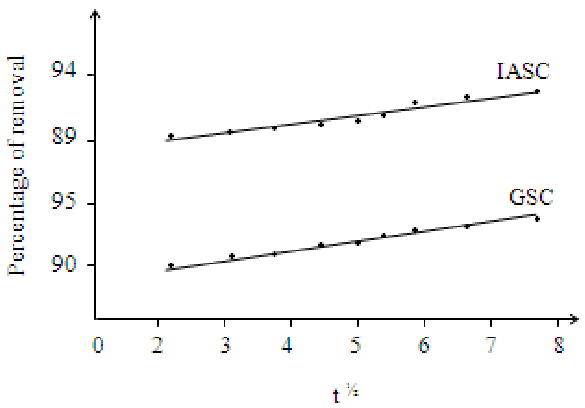

Figure 9. Effect of contact time variation: Intraparticle Diffusion Model

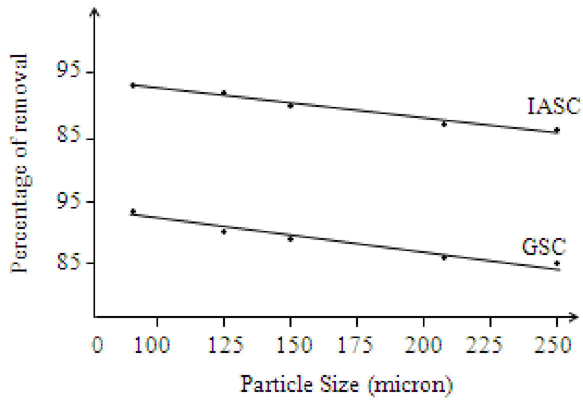

Figure 12. Effect of particle size on the percentage of removal of dye

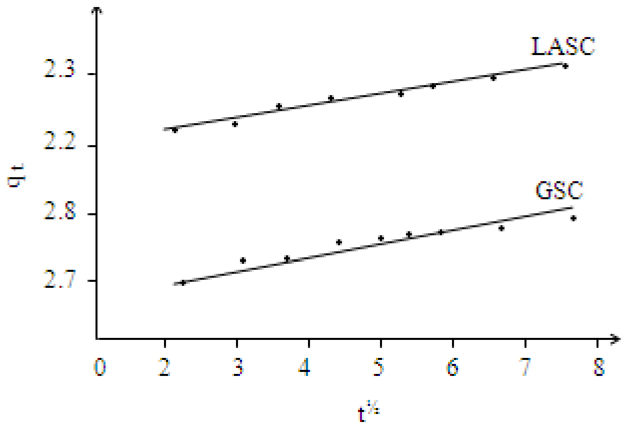

Figure 13. Effect of contact time variation: Intraparticle Diffusion Model

CONCLUSION

The experimental data were fitted with Freundlich, Langmuir adsorptions isotherms and the process is found to be first order by applying first order kinetic equations. The raw materials for groundnut shell and Indian Almond Shell are agricultural waste and hence they are low cost adsorbents. The experimental result reveal that GSC and IASC can be used as an adsorbents alternative to CAC for the removal of Azure A from the aqueous solution.

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