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Efficient Usage of Rice Husk Carbon and Chitosan Composite for Adsorption of Rhodamine B from Waste Water

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ARTICLE INFORMATION

Received January 30, 2018

Revised March 12, 2018

Accepted April 20, 2018

Published August 22, 2018

ABSTRACT

A new composite material of rice husk with chitosan was prepared and found the adsorption efficiency with a dye Rhodamine B from aqueous solution. A batch mode adsorption study was carried out to evaluate the effectiveness of the chitosan / rice husk composite for the removal of dye pollutants. The composite material was characterized with IR Spectroscopy and series of experiments were performed to validate synthesis optimization, adsorption kinetics, isotherms and thermodynamics. Various parameters such as pH, temperature, dosage rate have been studied in comparison with bio-adsorbent chitosan and its composite material. The dye uptake capacity of Rhodamine-B ions at pH 6 was the minimum, and a significant uptake was obtained at pH 3. The results obtained from pseudo-first order rate constant coefficient values are very low while compared with pseudo second order kinetic values. The Gibbs free energy change illustrates a negative value which reveals that the dye adsorption process is spontaneous in nature for the adsorption of Rhodamine-B dye. The study indicates that the rice husk carbon and its composite is an effective adsorbent for the removal of Rhodamine-B from aqueous solution.

KEYWORDS: Rice Husk; chitosan; activated carbon, Rhodamine –B

INTRODUCTION

Removal of colored effluents of dyeing units from industries is one of the growing needs of the environmental concern. Generally dye-containing waste water are discharged from various industrial outlets, specifically dye manufacturing and textile finishing industries are discharged into river streams, even in low concentrations; dyes affect aquatic life disturbing its process of photosynthesis and damage the ecosystem and the food cycle [1,2].

Because numerous organic dyes are dangerous to human beings, the removal of colour from process or waste effluents is environmentally imperative one. Further, the dyes are challenging to decolorize due to their complex molecular structure containing aromatic rings which make them mutagenic and carcinogenic [3]. To tackle this problems many techniques like oxidative degradation, photo degradation and biochemical degradation [4] have been employed but it as certain restrictions.

Adsorption is a technique which finds extensive use in removal of colour from effluents due to excellent properties such as high adsorption capacity and easy in operations. Many low cost adsorbents such as orange peels, banana peels, nutshells, wood [5] etc., were used. The outstanding ability and economic promise of the activated carbons made from biomass showed high sorption properties. Conversely, the adsorption capabilities of carbons be influenced by the sources of the raw materials employed, the account of its research and treatment conditions such as pyrolysis temperature and activation period. Several other factors are similarly affect the adsorption ability in the same sorption circumstances such as surface attraction (heteroatom content), charge and pore structure. An appropriate carbon should have not only a porous texture, but also have large surface area.

Chitosan is a non-toxic, decomposable and biocompatible polysaccharide prepared from deacetylation of chitin seems to compromise numerous advantages [6]. Chitosan as a biopolymer adsorbent has an advantages over other adsorbent because of its chelating ability to pollutants and inexpensive [7-9]. The excellent adsorption capacities are due to the presence of hydroxyl groups and amino group in the flexible structure of its polymer chain [10]. Further the beneficial features of chitosan are abundance in nature, non-toxic nature, hydro-philicity, bio decomposability and anti-bacterial property. The adsorption of all dyes in neutral solutions using chitosan show outsized adsorption capacities. The role of pH may be an vital factor on the dye binding capability of chitosan because at small pH, the amino groups of chitosan are much easily cationized and they adsorb the anion of dye molecules strongly by electrostatic attraction.

Numerous adsorbents have been studied to remove different kinds of dyes from wastewater specifically those are harmful to mankind. Activated carbons, plant or lignocellulose wastes, clay materials and biopolymeric materials, rice husk, are among the common adsorbents used. Current study focuses rice husks have been employed as an adsorbent material for the removal of Rhodamine B from aqueous solutions. Rice husks is a by-product of the rice mills, an account for about 20% of rice as a whole. It is estimated annual rice production of

500 million metric tons in developing nations such as India, roughly 100 million tons of rice husks are obtainable annually for utilization in these countries alone. In fact, the quantity of rice husks available is far in excess of any local uses and, thus, has some disposal problems. Rice husks were chosen for the investigation as a predecessor material due to their coarse structure, insolubility in water, chemical constancy, excellent mechanical strength and ease of availability with cost effective.

In this current investigation an attempt was made to overcome various limitations with synthesizing a bio-sorbent by coating of chitosan over the surface of rice husk activated charcoal and assessing its equilibrium adsorption properties. The blending of the useful properties of rice husk charcoal and natural chitosan, could bring together a composite matrix material with many useful application and greater adsorption abilities. Using synthetic wastewater, the removal RhB by rice husk charcoal coated chitosan and acid treated rice husk charcoal adsorbents were statically compared.

MATERIALS AND METHODS

Chemicals

The chitosan flakes (molecular weight, MW=400,000Da, degree of deacetylation, DD=90%) was purchased from Pelicon Biotech and chemical Labs Pvt, Ltd., Cherthala, India. The dye Rhodamine B was obtained from Merck Company. The other chemical reagents such as sulphuric acid, sodium hydroxide, acetic acid were obtained from Qualigen Fine chemicals India Ltd. The different range of dye concentration was prepared from the stock solution between 10 and 100 ppm. These test solutions were prepared from dye stock solution of 1g/l. Deionised water was used throughout this study.

Preparation of Rich Husk activated carbon(RHAC)

Rice husk materials was received from a rice mill located in Vyasarpadi area, Chennai and washed with running water followed by distilled water through a sieve of 16mesh to remove all kinds of impurities. The husk was placed in trays and kept to dry in exposed air at room temperature to constant weight. The adsorbent was prepared in a clean air-dried rice husk was weighed in a clean dry beaker. 100 ml of 13M

sulphuric acid were added to the rice husk and the mixture and was heated to 175-180°C for 20 min with infrequent stirring. The similar temperature was maintained for another 20 min without disruption. The resulting black coloured mixture was allowed to cool for some time, and then it was filtered using a Buchner funnel under vacuum condition. The black expended sulphuric acid was filtered off and the carbonized material was washed several times with distilled water and then it was stored under dilute acidic conditions (diluted sulphuric acid, pH 1.5-2) to avoid any kind of bacterial growth.

Preparation of chitosan-RHAC composite

2 g of chitosan powder and 2 ml of acetic acid were added to 100 ml de-ionised water and stirred for 24 hrs. 1 g of prepared RHAC powder also added into the solution under constant stirring for another 24 hrs to obtain chitosan-RHAC composite. The composite was transferred to 0.65 M NaOH drop wise through micropipette to form smaller beads and was dried up at room temperature.

Preparation of Rhodamine-B (RhB) Stock Solution

Stock solution of RhB was prepared by accurately weighed samples of dye was dissolved in distilled water to give a concentration of 250 mg/litre. By diluting, where necessary, the dye stock solution (250ppm) with distilled water to the required concentrations the test solutions were obtained. All the experiments were conducted with pH adjustment.

Adsorption studies

For adsorption studies of each experimental run, 20 ml dye solution of known concentration was taken in 125 ml conical flask containing 0.4g of adsorbent. The flasks were shaken in a shaker for required period of time. The adsorption experiments were accompanied by varying pH, temperature, sorbent dose and contact time.

The pH was altered by adjusting the pH value with dilute HCl and NaOH solution. The kinetics experiments on adsorption were carried out by investigating solution in 0.4 gm of adsorbent in 20 ml of solution at applicable time intervals at various concentrations (20-100 mg/l). Finally, the solution samples were withdrawn and centrifuged at 3500 rpm for 15 minutes and then the dye absorbance was determined using spectrophotometer (model Elico Double beam SL191 UV-Visible spectrometer). The BRUKER TENSOR 27 FT-IR spectrometer (Bruker Optick GmbH, Germany) was used to analyze FTIR.

RESULTS AND DISCUSSION

FTIR Studies

FTIR studies are generally used for prediction of different types of functional groups present in an adsorption material. The FTIR spectrum of activated carbon RHAC, RHAC composite and Rhodamine-B adsorbed carbon are presented in Fig 1 to 3.

The RHAC spectrum indicates the peaks in the positions of 3438 cm^{-1} , 1616 cm^{-1} , 1074 cm^{-1} , 795 cm^{-1} . The peak position of 3438 cm^{-1} indicates that the occurrence of both free and hydrogen bonded OH groups on the adsorbent molecule. Peak positions at 1616 cm^{-1} , 1074 cm^{-1} , 795 cm^{-1} shows that the presence of conjugated hydrocarbon bonded carbonyl groups, C-C bond in aromatic conjugation, C-N peptide bond and S, O interaction respectively [11].

The band at 1601 cm^{-1} shows COO and C=C groups, the peaks at 1578 cm^{-1} indicates amine groups and the N-H bending vibrational modes in primary amine groups ($-\text{NH}_2$) were observed, and also presence of chitosan in the composite. The reduction of peaks widths in Figure 3 clearly shows that the Rhodamine-B dye adsorbed well in the composite adsorbent. The active functional groups in the composite adsorbent bind the dye molecule and increase the rate of adsorption.

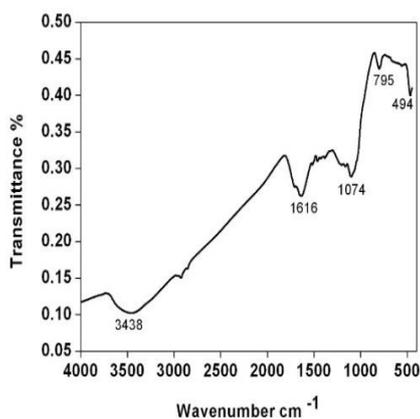


Fig. 1: FTIR spectrum of RHAC

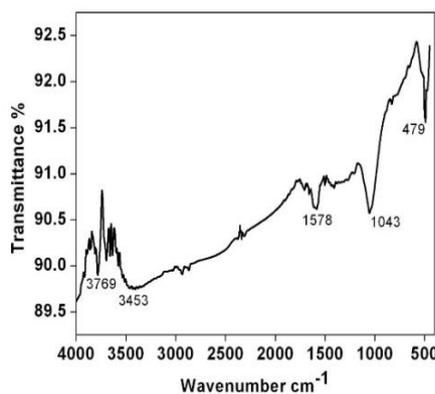


Fig.2: FTIR spectrum of RHAC/Chitosan composite

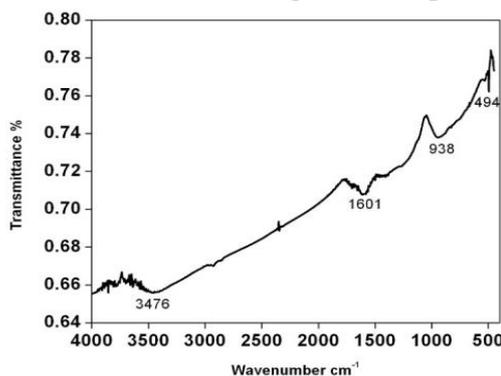


Fig.3: FTIR spectrum of composite after adsorbed RhB dye

Sorption Studies

Adsorption Studies on RHAC and RHAC/Composite

Adsorption experiments were carried out with different concentrations of dyes from 4mg L⁻¹ to 20 mg L⁻¹ with 4 mg L⁻¹ variation. Increase of initial concentration of RhB increases adsorption capacity, further enhancement of concentration leads to decrease in removal percentage due to non-availability of active sites in the adsorbent [12].

$$\text{Percentage Removal} = [(C_i - C_f) / C_i] \times 100$$

.....[1]

Where, C_i and C_f are initial and final concentration of dye solution, before and after sorption process.

Effect of pH on RHAC, Chitosan and RHAC/Composite

The effect of pH of the dye solution on RHAC and composite was determined and the results are shown in Figure 4. pH is one of the significant parameter to controlling the adsorption process [13]. The uptake of RhB ions was minimum at pH 6 and shows a maximum uptake at pH 3. Although, with the increase in pH of the dye solution (more than 6), the uptake

of RB ions were also gradually increased. It seems that a change in pH of the solution marks in the formation of various ionic species, and changed carbon surface charge.

If pH values lesser than 4, the Rhodamine-B ions become cationic and monomeric molecular in nature[14]. Therefore Rhodamine-B ions come closure into the pore structure, but a pH value become greater than 4, Rhodamine-B become zwitter ionic form in water which may increase the accumulation of Rhodamine-B to form a larger molecular form and become incapable to enter into the pore, Ghanadzadeh[15] have studied the aggregation of Rhodamine-B in the micro-porous solid hosts. Lopez Arbeloa and Ruiz Ojeda [22] determined the equilibrium constant for the dimer-monomer transition of Rhodamine - B in aqueous solution.

The larger aggregation of the zwitter ionic form is due to the strong electrostatic interactions between the carboxyl and xanthene groups of the monomers [22]. At a pH value greater than 6, the superiority of OH⁻ generates a rivalry between -N⁺ and -COO⁻ and it will decrease the accumulation of Rhodamine-B, which causes an increase in the adsorption of Rhodamine-B ions on the adsorbent surface. The effect of the

charge on the carbon surface and the electrostatic force of attraction and repulsion between the adsorbent surface and the Rhodamine - B ions do not contribute to the result. The figure shows the percentage removal of chitosan was high at pH 4. After pH 4, percentage removal was gradually decreased. But when compared to the removal of RHAC and

composite, chitosan showed lower percentage removal that happened at pH 3. From these studies all the adsorbent showed a maximum removal is at pH 3. However when comparing percentage removal of the adsorbents RHAC/ chitosan composite showed higher percentage removal of 96% indicates the efficiency of adsorption characteristics.

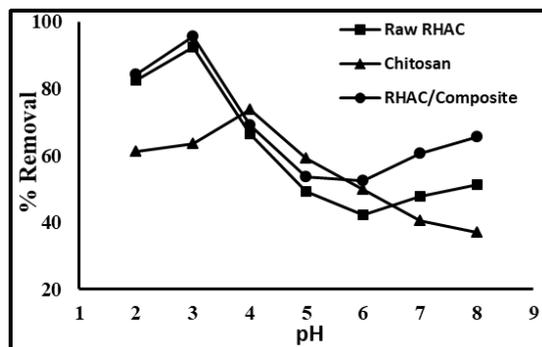


Fig. 4: Effect of pH on RHAC, Chitosan and RHAC/Composite

Effect of temperature on RHAC, Chitosan and RHAC/Composite

The role of temperature on adsorption experiments were conducted at temperatures of 303K, 313K, 323K, 333K, and 343K. These experiments were carried out with optimum concentration of 8ppm on various adsorbents under investigation. The figure 5 indicates the amount of adsorbed Rhodamine-B dye was diminished with rising temperature this can be described by the fact that the mobility of Rhodamine-B dye molecules increases with increase in temperature. Further the figure shows a slightly decrease in dye removal percentage, this might be due to the decreasing of the physical forces of attraction between dye and an adsorbent.

The experimental results exhibited that the removal of dye is reduced with rise in temperature onto the adsorbent RHAC is a kinetically controlled exothermic process. Chitosan showed better result at room temperature (303 K) removal decreases with increase in temperature.

Similar to RHAC and chitosan RHAC/Chitosan composite showed a maximum percentage removal 303K. From the figure 5, the reduction in percentage removal of dye with increasing temperature is ascribed to weakening of the bonds between the dye molecules and adsorbent [17]. The observed trend also suggests that adsorption of Rhodamine-B is kinetically controlled by exothermic process. It is noteworthy to view RHAC/Chitosan composite has a percentage removal above 90.

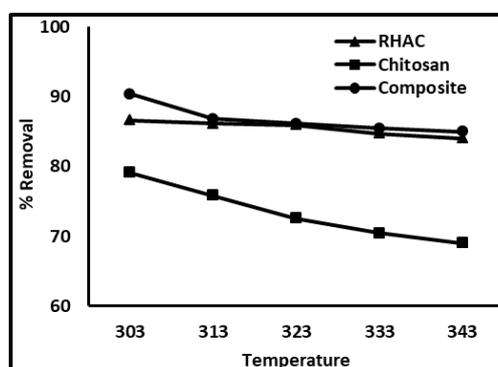


Fig. 5: Effect of temperature RHAC, Chitosan and RHAC/Composite

Effect of dosage on RHAC, Chitosan, and RHAC/Chitosan Composite

The dose of the adsorbent is an important parameter that powerfully influences the adsorption process by affecting adsorption capacity of the adsorbent materials. Hence the

effect of adsorbent dose on Rhodamine-B adsorption by various adsorbent was investigated in the range of 0.1- 1.2 g. The effect of adsorbent dose on the percentage removal of Rhodamine-B for RHAC, chitosan and composite is shown in Figure 6.

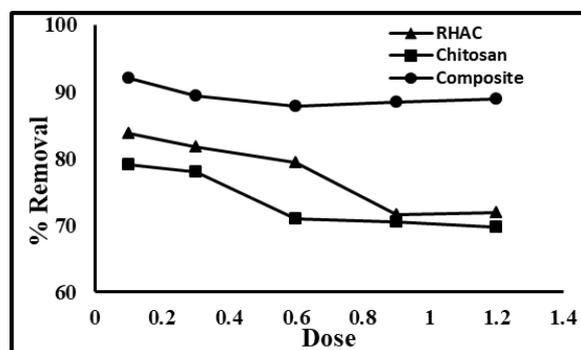


Fig. 6: Effect of dosage on RHAC, Chitosan, RHAC/Composite

Raw RHAC showed more percentage removal in various dose studies when compared to chitosan. Further, in all the cases, sorption was found to be attained more rapidly at lower adsorbent dosage 0.1g this result predicts a less amount is need to remove dye solution which in turn shows cost effectiveness of the adsorbent. This dosage is fixed as optimum dose that is used for further investigation.

Here also, RHAC/ Chitosan composite showed more percentage removal at dosage 0.1 g L⁻¹ when compare with raw RHAC. This further confirms that low dosage is enough for effective removal of dye from the aqueous solution. The increase in adsorbent dose reduced the higher removal of Rhodamine-B. The reduction in sorption capacity with rising dose of adsorbent at constant dye concentration and volume could be familiar to saturation of adsorption sites due to dye interaction such as accumulation [18]. Such accumulation would lead to a reduce in total surface area of the adsorbent and increase in diffusional path length [19].

Effect of contact time on RHAC, RHAC/Chitosan Composite

By using optimum concentration of 8 ppm a contact study was conducted for one hour at an interval of 10 minutes duration. The significance of contact time on the elimination of Rhodamine-B by the RHAC for dose 0.1g L⁻¹ showed rapid adsorption of Rhodamine-B in the first 40 min and subsequently, the adsorption rate slightly reduced.

Figure 7 shows with rise in time the quantity of dye adsorbed per unit mass of adsorbent slightly increases and attain constant thereafter. It is evident from the figure that the carbon is effective to adsorb Rhodamine-B with varied efficiencies. RHAC/ Chitosan Composite possess greater adsorption ability than RHAC at equilibrium. The dye adsorption process attains equilibrium gradually after 40 minutes. To achieve equilibrium, it requires 40 min. This could be due to the evidence that the carbon composed with macro and micro pores. In the progression of dye adsorption, primarily dye molecule taking to first come across the boundary layer film against adsorbent surface and then lastly it may diffuse on the porous structure of the adsorbent material. This occurrence will take comparatively long contact time.

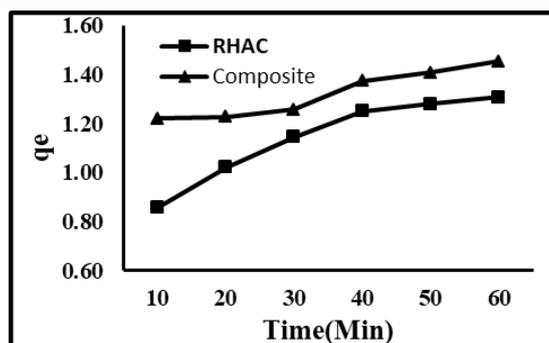


Fig.7: Effect of contact time on RHAC, RHAC/ Chitosan Composite

The adsorption of dye is mostly due to physisorption process although chemisorption possibly will not be carved off. Mohan [20] stated that the of adsorption of Direct brown from aqueous solution onto commercial activated carbon, Filtrasorb-400 was due to physisorption and the contact time is necessary to attain equilibrium and it was attained after 400 min. The required time to uptake of dye is a single, smooth, and continuous curve implies to saturation, signifying the probable monolayer coverage of dye molecule on the surface of the adsorbent material.

Adsorption Isotherm Of RHAC, RHAC/Chitosan Composite

The adsorption experimental data were analysed with an adsorption isotherm models, like Freundlich and Langmuir. Many forms of Langmuir and Freundlich were verified in their linear forms. The Langmuir adsorption isotherm model is based on the assumption that the adsorption process existed monolayer of the solute molecules on the adsorbent surface. The Langmuir isotherm is :

$$q_e = q_m K_a C_e / (1 + K_a C_e) \quad \dots\dots\dots(2)$$

The term q_e (mg g^{-1}) and C_e (mg L^{-1}) are the quantity of dye adsorbed per unit mass of sorbent and unadsorbed concentration of dye in solution. Where q_m is the highest amount of dye adsorbed per unit mass of sorbent at whole monolayer on surface bound, and K_a (L mg^{-1}) is a constant related to the attraction of the binding sites

The theoretical model of Langmuir isotherm [21] is usable for adsorption of a solute from a liquid solution such as monolayer adsorption on a surface containing a limited number of indistinguishable sites. Langmuir isotherm model accepts constant energies of adsorption onto the surface without transmigration of adsorbate in the surface [22]. Thus, the Langmuir isotherm model was selected for an assessment of the adsorption capacity resultant to whole monolayer coverage on the adsorbed surface.

Langmuir adsorption isotherms for RHAC, RHAC/Chitosan-Composite

Langmuir isotherm shows a superior correlation coefficient (r^2) value as compared to Freundlich isotherm. The higher q_m value of Langmuir confirms that the large quantity of adsorption at 303 K. The resultant equilibrium data were further examined using the linearized form of Freundlich equation using the same set of experimental data, by plotting $\log(q_e)$ vs $\log(C_e)$. It was seeming that at all solution temperatures. For RHAC/Chitosan composite the r^2 values is 1 suggest that the Langmuir isotherm is the most suitable isotherm than Freundlich isotherm given in Fig.8 to Fig.11. The predicted equilibrium curve linear method given in Table 1 to 3 for the two equilibrium isotherms of Freundlich and Langmuir at 303 K. It was observed that at different temperatures, 303 K was proven to be more suitable temperature as compared with other temperature.

Table 1: Isotherm Formulae

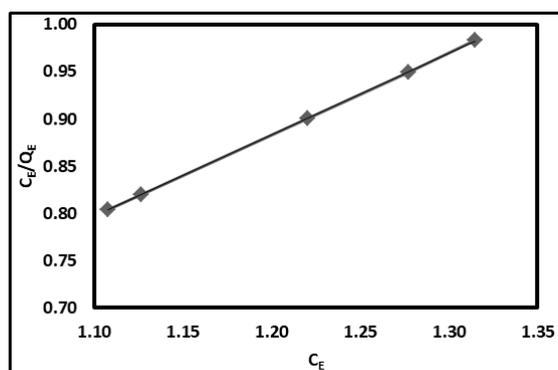
Isotherms	Linear	Plot	Reference
Freundlich	$\log q_e = \log K + 1/n \log C_e$	$\log q_e$ Vs $\log C_e$	Freundlich(1906)
Langmuir	$C_e/q_e = 1/q_e C_e + 1/K_a q_e$	C_e/q_e vs C_e	Langmuir(1916)

Table 2: Isotherm parameters obtained from Linear Method for RHAC

Isotherm	Parameters	Temperature(303 K)
Freundlich	1/n	0.1773
	K (mg g ⁻¹) (Lg ⁻¹)	1.1404
	r ²	0.9994
Langmuir	q _m (mg g ⁻¹)	1.153
	K _a (L mg ⁻¹)	5.515
	r ²	0.9999

Table 3: Isotherm parameters obtained from Linear Method for RHAC/ Chitosan Composite

Isotherm	Parameters	Temperature(K) (303 K)
Freundlich	1/n	0.419
	K (mg g ⁻¹) (Lg ⁻¹)	1.4554
	r ²	0.6739
Langmuir	Q _m (mg g ⁻¹)	1.1889
	K _a (L mg ⁻¹)	6.5919
	r ²	1.0000

**Fig.8: Langmuir adsorption isotherm of RHAC**

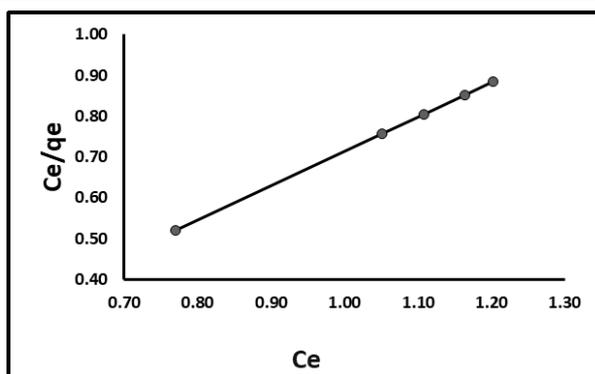


Fig. 9: Langmuir adsorption isotherms for RHAC/Chitosan Composite

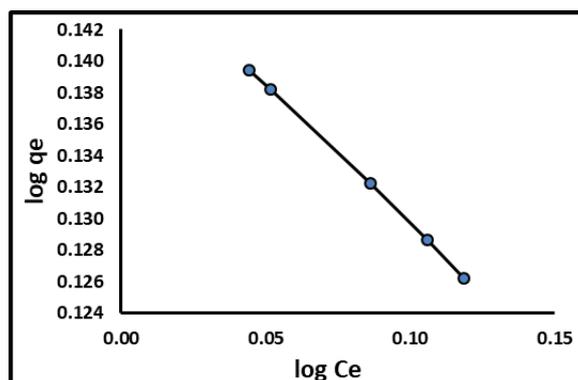


Fig. 10: Freundlich adsorption isotherms for RHAC

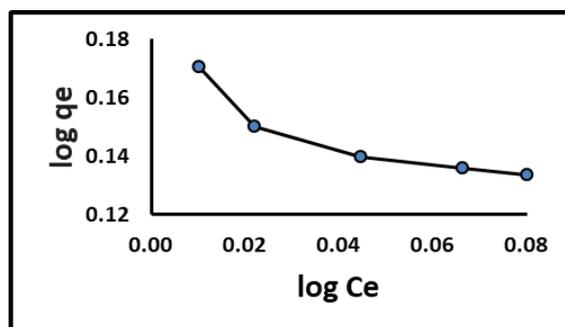


Fig.11: Freundlich adsorption isotherm for RHAC/Chitosan composite

Freundlich adsorption isotherms for RHAC, RHAC/Chitosan Composite

The familiar logarithmic form of Freundlich isotherm model is given in table 1. From the formula, C_e the concentration at equilibrium condition of the adsorbate (RhB) and K and n are constants for Freundlich, n gives an suggestion to favourability of the adsorption process and K shows the adsorption ability of the adsorbent. K is defined as the adsorption of dye or distribution coefficient of dye and also represents the amount of dye molecules adsorbed by the adsorbent material for an unit at equilibrium concentration. The slope values ($1/n$) are among 0 and 1, is a degree of adsorption intensity or surface heterogeneity, and initiate more dissimilar as its value gets

very closer to zero [23]. A value for $1/n$ is less than one specifies a normal Langmuir isotherm while $1/n$ is beyond one is revealing of cooperative adsorption.

As seen from Table 2, the Langmuir model yields a somewhat better fit ($r^2=0.9999$) than the Freundlich model (0.9994). As also showed in Table 2, the value of $1/n$ is 0.177, which specifies favorable adsorption.

Kinetic Studies

The adsorption kinetics were given by the Lagergren's pseudo first order model [24], which is a known equation that expressing the degree of adsorption based on the adsorption ability. Lagergren's pseudo first order and pseudo second order kinetic models were useful to study

the kinetics profiles. The pseudo first order linearized form of the equation is:

$$\text{Log}(q_e - q_t) = \log(q_e) - K_1 t / 2.303 \dots\dots\dots (3)$$

Where, K_1 is the pseudo first order rate constant, q_e is the quantity of dye adsorbed onto RHAC at equilibrium (mg g^{-1}), q_t quantity of dye molecules adsorbed onto RHAC at time t (mg g^{-1}). The pseudo second order linearized form is :

$$T/q = 1/K_2 q_e^2 + (1/q_e) t \dots\dots\dots (4)$$

where, K_2 is the pseudo second order rate constant, q_e is the quantity of dye adsorbed onto RHAC at equilibrium (mg g^{-1}); q_e^2 is the pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

The second order constant k_2 is found experimentally from the slope and intercept by plotting t/q_t vs t . Figure 14 & 15 for RHAC and RHAC/Composite. The found values are very closer agreement with second order kinetics model; thus the adsorption kinetics possibly will be estimated more positively by second order kinetic model for Rhodamine-B. The k_2 value is calculate from Figure are listed in Table 5 and Table 6 for RHAC and RHAC/Composite respectively.

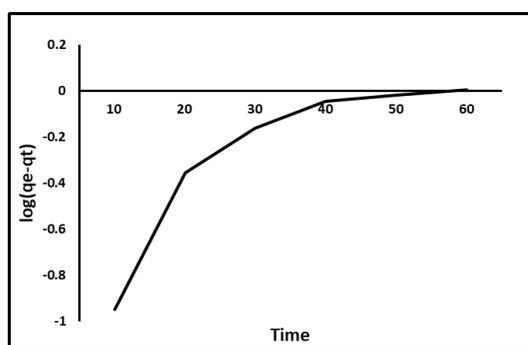


Fig. 12: Pseudo first order kinetics plot for RHAC

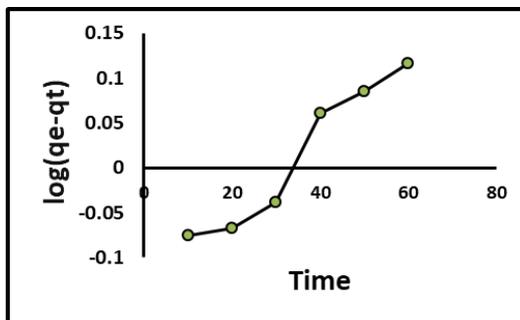


Fig. 13: Pseudo first order kinetics for RHAC/Composite

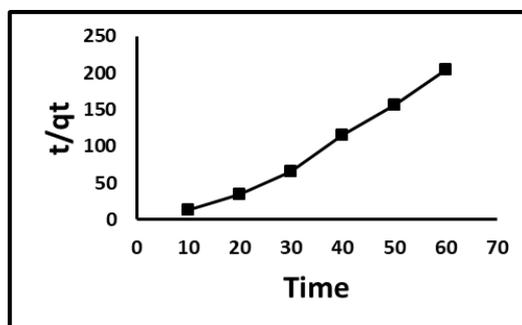


Fig. 14: Pseudo second order kinetics for RHAC

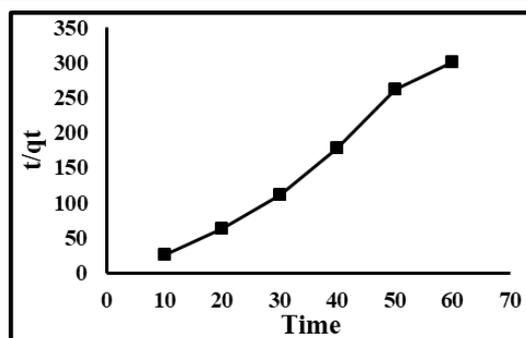


Fig. 15: Pseudo second order kinetics for RHAC/Chitosan Composite

The pseudo first order and second order models were verified to find the rate constants and equilibrium adsorption capacity. In addition, the hypothetical and experimental equilibrium adsorption capacities, q_e found from the kinetic model. These results indicate that adsorption of RhB on RHAC and its composite cannot be explained by the pseudo first order kinetic model [24].

From the table coefficient values of pseudo-first order rate constant values are very small while compared with pseudo second order values. Further the r^2 value is 0.9838 whereas pseudo-first order shows 0.7434. Therefore, the results tells that the sorption process follows second rate equation during the process. In addition, the rate of the reaction does not depending upon

the concentration factor (pseudo- first order) but it also depends on both concentration and time (pseudo-second order).

On the other hand, the kinetic values revealed an outstanding agreement with pseudo second order kinetic equation. The plots of t/q_t against t showed good linearity. The pseudo second order rate constant k_2 , the calculated q_e values and the agreeing linear regression coefficient of correlation values r^2 and are given in Table 6.

RHAC/Composite shows a pseudo first order rate constant coefficient values very low while compare with pseudo second order values. The r^2 value for second order is 0.9848 while that of first order shows 0.9359. From the r^2 values results the composite well suitable with Pseudo second order kinetics equation [25].

Table 4: Pseudo first order and second order rate equation and their formulae

Type	Linear	Plot
Pseudo-first order	$\log(q_e - q_t) = \log q_e - K_1 t / 2.303$	$\log (q_e - q_t)$ vs t
Pseudo-second order	$t/q_t = 1 / k_2 q_e^2 + 1/q_e t$	t/q_t vs t

Table 5: Pseudo-first order and second order rate constant for the sorption of Rhodamine-B onto Raw RHAC

C_0	Pseudo-First order kinetics			Pseudo- second order kinetics			
	K_1	q_e	r^2	q_e (Experimental)	K_2	q_e (calculated)	r^2
8	0.3878	6.959	0.7434	0.3216	0.3957	0.2552	0.9838

Table 6: Pseudo-first order and second order rate constant for the sorption of Rhodamine B onto RHAC /Chitosan Composite

C_0	Pseudo-First order kinetics			Pseudo-second order kinetics			
	K_1	q_e	r^2	q_e (Experimental)	K_2	q_e (calculated)	r^2
8	0.009902	1.3730	0.9358	0.1988	1.4283	0.1233	0.9848

Thermodynamic Studies

The thermodynamic influence of adsorption process was determined by the parameters like free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) and are calculated from the vant Hoff equation, which was shown below [27].

$$K_d = q_e / C_e \dots \dots \dots (5)$$

$$\Delta G = -RT \ln K_d \dots \dots \dots (6)$$

$$\ln k_d = \Delta S^0 / R - \Delta H^0 / RT \dots \dots \dots (7)$$

Where, K_d = distribution coefficient, T = temperature and R = gas constant (8.314J mol⁻¹ K⁻¹). From the Figure 16, 17 the parameters ΔS^0 and ΔH^0 were calculated using van't Hoff plot with the parameters of $\ln K_d$ vs $1/T$.

Table 7 and 8 gives the thermodynamic parameters of RHAC and RHAC/Composite respectively. The positive value of the change in enthalpy ΔH^0 shows that the endothermic nature of the adsorption reaction involved throughout the process. The adsorption in the solid-liquid system is a composed of two

processes: they are (1) the desorption of solvent (water and (2) the adsorption of dye species [28]. The Rhodamine-B ions are displace more than that of water molecule for the process and its result shows endothermic nature of the adsorption process.

The change of entropy shows positive value, it specifies that there was a increased disorderness at the Solid /Solution interface with some physical variations in the adsorbate and adsorbent molecules and an attraction of the RHAC towards Rhodamine-B. Furthermore, a positive ΔS^0 value show that an increase in the degree of disorderness of the adsorbed species [29].

The Gibbs free energy shows a negative value and it shows that the adsorption process is spontaneous in nature for the adsorption of Rhodamine-B dye onto RHAC. Generally the kinetic models do not give enough evidence of a diffusion mechanism that is also involved during the process and the rate controlling steps, which disturb the nature of adsorption process [30].

Table 7: Thermodynamic parameters for RhB onto Raw RHAC

T(K)	ΔG^0 (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (Jmol ⁻¹ K ⁻¹)
303	-0.55		
313	-0.52		
323	-0.78	0.13	2.35
333	-0.14		
343	-0.05		

Table 8: Thermodynamic parameters for RhB onto RHAC/Chitosan Composite

T(K)	ΔG^0 (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (Jmol ⁻¹ K ⁻¹)
303	-0.98		
313	-0.73		
323	-0.59	0.15	3.55
333	-0.44		
343	-0.15		

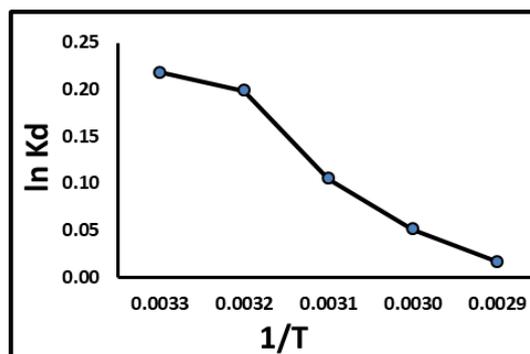


Fig. 16: Vant Hoff plot for RHAC

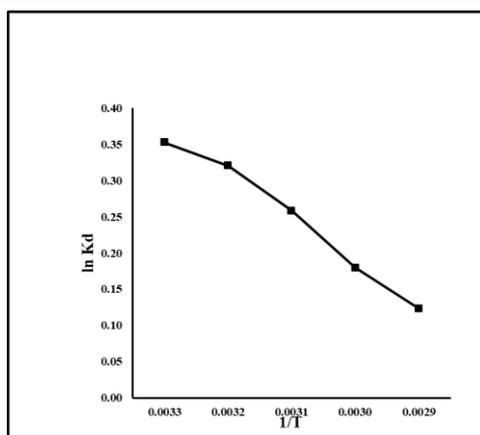


Fig.17: Vant Hoff plot for RHAC/Chitosan Composite

Intra-particle diffusion mechanism

The best suited model for ascertaining the mechanism involved in the sorption process is intraparticle diffusion model. The experimentally obtained data are correlated with an intraparticle diffusion plot, which was proposed by Weber and Morris [31], an intraparticle diffusion coefficient K_p is given by the equation:

$$K_p = q_t / t_{1/2}$$

So the K_p value could be obtained from the slope of the plot of q_t vs $t_{1/2}$ for Rhodamine-B, it was illustrated that the sorption process have a tendency to to be followed by two segments.

The two segments in the intraparticle diffusion plot suggest that the sorption process proceeds

by surface adsorption and intraparticle diffusion [32].

The plot between q_t vs $t_{1/2}$ shows a linear line and the parameters of k_d and C are calculated from the linear regression analysis of the obtained slope and intercept. The experimental values are showed in the Fig 18 and 19 for RHAC and composite. The expected plot does not show linearity at different time interims, which represents that adsorption, comprises a number of modes of sorption rather than a single mode. The results put forward that an intra-particle diffusion process is not only at a rate measured step but also some unexpected mechanism involved during the process of diffusion

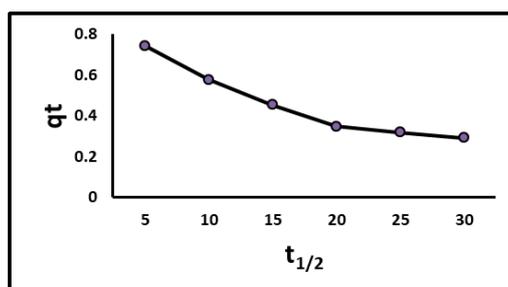


Fig. 18: Intra-particle diffusion model for RHAC

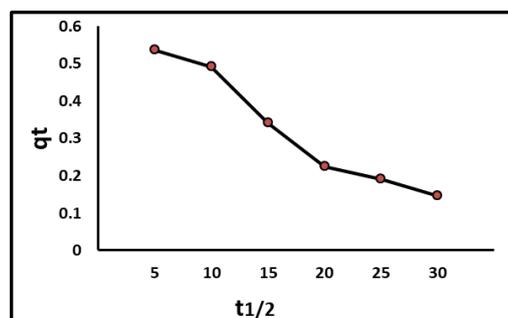


Fig. 19: Intra-particle diffusion model for RHAC/Chitosan Composite

CONCLUSION

The rice husk is by product of agricultural materials and has been prepared into a possibly low cost biosorbent material for the dye removal process. The present study demonstrates that the rice husk is an efficient adsorbent material for the removal of Rhodamine-B from aqueous solution. The acceptance of Rhodamine-B ions at pH 6 was the meager, and a maximum in uptake was attained at pH 3. Variant in temperature exhibited a slight decrease in percentage removal with rise in temperature for the adsorbent could be due to the reduction of the physical forces of attraction between Rhodamine-B dye and adsorbent. The kinetics of adsorption process was studied for its significance in the treatment of dye containing industrial waste water. RHAC/Chitosan Composite has excellent adsorption capacity than RHAC at equilibrium adsorption. To reach equilibrium, it takes 50 min. This could be due to the idea that the activated carbon produces some macro and micro pores in the composite form. Langmuir isotherm confirms a better correlation coefficient (r^2) value as compared with Freundlich isotherm. From the kinetic studies, results obtained from the coefficient values of pseudo-first order rate constant are very low while compared with pseudo second order kinetic values. Therefore, the results indicate that the sorption process follows second rate equation during the process. The Gibbs free energy change value is negative which reveals that the adsorption process is spontaneous in nature for the adsorption of Rhodamine-B dye by RHAC and composites. It is proven on the above investigation, the RHAC/Composite is an efficient adsorbent and it fulfills all the essential criteria for the removal of Rhodamine B dye. So, it may be concluded that RHAC/Composite is a best suitable and cost effective substituent for effective removal of dye for the adsorption mechanism. The composite adsorption beads may be used in fixed and fluidized bed reactors in industrial effluent treatment plants.

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Cite this article as:

T.K. Arumugam, P. Krishnamoorthy, R.Tamilarasan, N.R.Rajagopalan. Efficient Usage of Rice Husk Carbon and Chitosan Composite for Adsorption of Rhodamine B from Waste Water. *J Pharm Chem Biol Sci* 2018; 6(2):107-121