

Removal of a Basic Dye (Rhodamine-B) From Aqueous Solution by Adsorption Using Timber Industry Waste

V. K. Garg*, R. Gupta, and T. Juneja

Department of Environmental science and Engineering,
Guru Jambheshwar University, Hisar 125001, Haryana, India

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Sorption of rhodamine-B from aqueous solutions on formaldehyde treated saw dust (SD) and sulphuric acid treated saw dust (SDC) of Indian Rosewood, a timber industry waste, was studied. Aqueous solutions of various mass concentrations ($50 - 250 \text{ mg l}^{-1}$) were shaken with certain amounts of adsorbent to determine the adsorption capacity of rhodamine-B on SD and SDC as well. Similar experiments were carried out with commercially available activated carbon (ACR) to compare the adsorption capacity of SD and SDC. The influence of several individual variables (initial adsorbate concentration, adsorbent mass, pH etc.) on the rate of uptake of dye by the adsorbents was determined using the batch mode. The adsorption capacity of the studied adsorbents was in the order $\text{ACR} > \text{SDC} > \text{SD}$. Initial pH had negligible effect on the adsorption capacity. Maximum dye was sequestered from the solution within 30 – 45 min after the beginning for every experiment. After that, the concentration of rhodamine-B in the liquid phase remained almost constant. The adsorption of rhodamine-B on SD and SDC followed a first order rate expression and fit the Lagergren equation well. The results showed that SDC and SD can be considered as potential adsorbents for rhodamine-B removal from dilute aqueous solutions.

Key words:

Rhodamine-B, formaldehyde, sulphuric acid, treated sawdust, adsorption

Introduction

Dyes are aromatic organic colorants having potential applications in textile, paper and leather industries. The textile sector alone consumes approximately 60 % of the total dye production, for coloration, about 10 – 15 % of the dyes used come out through the effluent.¹ The dye laden wastewater is characterized by persistent color coupled with high chemical and biological demands (COD and BOD). Discharge of such effluents imparts color to the receiving water and interferes with its intended beneficial use. Color impedes light penetration, retards photosynthesis, inhibits the growth of aquatic biota, and interferes with gas solubility in water bodies.² The metal complex dyes are based on chromium and are known or suspected to be carcinogenic.³

Current methods for removing dyes from wastewater include flocculation, electro-flotation, precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation, and ozonation. However, these processes are costly and can not effectively be

used to treat the wide range of dye wastewater. The alum coagulation process is ineffective for the treatment of azoic, reactive, acidic and basic dyes. Conventional biological processes are effective only against basic dyes.⁴ The stringent and rigid national effluent disposal standards call for advance treatment among which liquid-phase adsorption has been found highly efficient for removal of color in terms of initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances. Activated carbon (powdered or granular) is the most widely used adsorbent, because it has excellent adsorption efficiency for organic compounds, but its use is usually limited due to its high cost.⁵ Consequently a number of non-conventional low cost adsorbents are being studied for the dye removal. These include vermiculite, rice husk, orange and banana peels, chitin, Fuller's earth, fly ash, coal, china clay, saw dust, natural clay, waste coir pith, biogas slurry, banana pith, bagasse pith etc.^{6–17}

In our laboratory, the work is in progress to evaluate the possibility of the use of waste biomass for industrial pollution control. The aim of the present study was to determine the optimum conditions for the removal of a dye, rhodamine-B, from an aqueous solution by formaldehyde treated sawdust (SD) and sulphuric acid treated sawdust (SDC) carbon of Indian Rosewood. Timber of this tree is

*Address for communication: Dr. V. K. Garg, Department of Environmental science and Engineering, Guru Jambheshwar University, Hisar 125001, Haryana, India
Corresponding author: e-mail: vinodkgarg@yahoo.com,
Fax: +91-1662-276240

widely grown in the Northern India for furniture making and presently the sawdust of this tree is either used as cooking fuel or a packing material. Similar experiments were undertaken with commercially grade activated carbon (ACR) to compare the results.

Experimental

Coconut shell based commercial grade ACR was procured from S.D. Fine Chemicals, Mumbai, India and used as such without further grinding and sieving. The physico-chemical characteristics of the adsorbent are summarized in Table 1.

Table 1 – Physico-Chemical Characteristics of adsorbents

Parameter	ACR	SDC
Source	Coconut shell	Indian Rosewood
Colour	Black	Black
Moisture content (%)	8.0	3.82
Ash content (%)	2.5	1.68
Methylene blue adsorption (mg/g)	150	51.4
Surface area (m ² /g)	800	98
pH	7.0	6.5
Acid soluble content (%)	1.0	9.34
Water soluble content (%)	0.2	1.68
Chloride (%)	0.01	0.13
Sulphate (%)	0.01	0.25
Phosphate (%)	BDL*	0.02
Iron (%)	0.01	–
Zinc (%)	0.001	–
Acidic surface functional groups		
Carboxylic	present	present
Lactonic	present	present
Phenolic	present	present
Carbonyl	present	present

* BDL = Below detection limit

Preparation of formaldehyde treated sawdust (SD)

Dalbergia sissoo (Indian Rosewood) tree sawdust collected from a local sawmill was dried in sunlight until all the moisture evaporated, and

ground to a fine powder in a steel blender. To polymerize and immobilize the color and water-soluble substances the ground sawdust was treated with 1 % formaldehyde in the mass ratio of 1: 5 (sawdust: formaldehyde, $\zeta_{s/t}$) at 50 °C for 4 h. The sawdust was filtered out with a Büchner funnel, washed with distilled water to remove free formaldehyde, and activated at 80 °C in an air oven for 24 h. The resulting material was sieved in the size range of 20 – 50 mesh ASTM. The methylene blue removal capacity of SD is 46.1 mg g⁻¹ for 250 mg l⁻¹ solution.¹⁶ The material was placed in an airtight container for further use.

Preparation of sulphuric acid treated sawdust carbon (SDC)

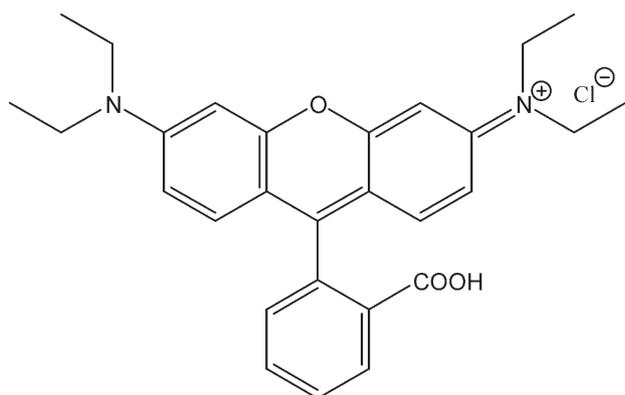
One part of dried sawdust was mixed with one part of concentrated sulphuric acid and heated in a muffle furnace for 24 h at 150 °C. The heated material was washed with distilled water and soaked in 1 % sodium bicarbonate solution overnight to remove residual acid. The material was dried in an oven at 105 °C for 24 h and sieved in the size range of 20 – 50 mesh ASTM for further processing. SDC was characterized by adopting the standard procedures.^{18,19} The various physico-chemical characteristics of SDC are given in Table 1. All adsorbents were dried at 110 °C overnight before the adsorption experiments.

Dye solution preparation

The commercial-grade basic dye rhodamine-B [C. I. = 45170; CAS no. = 81-88-9, chemical formula = C₂₈H₃₁ClN₂O₃; M_r = 479.02; class = basic dye; color = basic violet 10; electrical conductivity (20 mg l⁻¹ solution) K = 0.015 s m⁻¹, melting point T_m = 165 °C, molar extinction coefficient in ethanol = 106,000 l mol⁻¹ at 542.72 nm, purity w ≈ 80 % and λ_{\max} = 543 nm], was used as supplied by S. D. Fine Chemicals, Mumbai, India. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (500 mg l⁻¹). Experimental solutions of the desired concentrations were obtained by successive dilutions.

Rhodamine-B has been tested on mice and rats by subcutaneous injection and, in inadequate studies, by oral administration. It was carcinogenic in rats when injected subcutaneously, producing local sarcomas. The intravenous LD₅₀ in rats is 89.5 mg kg⁻¹ [www.osha-slc.gov/dts/sltc/methods]

IUPAC name of rhodamine-B is *N*-[9-(2-carboxyphenyl)-6-(diethylamino)-3*H*-xanthen-3-ylidene]-*N*-ethylethanaminium.



Chemical structure of Rhodamine-B

Batch mode experiments

In each adsorption experiments, 100 ml of dye solution of known concentration and pH was added to 400 mg of SD, SDC or ACR in a 0.25 l glass-stoppered flask at room temperature (26 ± 1 °C) and the mixture was stirred on a mechanical shaker at 160 rpm. The samples were withdrawn from the shaker at the pre-determined time intervals, and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 min. The absorbance of the supernatant solution was, estimated to determine the residual dye concentration, measured before and after treatment at 543 nm with an ELICO spectrophotometer (Model SL-150). Effect of initial pH of the dye solution was studied in the pH range of 2 to 10. Initial pH of the dye solution was controlled by addition of 0.01 mol l^{-1} HCl or NaOH solutions as required. Two main system variables, initial dye concentration in the test solution and adsorbent dosage, were varied to investigate their effect on the adsorption kinetics. Each experimental point is the average of three independent runs and all the results were reproducible with ± 3 % error limit.

Results and discussion

Neither changes appeared in the absorption spectrum nor additional peaks formed for the dye solution after shaking it with the adsorbent. This indicated that there were no breakdown product(s) of the dye and also supported the fact, that the dye removal from the solution in this study was through the mechanism of adsorption.

Adsorption capacity of different adsorbents

Experiments on adsorption capacity of ACR, SDC and SD were conducted at different dye concentrations ($50 - 400 \text{ mg l}^{-1}$) whilst maintaining the temperature (26 ± 1 °C), pH (7.0) and equilibrium time (3h) constant. Fig.1 shows that for the same

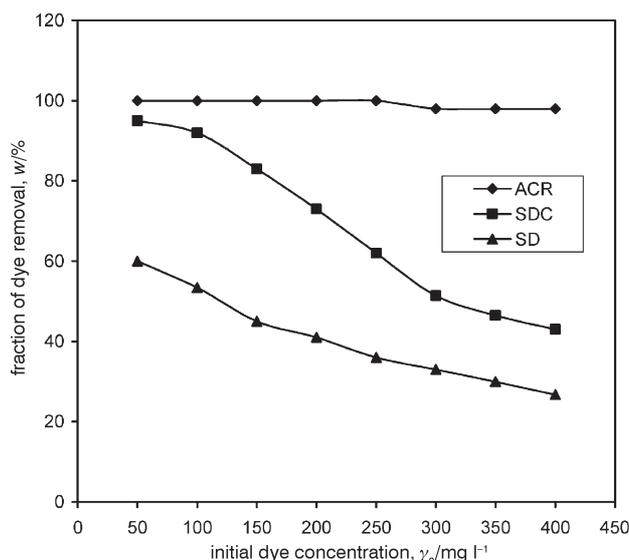


Fig. 1 – Effect of adsorbent change on dye removal (pH 7.0, adsorbent dose $\gamma_{ad} = 4.0 \text{ g l}^{-1}$, equilibrium time, $t = 3 \text{ h}$)

amount of dye, maximum adsorption capacity of these adsorbents was in the order $\text{ACR} > \text{SDC} > \text{SD}$. At 50 mg l^{-1} dye concentration, ACR had 1.1 and 1.7 times more adsorption capacity than SDC and SD, respectively. Whereas at 400 mg l^{-1} dye concentration, ACR had 2.5 and 3.7 times more adsorption capacity than SDC and SD, respectively. This suggests that an increase in the initial dye concentration decreased the adsorption capacity of SDC and SD.

Effect of pH on dye adsorption

To study the effect of pH on rhodamine-B adsorption on ACR, SDC and SD, the experiments were carried out at 250 mg l^{-1} dye concentration with $0.4 \text{ g}/100 \text{ ml}$ adsorbent mass at 26 ± 1 °C temperature for 180 min equilibrium time. The initial pH of the solution was varied from 2 to 10. The pH of dye solution was slightly higher at equilibrium time than adjusted value. It may be due to hydrolysis of the adsorbent in water, which creates positively charged sites.¹⁶ The dye adsorption by ACR was 100 % in the studied pH range followed by SDC (73.4 – 62 %) and SD (37.6 – 34.6) (Fig. 2). Different trends for the adsorption of rhodamine-B on different adsorbents have been reported. The adsorption capacity of banana peel⁸ increased, when the pH was increased with maximum adsorption at pH 6–7. For orange peel,⁸ the amount of dye adsorbed reached the plateau at pH > 7. Waste coir pith removed the maximum amount of rhodamine-B at pH 3.03, which decreased up to pH 11.03.¹⁷ Coal¹² adsorbed the maximum dye in pH range of 3.8 – 5.8. Our results are similar to those reported for waste coir pith¹⁷ as adsorbent. ACR and SDC

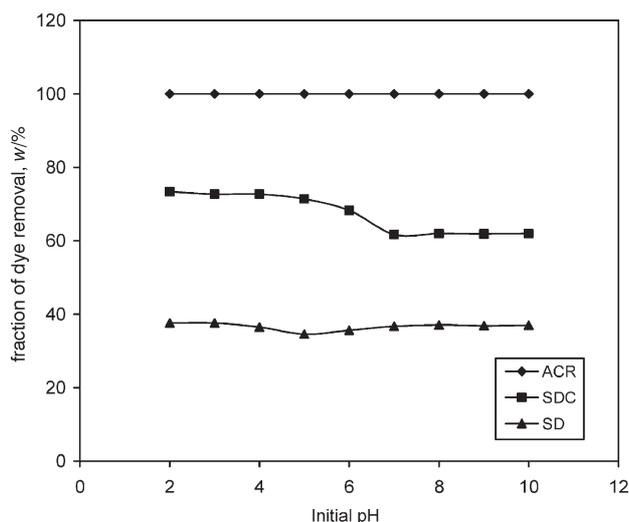


Fig. 2 – Effect of pH on dye mass adsorption (Dye mass concentration $\gamma_d = 250 \text{ mg L}^{-1}$, adsorbent dose $\gamma_{ad} = 4.0 \text{ g l}^{-1}$, equilibrium time $t = 3 \text{ h}$)

had more adsorption capacity than SD at all the initial pH values. This can be attributed to better physical structure and surface area of ACR and SDC.

Influence of the initial dye concentration

The influence of the initial concentration of rhodamine-B in the solutions on the rate of adsorption on ACR, SDC and SD was studied. The experiments were carried out at 160 rpm, $0.4 \text{ g}/100 \text{ ml}$ mass of sorbent, $26 \pm 1 \text{ }^\circ\text{C}$ temperature, 7.0 pH, and initial mass concentrations of rhodamine-B 50, 100, 150, 200 and 250 mg l^{-1} for different time intervals. Dye removal by ACR was 100 % at all the studied dye concentrations. Percent decolourization efficiency of SDC and SD decreased with increase in dye concentration (Fig. 3 & 4). Adsorption and initial dye concentration correlation is exponential in nature for SDC and SD. This is well in accord with the findings of other investigators.²⁰ Though the percentage removal decreased with increase in concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye mass concentration. The equilibrium was established quickly within 15 min at all the studied concentrations by ACR. However, SDC and SD took about 60 and 120 min, respectively, for equilibrium attainment.

Influence of adsorbent mass on dye adsorption

The adsorption rate of rhodamine-B on ACR, SDC and SD was studied by changing the quantity of the sorbent added 4.0, 6.0, 8.0 and 10.0 g in 1 l , while keeping the initial dye mass concentration 250 mg l^{-1} , temperature $26 \pm 1 \text{ }^\circ\text{C}$ and pH 7.0 constant at different contact times up to 180 min. The fraction adsorption was increased and equilibrium

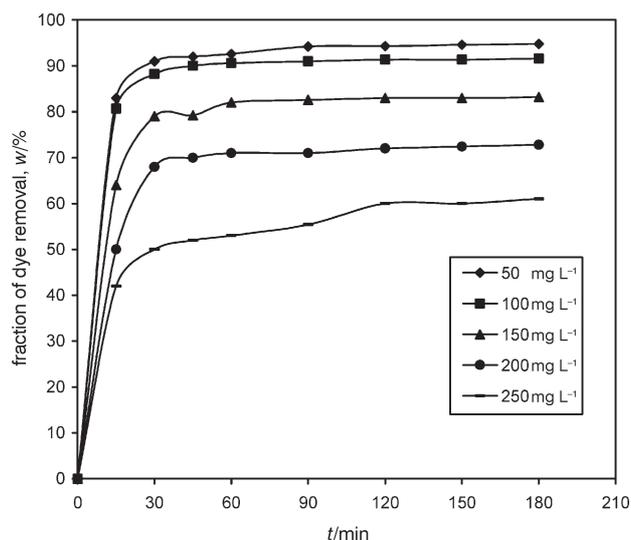


Fig. 3 – Effect of initial dye mass concentration on the adsorption of rhodamine-B on SDC (adsorbent dose $\gamma_{ad} = 4.0 \text{ g l}^{-1}$, pH 7.0)

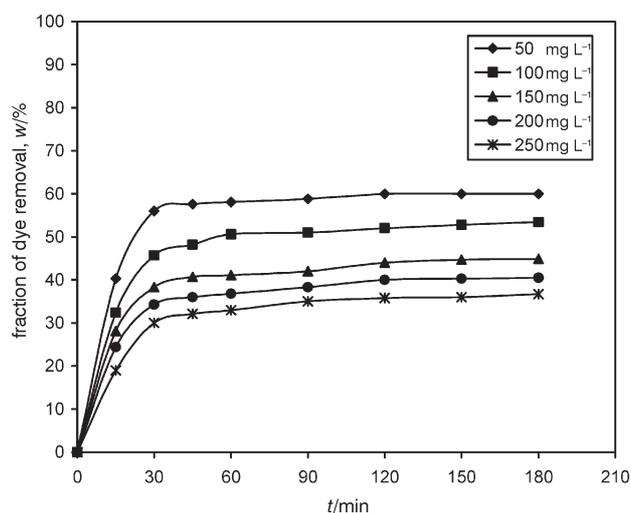


Fig. 4 – Effect of initial mass concentration on the adsorption of rhodamine-B on SD (adsorbent dose $\gamma_{ad} = 4.0 \text{ g l}^{-1}$, pH 7.0)

time was decreased with sorbent dosage (Fig. 5 & 6). The adsorption was 100 % by ACR at the minimum studied adsorbent dosage (4.0 g l^{-1}) within 15 min. The fraction adsorption increased from 61.7 to 94.6 %, as the SDC dose was increased from 4.0 to 10.0 g l^{-1} after 180 min. For SD, adsorption increased from 36.7 to 77.0 % with same adsorbent dosages. Maximum dye was sequestered from the solution within 30 – 45 min after the beginning for every experiment. After that, the mass concentration of rhodamine-B in the liquid phase remained almost constant. Increase in the adsorption with adsorbent dosage can be attributed to increased surface area and availability of more adsorption sites. But unit adsorption was decreased with increase in adsorption dosage. For SDC, unit adsorption was

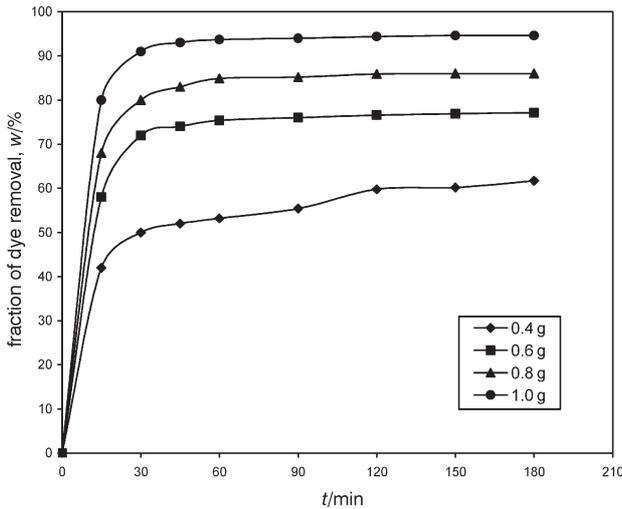


Fig. 5 – Effect of adsorbent mass on the adsorption of dye on SDC (Dye mass concentration $\gamma_d = 250 \text{ mg L}^{-1}$, volume of sample $V = 100 \text{ ml}$, pH 7.0)

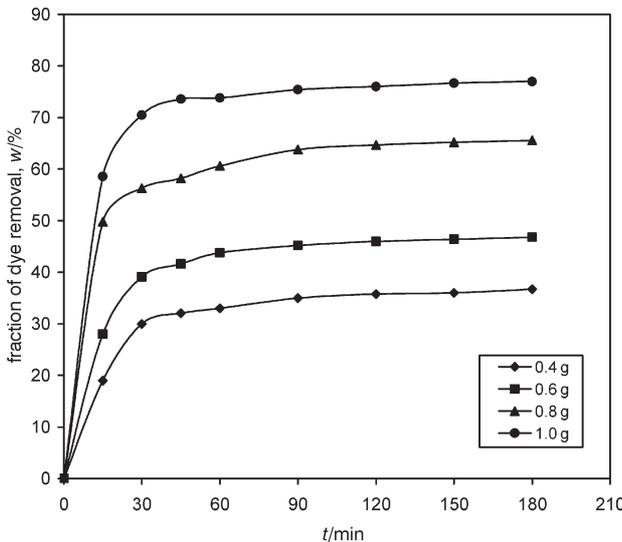


Fig. 6 – Effect of adsorbent mass on the adsorption of dye on SD (Dye mass concentration $\gamma_d = 250 \text{ mg L}^{-1}$, volume of sample $V = 100 \text{ ml}$, pH 7.0)

decreased from 38.7 mg g^{-1} to 23.6 mg g^{-1} as the adsorbent dosage was increased from 4.0 to 10.0 g l^{-1} in solution. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles.^{15–17} For SD, the unit adsorption was decreased from 23.0 to 19.3 mg g^{-1} as the dosage was increased.

Adsorption dynamics

The coefficient rate, k_{ad} , for the adsorption of rhodamine-B on SDC and SD, was calculated using the pseudo-first order Lagergren equation.

$$\log(w_e - w) = \log w_e - \frac{k_{ad} \times t}{2.303}$$

where w_e and w (both in mg g^{-1}) are the amounts of rhodamine-B adsorbed at equilibrium time and at any time “ t ”, respectively. The straight-line plot of $\log(w_e - w)$ vs. t at different dosages indicated the validity of Lagergren equation for the present system and explained that the process follows the first order kinetics. The values of k_{ad} , calculated from the slopes of the plots, were 0.0302 min^{-1} and 0.0133 min^{-1} for SDC and SD, respectively, at 4.0 g l^{-1} dosage.

There is a possibility of transport of adsorbate ions from solution to pores of adsorbent due to stirring in batch processes in addition to adsorption on the outer surface of adsorbent. The plot of adsorbate uptake versus square root of time ($t^{1/2}$) has commonly been used to describe whether the adsorption process is controlled by diffusion in the adsorption particles and consecutive diffusion in the bulk of solution²¹. In order to explore the existence of intraparticle diffusion in this study, the amount of rhodamine-B sorbed per unit mass of adsorbents (q) at time “ t ” was plotted as a function of square root of time, $t^{0.5}$. The rate constant for the intraparticle diffusion was obtained using the following equation

$$w = K\rho \cdot t^{1/2}$$

where w (in mg g^{-1}) is the amounts of rhodamine-B adsorbed at any time “ t ” and $K\rho$ ($\text{mg g}^{-1} \text{ min}^{-1/2}$) is the intraparticle diffusion rate constant.

The shape of the w versus $t^{1/2}$ plot is curved (Fig. 7) at a small time limit which might be due to mass transfer effect.²² There are two separate regions in the curves. The initial curved portion reflects film or boundary layer diffusion effect and the linear portion to the intra-particle diffusion-effect.²² The values of $K\rho$ were obtained from the slope of the straight lines, and were $1.765 \text{ mg g}^{-1} \text{ min}^{1/2}$ for SDC and $1.433 \text{ mg g}^{-1} \text{ min}^{1/2}$ for SD. Fig. 7 depicts that intra-particle diffusion is slow and rate determining step. The linear portions of the

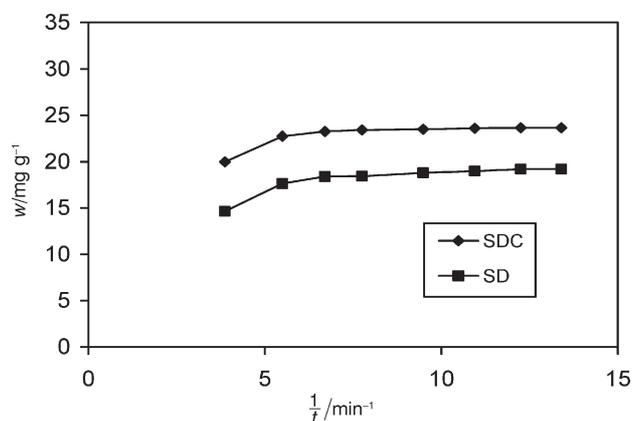


Fig. 7 – Test of intra-particle diffusion model for adsorption of dyes using SDC and SD

curves (Fig. 7) do not pass through the origin. This indicates that mechanism of dye removal on SD and SDC is complex and both, the surface adsorption as well as intra-particle diffusion contribute to the rate determining step.^{23, 24}

Conclusion

The removal of rhodamine-B from simulated aqueous solutions using ACR, SD and SDC has been investigated under different experimental conditions in batch mode. The adsorption of rhodamine-B was dependent on adsorbent surface characteristics, adsorbent dose, and adsorbate concentration in the solution. Results indicate that SDC and SD had lower adsorption of rhodamine-B than ACR at higher dye concentrations. Initial pH of solution had no marked effect on the adsorption for this dye. Adsorption kinetics followed Lagergren first-order kinetics model. Higher dye adsorption by SDC and SD was possible provided the initial dye concentration was low in the solution. ACR is an expensive material and regeneration is essential, where as SD and SDC are economically cheap, so regeneration is not necessary. Indian Rosewood is a common tree in India and its sawdust is easily available in the countryside at zero or negligible price. The data may be useful for designing and fabricating an economically cheap treatment process for small-scale dyeing reactors using batched or stirred-tank flow reactors.

List of symbols

- K_p – diffusion rate constant, $\text{mg g}^{-1} \text{min}^{1/2}$
 k_{ad} – rate coefficient of adsorption, min^{-1}
 t – time, min
 V – volume, l
 w – mass fraction, 10^{-3}
 γ – mass concentration, g l^{-1}
 $\zeta_{s/f}$ – mass ratio, m_s/m_f

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