Preparation, characterization and removal of hazardous reactive violet dye from aqueous solution using activated carbon and electroactive conducting polymer – a comparative study

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ABSTRACT

The present study investigates the feasibility of removing Reactive Violet 5 (RV5) from aqueous solution using two different adsorbents namely phosphoric acid activated carbon (PAC) and electroactive conducting polypyrrole coated sawdust (PPy/SD) prepared from *Casuarina* wood. The parameters like initial dye concentration, temperature, contact time and pH were evaluated and optimum experimental conditions were verified. The experiments were carried out using batch mode adsorption systems at 30°C, 35°C and 40°C. Surface morphology was studied through scanning electron microscopy. X-ray diffraction technique was used to analyze the nature of the adsorbent material. Adsorption of RV5 onto PAC and PPy/SD under different conditions was predicted using various kinetic models like pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models. The experimental data were also analyzed by Langmuir, Freundlich, D–R and Temkin isotherm models. The adsorption isotherm data for RV5 were best fitted to the Langmuir isotherm. The maximum monolayer adsorption capacity was found to increase from 10.39 to 12.35 mg/g for PAC and 11.19 to 13.59 mg/g for PPy/SD on increasing the temperature from 30°C to 40°C which accounts for the endothermic nature of the process. The results revealed that PPy/SD can act as an excellent adsorbent than PAC for removal of anionic dye namely RV5.

Keywords: Phosphoric acid activated carbon; Electroactive conducting polymer; Reactive Violet; Batch mode adsorption; Intraparticle diffusion; Adsorption isotherm

1. Introduction

Rapid pace of industrialization, population expansion and urbanization have largely contributed to severe water pollution. The main sources of freshwater pollution can be attributed due to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluents and run-offs from agricultural fields. Nowadays, urbanization and industrialization are making a heavy demand for water resources, which need to be conserved. The high level of production and usage of dyes generates coloured wastewaters, which has aroused people's concern about environmental protection.

The runoffs from the manufacturing and textile industries are discarded into rivers and lakes, altering the biological stability of surrounding ecosystem. Therefore, removal of dyestuffs from wastewater has received considerable attention over the past decades. Water pollution is a continuing threat to human and their environment due to the abusive use and uncontrolled release of toxic substances. Many industrial activities consume large amounts of water and some of them, particularly the textile, paper, plastics, coal, food, petrochemical, pharmaceutical and dye industries. These industrial activities discharge effluents containing various chemicals,

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most of which are toxic to human and harmful to the environment [1].

Reactive dyes are used primarily on cotton and rayon. They are highly soluble in water and with the help of large amount of salt; the exhaustion of the dyes is improved. The wastewater produced by a reactive dye contains hydrolyzed reactive dyes responsible for the colouration of the effluents and cannot be recycled.

The dye also contains organic substances, which are non-recyclable and responsible for the high biological oxygen demand and chemical oxygen demand (COD) of the effluents, textile fibres and electrolytes, essentially sodium chloride and sodium carbonate, which are responsible for the very high saline content of the wastewater [2]. In addition, these effluents exhibit a pH of 10–11 and high temperature (50°C–70°C). Due to the toxic nature of most dyes to plants and microorganisms, coloured wastewater should not be discharged without adequate treatment. Even if they are non-toxic, such wastewater obstructs light penetration, therefore, decreases the efficiency of photosynthesis in three aquatic plants, and raises the COD [3].

Residual colour is a problem with reactive dyes because, in current dyeing processes, as much as 50% of the dye is lost in the wastewater. These losses are due to the relatively low levels of dye–fiber fixation and the presence of unreacted hydrolyzed dye in the bath. Dye hydrolysis occurs when the dye molecule reacts with water rather than with the hydroxyl groups of the cellulose [4]. The reason behind this phenomenon is that in the process of dyeing cellulosic fibers with reactive dyes, the use of alkalis is required to promote formation of covalent bonds between the dye and cellulosic substitute. However, the uses of alkalis result in hydrolysis of reactive groups in the dye, and the reaction necessary to introduce the substitute on the fiber do not go to completion. Therefore, residual reactive hydrolyzed dyes remain in the process water. These problems are compounded by the high water solubility and characteristic brightness of the dyes [5].

Removal of dyes from industrial effluent is a challenge since some processes are not economical while others are not so effective. In view of the importance of water pollution control, number of technologies has been developed. But colour removal from industrial wastewater by adsorption technique has been of growing importance due to the chemical and biological stability of dyestuffs to the conventional water treatment methods and the growing need for high quality treatment. Conducting polymers such as polypyrrole and its derivatives have attracted a great deal of attention in recent years due to their interesting electrical conductivity, electroactivity, environmental stability, low cost of raw materials and easy synthesis [6]. This class of new polymeric material can be easily synthesized from both aqueous and non-aqueous solution. These polymers can effectively remove or uptake heavy metal ions and dyes from aqueous solutions [7].

Application of activated carbon and polypyrrole conducting polymer doped with releasable or exchangeable counter ions for the removal of anionic dyes from aqueous solutions based on anion-exchange property of this polymer is a novel research work that can be considered as a highly efficient, cost-effective and green way in dye removal technology. Thus, the safe removal of toxic dyes is the prime aim of our present research and this is accomplished by using novel adsorbents.

2. Materials and methods

2.1. Preparation of activated carbon

The seeds and branches of *Casuarina* wood were collected and cut into small pieces (2 cm), washed with distilled water and dried in sunlight for 10 d. The dried material was soaked in a boiling solution of 40% H_3PO_4 for 1 h and kept at room temperature for 24 h. After 24 h, the wood material was separated, air dried and carbonized in muffle furnace at 400°C. The carbonized material was then powdered and activated in a muffle furnace at 800°C for a period of 10 min. After activation, the material was repeatedly washed with plenty of distilled water. The characteristics of phosphoric acid activated carbon (PAC) and polypyrrole coated sawdust (PPy/SD) are analyzed as per the standard procedures [8,9] and are given in Table 1.

2.2. Preparation of electroactive polypyrrole polymer

Sawdust prepared from *Casuarina* wood was used for the preparation of PPy/SD. The sawdust was first washed with distilled water in order to remove the impurities and finally dried at 60°C for 2 h. In order to prepare polymer coated sawdust, 5.0 g of sawdust was immersed in 50 mL of 0.20 M freshly distilled pyrrole solution for 12 h before polymerization. 50 mL of 0.5 M $FeCl_3$ as the oxidant solution was added into the mixture gradually and the reaction was allowed to continue for 4 h at room temperature [10]. The polymer coated sawdust was filtered, washed with distilled water, dried in an oven at 55°C–60°C and sieved before use [11].

2.3. Preparation of dye solution

Reactive Violet 5 (molecular weight: 735.58, molecular formula: $C_{20}H_{16}N_3Na_3O_{15}S_4$, λ max: 545 nm) used in this study is of commercial quality and used without further purification. Different initial concentrations were prepared by diluting the stock solution using double distilled water

Table 1
Physicochemical characteristics of PAC and PPy/SD

Properties	PAC	PPy/SD
pH	6.17	7.14
Conductivity, mS/cm²	0.12	6.25
Moisture content, %	11.30	10.12
Ash, %	10.3	1.3
Volatile matter, %	10.7	21.2
Matter soluble in water, %	0.19	0.13
Matter soluble in 0.25 M HCl, %	0.80	0.18
Bulk density, g/L	0.42	0.25
Specific gravity	1.87	0.23
Porosity, %	58.15	41.3
Surface area (BET), m²/g	963	287
Methylene blue number, mg/g	525	67
Iodine number, mg/g	1,186	128
Fixed carbon, %	67.7	22.4
Yield, %	69.2	94.4

as solvent. Dye concentration was analyzed by measuring the absorbance values with UV–VIS spectrophotometer (Model: JASCO V-570). The pH measurements were made using pH meter (Model LI 610 ELICO). The pH adjustments of the solution were made by 0.1 M HCl or 0.1 M NaOH. The chemicals were of AnalaR grade and all the adsorption experiments were carried out at room temperature (27°C ± 2°C). The structure of RV5 dye is shown in Fig. 1.

2.4. Batch mode adsorption experiments

The batch technique was selected because of its simplicity. The experiments were carried out in a mechanical shaker (KHAN shaker – KEMI make) working at a speed of 150 rpm. Dye solutions (50 mL) of desired concentrations and initial pH values were used. Blank samples were run under similar experimental conditions without using adsorbents. After shaking, the adsorbents were separated by centrifugation and the supernatant solutions were estimated by measuring absorbance at maximum wavelengths using UV–Visible spectrophotometer (Model: JASCO V-570) at the desired wave length. The effect of each parameter like adsorbent dose, adsorbent particle size, different dye concentrations and agitation time was studied by fixing the values of other parameters [12]. The amount of dye adsorbed by PAC and PPy/SD was calculated using the following equation:

$$q_e = \frac{(c_0 - c_e)}{w} v \qquad (1)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium onto PAC and PPy/SD; C_0 and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations of dye; V (L) is the initial volume of dye solution and W (g) is the weight of PAC and PPy/SD. The adsorbents PAC and PPy/SD of 2 g were added to each flask and then the flasks were sealed to prevent any change in volume during the experiments. It was agitated for predetermined time intervals at room temperature in the mechanical shaker.

3. Results and discussion

3.1. Physicochemical characteristics of adsorbents

Physicochemical characteristics of PAC and PPy/SD were studied as per the standard testing methods [13] and are summarized in Table 1.
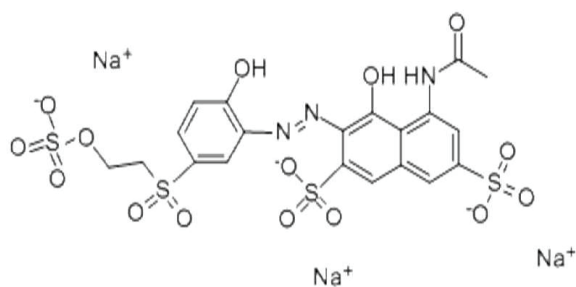

Fig. 1. Structure of Reactive Violet 5.

The pH value of PAC is found to be slightly acidic in nature due to the incorporation of acidic group in the carbon structure and that of PPy/SD is found to be basic in nature due to the presence of basic pyrrole group on the surface. Conductivity measurements are important as they indicate the presence of leachable ash which is considered as an impurity and undesirable matter in the adsorbent. Conductivity values of PAC are observed to be less indicating that substantial amount of water soluble minerals still remains in the carbon. The conductivity values exhibited by PAC might be due to the presence of uniform exchangeable site on the porous surface of the activated carbon. The conductivity of PPy/SD is due to the positively fixed charged sites on the surface which are balanced with the anion. PAC and PPy/SD have low moisture content of 11.30 and 5.12, respectively. High ash content ultimately reduces the percentage of fixed carbon. Very less percentage of ash content present in PPy/SD indicates the higher adsorptive capacity of the adsorbent when compared with PAC. Solubility studies of activated carbon and polymer coated sawdust in water and acid were carried out to evaluate the amount of impurities present in the adsorbents which could affect the quality of water during treatment processes.

From Table 1, it is evident that PAC and PPy/SD exhibits very less amount of impurities. PAC is found to possess high porosity when compared with PPy/SD. This fact could be supported from the surface area value that the H_3PO_4 activated carbon, PAC has highest surface area 963 m^2/g. Surface area increases with increase in porosity. Methylene blue value not only provides some insight into the surface properties and affinity of an adsorbent, but it also indicates the macropore and mesopore capacity of an activated carbon, which for dye adsorption, places mesoporous carbon in a leading position [14]. Iodine number is an important parameter used to characterize the efficiency of activated carbon as an adsorbent. From the results obtained, it is clear that PAC has an excellent iodine number when compared with PPy/SD. But the presence of ion-exchangeable sites on PPy/SD indicates that it could also be used as an efficient adsorbent in water treatment. Based on this characterization analysis, it is concluded that the activated carbon and polymer coated sawdust possess high adsorptive efficiency for the removal of textile dyes.

Scanning electron microscopy (SEM) reveals the surface texture and porosity of adsorbent. It also plays an important role in determining the surface availability for the adsorption of dye on adsorbents. The SEM photographs of activated carbon and PPy/SD are presented in Fig. 2. The surface of PAC has a structure similar to that of a honey comb with large number of pores indicating larger surface area and PPy/SD reveals that the surface consists of well developed, smooth, glassy spherical particles containing small holes in the centre of the spheres.

X-ray diffraction (XRD) technique is a powerful tool to analyze the crystalline and amorphous nature of the material under investigation. In crystalline material, well-defined peaks are observed whereas non-crystalline or amorphous material shows broad peaks instead of sharp peaks. X-ray diffractograms obtained ensure the small crystalline domains [15] and are presented in Fig. 3.

The broadness of the peaks indicates the amorphous nature of the carbon. Several sharp and intense diffraction
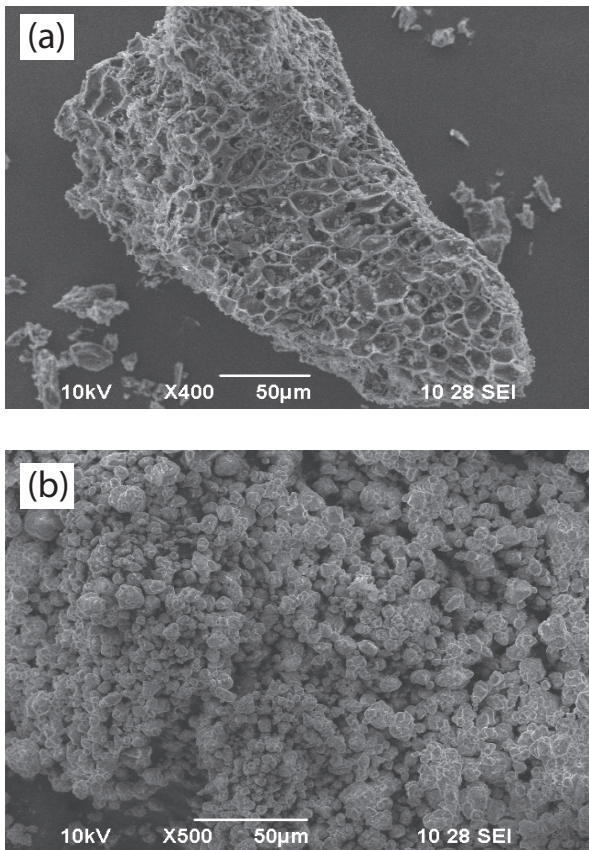
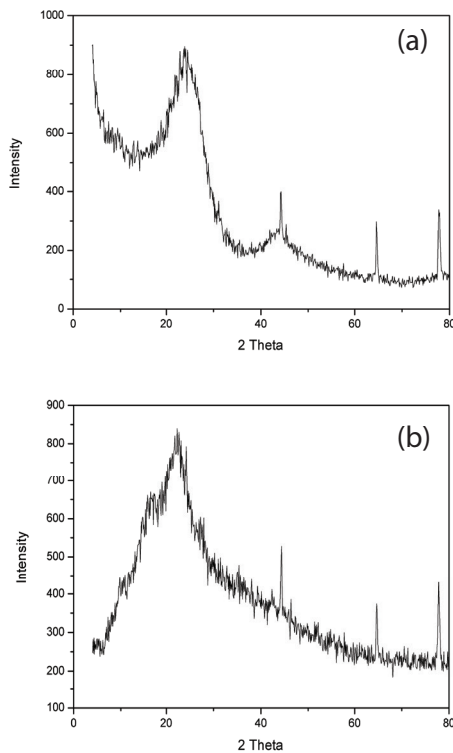Fig. 2. SEM images of (a) PAC and (b) PPy/SD.

Fig. 3. XRD image of (a) PAC and (b) PPy/SD.

peaks were also observed in the XRD profile and they might be due to the presence of some silica and other typical mineral matter present in the plant tissues which remain intimately bound with carbon material.

3.2. Effect of initial dye concentration and contact time

Initial dye concentration of RV5 ranging from 25 to 100 mg/L was prepared and adsorption experiments were conducted using 2 g of PAC and PPy/SD. The percentage removal of the dye was found to decrease from 89.6% to 67.1% for PAC and 90.2% to 69.2% for PPy/SD at 30°C with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of RV5 [16] and hence, the overall removal percentage decreases with increase in concentration [17]. The amount of RV5 dye removal by PAC is less than PPy/SD. This increase in dye removal capacity might be due to the ion-exchange mechanism taking place between the oppositely charged functionalities originating from monomer and the ionic dye molecules.

The effect of contact time was studied by agitating 2 g of PAC and PPy/SD separately with 50 mg/L of RV5 solution. The adsorption efficiency increases with increase in time (Fig. 4). PAC shows 82.7% removal of RV5 whereas PPy/SD shows 90.3% removal of RV5. The adsorbent PAC attains equilibrium at 100 min and PPy/SD at 80 min. In the process of adsorption, initially, the dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface. Finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time.
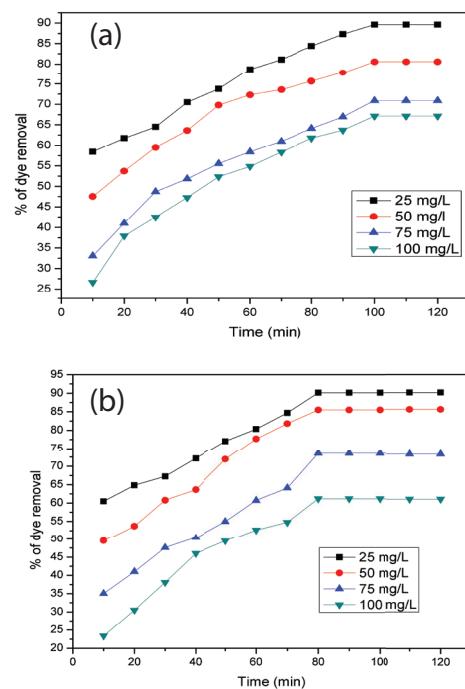

Fig. 4. Effect of time for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

3.3. Effect of pH

Adsorption process for the treatment of dye containing waste water is pH dependent. The effect of initial pH on adsorption capacity was studied in the pH range of 2–12 at 50 mg/L initial dye concentration. The removal of RV5 onto PAC and PPy/SD was found to be in the acidic range of pH 2–3 (Fig. 5) with maximum uptake at 93.4 mg/g for PAC and 97.1 mg/g for PPy/SD, after which, the uptake declined significantly.

At lower pH values, the adsorbent will have a net positive charge. Higher uptakes obtained at lower pH may be due to the electrostatic attractions between negatively charged functional groups located on the reactive dye and positively charged adsorbent surface. Hydrogen ion also acts as a bridging ligand between the adsorbent wall and the dye molecule. The reduction in adsorption capacity of dye on adsorbent with increasing pH can be attributed to change in surface characteristics and charge.

As the pH of the system increases, the number of hydroxide ion increases and will compete with anionic ion of the dye on the adsorption site in the alkaline condition and could reduce the adsorption capacity since the number of positively charged sites decreases. Moreover, there are also no more exchangeable anions on the outer surface of the adsorbent. A negative charged surface site on the adsorbent does not favour the adsorption of dye ions due to electrostatic repulsion and abundance of OH^- ion.

3.4. Effect of temperature

The effect of temperature on dye adsorption was studied at 30°C, 35°C and 40°C. The amount of RV5 uptake increases from 80.6 to 85.8 mg/g onto PAC and 85.5 to 92.6 for PPy/SD on increasing the temperature from 30°C to 40°C. The percentage of colour removal is found to increase with increase in temperature implying that high temperature favours the removal of RV5 onto PAC and PPy/SD. The enhanced equilibrium adsorption capacity of RV5 with increase in temperature indicates that the adsorption process is endothermic in nature. In this regard, it is noteworthy that endothermic pore diffusion highly influences the adsorption process for the selected adsorbents at the studied temperatures.
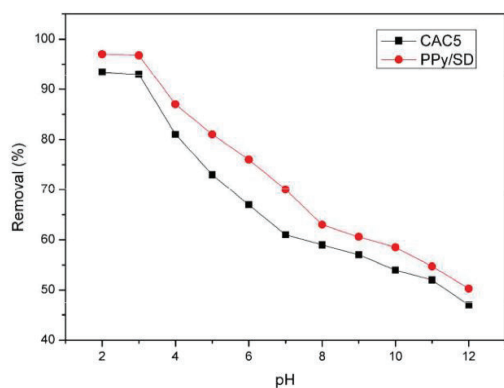

Fig. 5. Effect of pH on the percentage removal of RV5 by PAC and PPy/SD.

3.5. Adsorption kinetics

Adsorption kinetics provides an invaluable insight into the controlling mechanism of an adsorption process which in turn governs the residence time of adsorbate at the solid–liquid interface. Thus, in order to evaluate the kinetic mechanism that controls the adsorption of RV5 onto PAC and PPy/SD, four kinetic models such as pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models were tested to interpret the experimental data.

3.5.1. Pseudo-first-order kinetic model

The pseudo-first-order model of Lagergren [18] is based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount. The pseudo-first-order equation is expressed as given in Eqs. (2) and (3).

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{2}$$

The integrated form of equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity per unit weight of adsorbent at equilibrium and at time t (min), respectively. k_1 (min^{-1}) is the pseudo-first-order rate constant. Linear plot of $\log(q_e - q_t)$ vs. t gives the value of rate constant k_1. The values of first-order rate constant k_1 and q_e were calculated from the intercepts and slopes of the plot of $\log(q_e - q_t)$ vs. t (Fig. 6) and the results are summarized in Table 2. The correlation coefficients are low for both PAC and PPy/SD and it is found that the pseudo-first-order equation does not fit well with whole range of adsorption process, as it is only applicable for the initial stages of adsorption processes [19] and after that it starts deviating from the theory.

This infers that the adsorption of RV5 onto PAC and PPy/SD does not follow first-order mechanism.

3.5.2. Pseudo-second-order kinetic model

The pseudo-second-order model [20] is based on the assumption that the rate-limiting step involves chemisorption. The dye adsorption described by a second-order equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q e^2} + \frac{1}{q_e} \tag{4}$$

where k_2 is the pseudo-second order rate constant (g/mg/min). The value of k_2 was found to decrease with increase in dye concentration due to decrease in available vacant sites for adsorption. The values of second-order rate constant k_2 and q_e (Table 2) were calculated from the intercepts and slopes of the plot of t/q_t vs. t as shown in Fig. 7.

Considering the q_e (exp) and q_e (cal) values and high correlation coefficient values obtained for pseudo-second-order
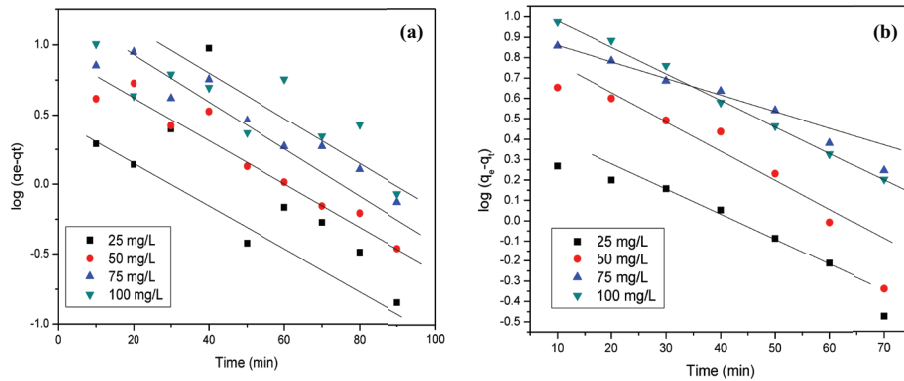
Fig. 6. Pseudo-first-order plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

Table 2
Calculated kinetic parameters for the adsorption of RV5 onto PAC and PPy/SD

Parameters	Initial dye concentration, mg/L							
	PAC				PPy/SD			
	25	50	75	100	25	50	75	100
q_e (exp) (mg/g)	5.601	10.072	13.301	16.785	5.635	10.692	13.782	18.288
Pseudo-first-order kinetic model								
$k_1 \times 10^{-2}$ (min^{-1})	32.1	37.93	25.77	29.18	26.9	36.47	22.9	30.67
q_e (cal) (mg/g)	0.7173	0.6072	0.8937	0.7893	0.856	0.6315	1.01	0.7509
r^2	0.8421	0.8231	0.8955	0.9167	0.8676	0.8548	0.9163	0.9083
Pseudo-second-order kinetic model								
$k_2 \times 10^{-4}$ (g/mg min)	11.789	6.524	2.987	1.895	13.5	5.14	2.388	1.9199
q_e cal (mg/g)	6.2454	11.2395	15.5739	20.4438	6.23	12.26	16.85	19.25
r^2	0.996	0.9982	0.9958	0.9968	0.9971	0.9964	0.99	0.9958
h	0.4598	0.7243	0.7919	0.8242	0.5276	0.6788	0.7114	0.7738
Elovich model								
α (mg/g/min)	1.383	1.1473	1.0598	1.0132	4.4315	2.6127	2.1748	1.5139
β (g/mg)	1.8491	1.9373	2.3028	3.0335	1.8961	2.1678	3.3885	4.2907
r^2	0.9908	0.9869	0.9952	0.9928	0.9962	0.9736	0.9897	0.9872
Intraparticle diffusion model								
K_{dif} (mg/g/min$^{1/2}$)	0.5838	1.0252	1.8571	2.6198	0.5543	1.3254	2.0949	2.5811
r^2	0.9839	0.9849	0.9928	0.9899	0.9863	0.9724	0.9893	0.9814
C	2.6165	3.3777	3.6779	4.3843	2.5652	2.8513	3.1976	4.1069

reaction, it can be concluded that the adsorption of RV5 onto PAC and PPy/SD follows second-order kinetics [21].

3.5.3. Intraparticle diffusion study

In a rapidly stirred batch reactor, the transport of adsorbent species takes place from the bulk of the solution into solid phase through intraparticle diffusion process. The expression for the intraparticle diffusion model is given by the following Eq. (5):

$$q_t = K_{dif}\, t^{1/2} + C \tag{5}$$

where C (mg/g) is the intercept and K_{dif} is the intraparticle diffusion rate constant (mg/g/min$^{1/2}$).

The values of q_t are found linearly correlating with values of $t^{1/2}$ for both the adsorbents and the rate constant K_{dif} was directly evaluated from the slope of the regression line. The values of intercept C provide information about the thickness of the boundary layer. The resistance to the external mass transfer increases as the intercept increases. The results are shown in Table 2.
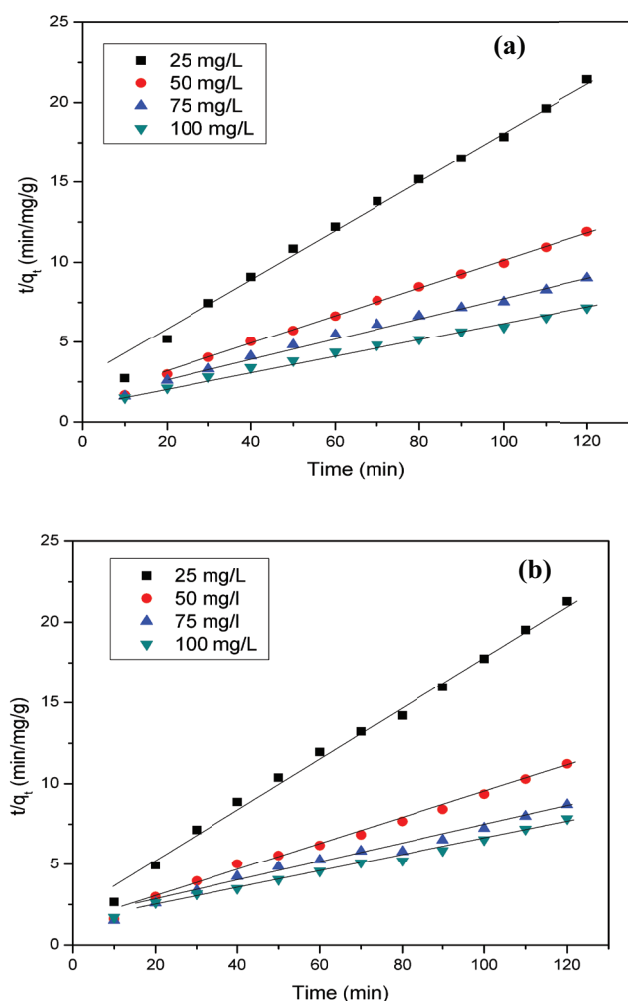
Fig. 7. Pseudo-second-order plot for adsorption of RV5 onto (a) PAC and (b) PPy/SD.

Fig. 8. Intraparticle diffusion plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

3.5.4. Elovich kinetic model

The Elovich plot for the adsorption of RV5 on PAC and PPy/SD at various initial concentrations and temperatures are shown in Fig. 9. The parameters of Elovich kinetic model are listed in Table 2. The initial adsorption rate (α) seems to decrease from 1.383 to 1.0132 (mg/g/min) for PAC and from 4.4315 to 1.5139 (mg/g/min) for PPy/SD while increasing the initial concentration from 25 to 100 mg/L. The desorption coefficient (β), which is related to surface coverage, increases with increase in the initial dye concentration indicating the decrease in availability of adsorption surface for the adsorbate [23].

If the intraparticle diffusion is involved in the adsorption process, then the plot of q_t vs. $t^{1/2}$ would result in a linear relationship and the intraparticle diffusion would be the controlling step if this line passes through the origin. When the plots do not pass through the origin, it indicates some degree of boundary layer control and it further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption. Such plots may present multi-linearity, indicating that two or more steps take place.

It is evident from Fig. 8 that initially the diffusion of adsorbate takes place through the solution and then to the external surface of adsorbent. Gradually, the intraparticle diffusion takes place and at the final equilibrium stage intraparticle diffusion starts to slow down due to extremely low adsorbate concentration in the solution. The correlation coefficient values from Table 3 indicate that pore diffusion [22] plays a major role for the adsorption of RV5 onto PAC and PPy/SD.
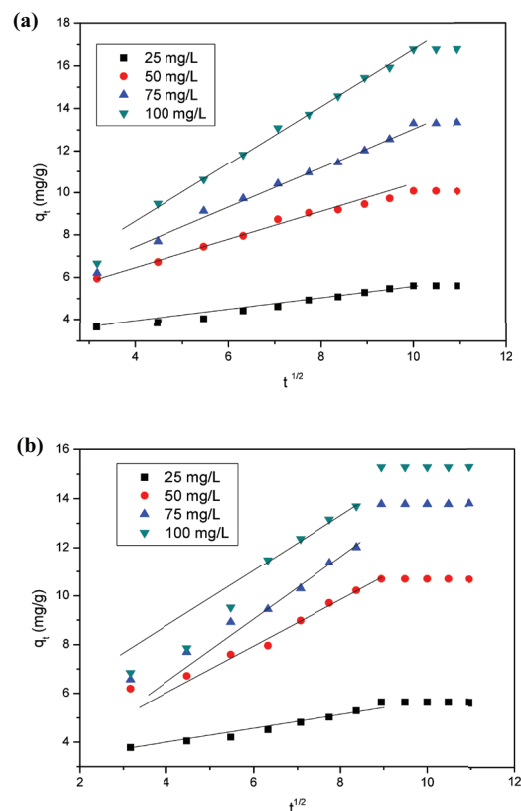
3.6. Adsorption isotherm studies

Adsorption isotherm indicates the relationship between the adsorbate in the liquid phase and the adsorbate on the surface of the adsorbent at equilibrium temperature [24]. The applicability of the isotherm equation is compared by judging the correlation coefficient (r^2). Langmuir [25], Freundlich [26], Dubinin–Radushkevich (D–R) [27] and Temkin isotherm models were used to describe the adsorption of RV5 onto PAC and PPy/SD.

3.6.1. Langmuir isotherm

Langmuir isotherm is used to determine the maximum capacity of the adsorbent.

Table 3
Results of isotherm plots for adsorption of RV5 onto PAC and PPy/SD

| Parameters	Temperature					
	PAC			PPy/SD		
	30	35	40	30	35	40
Langmuir isotherm model						
Q_0 (mg/g)	10.39	11.40	12.35	11.19	13.04	13.59
b_L (L/mg)	0.697	0.707	0.815	0.661	0.687	0.803
r^2	0.9945	0.9946	0.9958	0.9929	0.9985	0.9984
Freundlich isotherm model						
n	4.311	4.064	3.849	4.258	4.1304	3.481
K_f (mg$^{1-1/n}$ L$^{1/n}$/g)	2.7597	3.0863	3.7246	3.0033	3.6838	4.7847
r^2	0.8945	0.7938	0.9162	0.7945	0.8961	0.9259
Temkin isotherm model						
b_T (J/mg)	83.48	72.73	61.95	77.35	60.66	45.38
a_T (L/g)	1.9616	2.0929	2.1508	2.121	2.1312	2.3066
r^2	0.9887	0.9937	0.9907	0.9839	0.9921	0.9996
Dubinin–Radushkevich isotherm model						
Q_m (mg/g)	10.21	11.15	11.75	11.2116	12.2639	12.0915
E (kJ/mol)	21.92	22.36	24.25	22.36	24.25	30.43
r^2	0.9715	0.9875	0.9806	0.9855	0.9878	0.9918
$K \times 10^{-4}$ (mol^2/J^2)	10.4	10.0	8.5	10.1	8.5	5.4
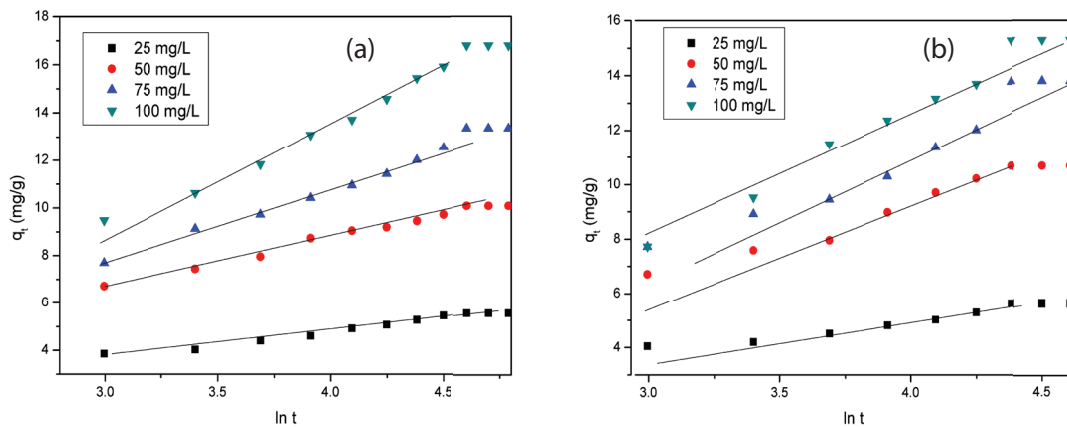
Fig. 9. Elovich plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

The Langmuir equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_{0b_L}} + \frac{C_e}{Q_0} \tag{6}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g)

and b_L (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The Langmuir isotherm is based on the assumption of structurally homogeneous adsorbent and monolayer coverage with no interaction between the sorbate molecules. Once a dye molecule occupies a site, no further adsorption can take place at that site [28].

The values of Q_0 and b_L for PAC and PPy/SD are calculated from the slopes and intercepts of the linear plots of C_e/q_e as shown in Fig. 10 and the results are summarized in Table 3.

The values of adsorption efficiency Q_0 and adsorption energy b_L increases with increasing temperature suggest that the maximum adsorption corresponds to a saturated monolayer of dye molecules on all the adsorbents. Further it confirms the endothermic nature of processes involved in the system.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L which could be defined by the following Eq. (7):

$$R_L = \frac{1}{(1 + bC_0)} \qquad (7)$$

where C_0 is the highest initial solute concentration. R_L value indicates the type of adsorption isotherm either to be unfavourable ($R_L > 1$), favourable ($R_L = 1$) or irreversible ($R_L = 0$). Langmuir model is more appropriate to explain the nature of adsorption of RV5 with very high correlation coefficient values.

3.6.2. Freundlich isotherm

The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. Linear form of Freundlich equation is expressed as follows:
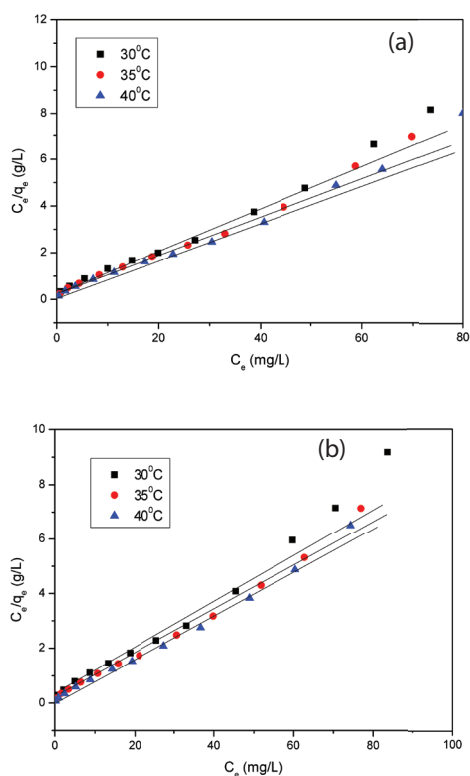
$$\log q_e = \log K_f + \log C_e \qquad (8)$$

where K_f is a constant related to the bonding energy. K_f can be defined as the distribution coefficient and represents the quantity of dye adsorbed onto the adsorbent for unit equilibrium concentration. Freundlich constant, n indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The data obtained by plotting $\log q_e$ vs. $\log C_e$ (Fig. 11) from linear Freundlich isotherm for the adsorption of RV5 onto PAC and PPy/SD is presented in Table 3. The correlation coefficient r^2 is found to be the least in comparison with Langmuir isotherm and is not in good agreement with the experimental data. Thus, it could be concluded that Langmuir isotherm model fits better to the equilibrium data obtained for the adsorption of RV5 onto PAC and PPy/SD [29].

3.6.3. Dubinin–Radushkevich (D–R) isotherm

The isotherm proposed by Dubinin and Radushkevich is useful in estimating the mean free energy and the energy of activation. From the energy of activation it can be predicted whether an adsorption is physisorption or chemisorption. The D–R model equation is as shown below:

$$q_e = Q_m e^{-K\varepsilon 2} \qquad (9)$$

where K is a constant related to the adsorption energy; Q_m is the theoretical saturation capacity; ε is the Polanyi potential, which is calculated from the following equation:

Fig. 10. Langmuir isotherm plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.
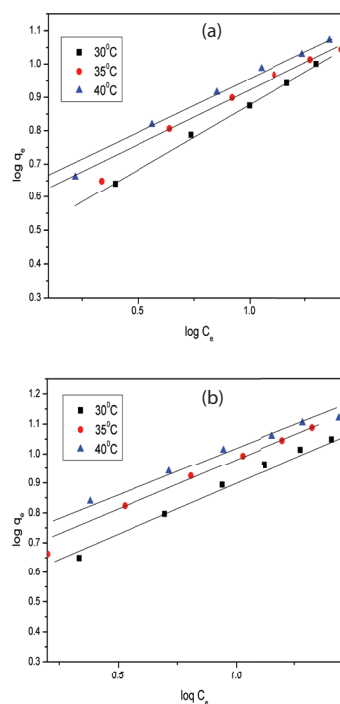

Fig. 11. Freundlich isotherm plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

$$\varepsilon = RT \, 1n\left(1 + \frac{1}{Ce}\right) \qquad (10)$$

The plot of $\ln q_e$ vs. ε^2 (Fig. 12) gives the slope K (mol²/J²) and the intercept yields the adsorption capacity Q_m (mg/g). The mean free energy of adsorption (E), defined as the free energy change, when 1 mol of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relationship:

$$E = \frac{1}{\sqrt{2k}} \qquad (11)$$

The calculated value of D–R parameters is given in Table 3. If the energy of activation is <8 kJ/mol, the adsorption is physisorption and if it is >16 kJ/mol, the adsorption is chemisorption in nature [30]. The values of E, calculated using Eq. (11) are 21.92–24.25 kJ/mol for PAC and 22.36–30.43 kJ/mol for PPy/SD. This indicates that the adsorption of RV5 onto PAC and PPy/SD is chemisorption in nature.

3.6.4. Temkin isotherm model

Temkin isotherm contains a factor that explicitly takes into account the adsorbent–adsorbate interactions. This isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and the adsorption is characterized by uniform distribution of binding energies up to some maximum binding energy.
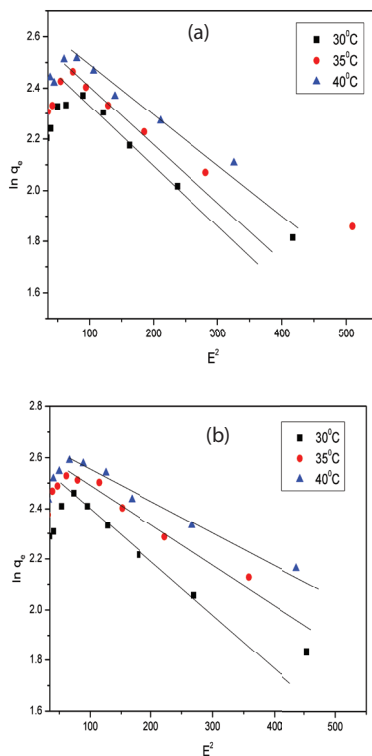
Temkin isotherm constants at different temperatures show that there is a linear fall in the standard enthalpy of adsorption with surface coverage [31]. The values obtained for Temkin sorption potential (a_T) and the Temkin constant (b_T) shows linearity while increasing the temperature. Fig. 13 shows the linear plots between $\ln C_e$ vs. q_e.

Furthermore, the model explains the adsorption isotherm of RV5 onto PAC and PPy/SD by its better fit into the experimental data at high temperatures and also with high correlation coefficient values.

4. Conclusion

The present study reveals that PAC and PPy/SD prepared from the seeds and woods of *Casuarina* were used effectively as adsorbents for the removal of RV5 from aqueous solution. The amount of dye adsorbed is found to vary with initial pH, temperature and contact time. Maximum adsorption occurs at pH 2–3 for RV5. Kinetic studies predict that the adsorption of RV5 onto PAC and PPy/SD follows pseudo-second-order kinetics. The adsorption isotherms like Langmuir, D–R and Temkin isotherm were found to fit well with experimental data whereas the Freundlich isotherm does not agree with the adsorption of RV5 onto PAC and PPy/SD. D–R isotherm predicts that the adsorption is chemisorption in nature. The equilibrium data fits very well into the Langmuir isotherm model which indicates monolayer adsorption. The adsorption capacity of PAC and PPy/SD increased with rise in temperature indicating endothermic nature of adsorption. Intraparticle diffusion model predicts that pore diffusion plays a major role for the adsorption of RV5 onto PAC and PPy/SD. On comparing the

Fig. 12. D–R isotherm plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.
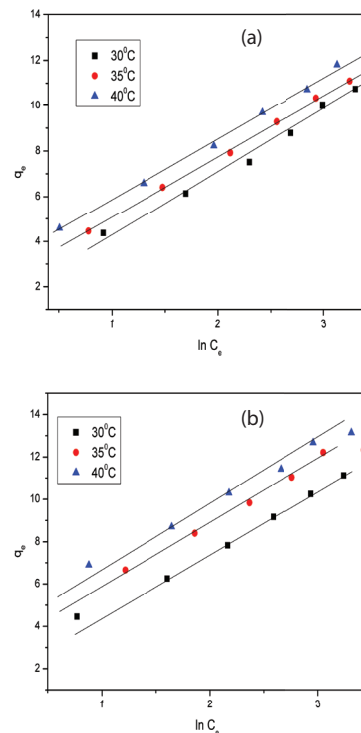

Fig. 13. Temkin isotherm plot for the adsorption of RV5 onto (a) PAC and (b) PPy/SD.

results, it is obvious that for the adsorption of Reactive Violet 5, PPy/SD is found to be an efficient adsorbent than PAC.

Symbols

C_0	—	Initial dye concentration, mg/L
C_t	—	Final dye concentration, mg/L
C_e	—	Equilibrium concentration of dye solution, mg/L
K_f	—	Freundlich adsorption constant, mg/g
q_t	—	Amount of dye adsorbed per gram of adsorbent at any time, mg/g
q_e	—	Amount of dye adsorbed per gram of adsorbent at equilibrium, mg/g
t	—	Time
r^2	—	Correlation coefficient
n	—	Freundlich adsorption constant
k_1	—	Equilibrium rate constant of pseudo-first-order adsorption, min^{-1}
k_2	—	Equilibrium rate constant of pseudo-second-order adsorption, g/mg min
h	—	Initial sorption rate
α	—	Initial adsorption rate
β	—	Desorption coefficient
K_{dif}	—	Diffusion constant
C	—	Thickness of the boundary layer
Q_0	—	Langmuir adsorption capacity
Q_m	—	Maximum amount adsorbed, mg/g
R_L	—	Dimensionless constant
b_L	—	Langmuir constant, L/mg
a_T	—	Temkin sorption potential, L/g
b_T	—	Temkin constant, J/mg
q_D	—	Theoretical saturation capacity, mg/g
ε	—	Polanyi potential
E	—	Mean free energy, kJ/mol
PAC	—	Phosphoric acid activated carbon
PPy/SD	—	Polypyrrole coated sawdust
RV5	—	Reactive Violet 5
XRD	—	X-ray diffraction

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