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Utilization of fluidized bed reactor for the production of adsorbents in removal of malachite green

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Abstract

Activated carbon was prepared from rubberwood (*Hevea brasiliensis*) sawdust by steam and chemical treatments. Steam activation was carried out in high temperature fluidized bed reactor (FBR) using steam as quenching medium. Chemical activation was carried out by using phosphoric acid. The adsorption capacity was determined by using iodine number and methylene blue number and surface area by ethylene glycol mono ethyl ether (EGME) method. Further the adsorption studies were carried out using malachite green dye. Langmuir, Freundlich and Temkin adsorption isotherms were analyzed and Langmuir isotherm shows satisfactory fit to experimental data. The adsorption capacity was found to decrease in the order; steam activated carbon > acid + steam activated carbon > commercial activated carbon > acid activated carbon. Temperature effects on adsorption were carried out and it was found that the adsorption reaction was endothermic. Thermodynamic analysis of the process confirms its endothermicity. The adsorption kinetics was found to follow pseudo-second-order kinetic model.

Keywords: Rubberwood sawdust; Activated carbon; Malachite green; Adsorption isotherm; Mass transfer; Kinetics

1. Introduction

Activated carbon is predominantly an amorphous solid with a large internal surface area and pore volume. It consists of a basic structural unit built up of condensed aromatic rings. Its high adsorptive capacity makes it favorable for the removal of hazardous material from effluents, toxic and odor producing gas removal, water purification, colour removal, etc. The pores in the carbon contribute the increase in its surface area and textural properties before and after activation. Further, the surface chemistry of the carbon is altered during activation process. The extent of the changes in the surface groups and pore development differs during different activation conditions. These surface functional groups and textural properties play an important role in the removal of the toxic substance from the effluents even if they are present in low concentrations. Earlier studies show that the use of some low cost carbonaceous and non-carbonaceous materials such as coir pith [1], coal [2] blast furnace slag [3], banana and orange peels [4], pistachio shells [5] were used as adsorbents. Adsorption studies using malachite green (MG) as the adsorbate was carried on Prosopis Cineraria [6] and rice husk [7]. In the present work rubberwood sawdust is taken as the carbonaceous substrate for preparation of activated carbon. The rubber tree after a period of time stops yielding rubber latex and hence felled. This wood is hence chosen due to its low commercial value as the precursor for the preparation of activated carbon. Fluidized bed reactor (FBR) is notable for its excellent gas solid contact, high mass transfer rates, no hot spots even with highly exothermic reactions due to good gas to particle and bed to wall heat transfer and ease of solids handling [8]. Under fluidized conditions the temperature is uniform throughout the bed, the modification in the surface functionalities of the carbon is more or less uniform during activation. Intra particle heat and mass transfer is enhanced due to thorough fluidization and hence improves the pore and surface area development, which directly relates with its adsorption capacity.

About 20% of the dye stuff produced in the world is discharged into streams without treating. This poses a very great challenge to the environment, particularly to the water bodies into which it has been discharged. MG is one such dye which is used as a food coloring agent, as a medical disinfectant and in dyeing in silks, wool, paper, jute and leather industries [9]. MG has been extensively used as fungicide and also used to control protozoan growth in aquacultures and fish farming industries

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[10]. However, studies have shown this dye to be highly toxic to fresh water fish in both acute and chronic exposure. MG is a carcinogen and mutagen, causing chromosomal fractures in rainbow trout [11]. MG also acts as a respiratory enzyme poison [12] and causes respiratory distress in rainbow trout. The dye causes detrimental effects in liver, gills, kidney, intestine, gonads and pituitary gonodotropic cells [13]. It is also found to cause tumor in lungs, breast and ovary in rats [12]. The light penetration capacity into the water bodies is considerably reduced even when MG is present in very low concentrations because of its very high coloring capacity. It destroys the biotic habitat and causes a great threat to fauna and flora of the water bodies. This leads to the need to treat the polluted water to decrease the concentration of MG present in it. Adsorption is the most commonly used form of effluent treatment using various adsorbents of which activated carbon is one, having the advantage of large surface areas over other adsorbents.

2. Experimental

2.1. Preparation of activated carbon

Activated carbon was prepared using steam activation in a FBR as well as chemical activation in a packed bed reactor as well as in a FBR. The diagrammatic representation of the FBR is given in Fig. 1. The rubberwood sawdust was screened and a particle size of 1.5–2 mm was chosen for all the activation process. A known quantity of sawdust was subjected to thermal activation process under the flow of steam in a high temperature FBR. Here, the steam acts both as the fluidizing and quenching medium. The precursor was maintained at 800 °C (bed temperature) and at atmospheric pressure for a fluidization time of 1 h. During this period most of the volatile matter would be driven off leaving behind the carbon with a more complex network of pores. The steam activated carbon (SAC) is then cooled to room temperature.

In the case of chemical activation, the precursor was soaked with 50% (wt.%) phosphoric acid for 24 h. A part of this impregnated sawdust was then steam activated in a FBR all other conditions being the same as that of steam activation yielding steam phosphoric acid activated carbon (SPAC). Another part was subjected to thermal activation in a packed bed reactor at 400 °C for 1 h yielding phosphoric acid activated carbon (PAC). The phosphoric acid causes phosphorylation of the cellulose [14].

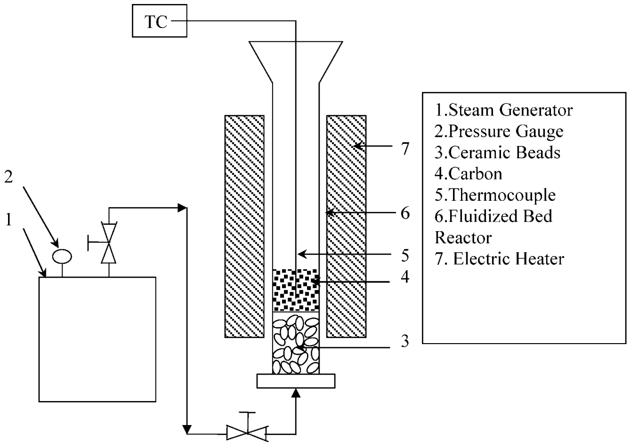

Fig. 1. Diagrammatic representation of high temperature fluidized bed reactor used in preparation of carbonaceous adsorbents.

All the above prepared activated carbons (SAC, SPAC and PAC) were washed well with ion free double distilled water at boiling conditions till the pH reached 7.0. The resulting carbons were dried in an oven at a temperature of 110 °C overnight to get rid of the moisture content. The activated carbon were ground and stored (<300 mesh) for further experimental studies.

2.2. Adsorption experiments

In each batch adsorption experiment, three key parameters were changed namely, carbon dosage, concentration of solution and temperature. For all experiments 100 ml solution of a known concentration was taken and 50 mg of the adsorbent was added. The effect of pH on the adsorption capacity was not carried out since addition of acid or alkali caused the colour of the adsorbate to change significantly. The mixture was stirred well in the rotary shaker. The samples were collected at predetermined time intervals. The residual concentration of the adsorbate was measured using a UV-spectrophotometer (Hitachi-U 2000). Experiments were also carried out using commercial activated carbon (CAC) supplied by e-Merck India Ltd. to compare the adsorption phenomena with the carbons prepared from rubberwood.

2.3. Dye solution

Malachite green dye (C.I. = 42,000; chemical formula = $C_{23}H_{26}ON_2$; formula weight = 346; melting point = 112–114 °C; and λ_{max} = 615–620 nm (reported) and 616 nm (experimentally obtained)) was supplied by Ranbaxy Ltd. (Analytical Grade), India. A stock solution of 1000 ppm (1 gm l^{-1}) was used for the experimental work and desired concentrations were obtained by successive dilutions.

3. Results and discussion

3.1. Characterization of activated carbon

The results of the proximate analysis of the rubberwood sawdust are given in Table 1. The characterization of the commercial and prepared activated carbon in terms of their iodine number [ASTM 4607-86], methylene blue number and methyl violet number [BIS 877-1977] are shown in Table 2. The surface

Table 1
Proximate analysis of rubberwood sawdust

Serial number	Characteristics	Values (%)
1	Carbon	62.91
2	Ash	4.96
3	Moisture	7.95
4	Volatile matter	24.15

Table 2
Characterization of activated carbon

Activated carbon	Iodine number (mg g^{-1})	Methylene blue number (mg g^{-1})	Methyl violet number (mg g^{-1})	Surface area (m^2 g^{-1})
SAC	1040	275	143	1095
SPAC	985	255	150	1045
CAC	834	210	150	1195
PAC	794	175	110	985

area was calculated using the EGME method [15]. The iodine number, methylene blue number and the methyl violet number presents the development of micro and meso pores since the molecular diameters of these molecules were 10, 15 and 21 Å, respectively [16].

Table 2 shows that the SAC was superior to other carbons. In case of SAC, as the temperature rises, initially the oxygen functionalities in the surface of the carbon increases due to the breakage of lignin materials [17]. Later at elevated temperatures, the hydrogen and the oxygen functional groups are removed gradually by the reaction with the steam imparting negative charge on the surface of the carbon. Hence the carbon surface becomes Lewis basic sites attracting the positive charge [18]. Further the reduction of the oxygen functionalities makes the carbon more hydrophobic in nature which repels the water molecules [7]. Here there will be no secondary contraction of the pore at elevated temperatures due to cleavage between the aromatic rings hence the pore size will not contract between the temperatures of 450 and 750 °C. Due to the good pore development, the advantage in the surface charge, and hydrophobic nature, the adsorption on the SAC is maximum.

In case of the SPAC, the dilation of the pores takes place in the soaking period since the amorphous lignin and hemicellulose reacts with the activating agent forming ketones and esters and the tar formation is comparatively retarded. At the temperature of 50 °C cleavage of aryl ether on the ligno-cellulosic material takes place which leads to the formation of ketones. At the temperature of 100–400 °C, at first cross linking and volumetric contraction takes place followed by cross linking and pore dilation. Cross linking occurs by the condensation and cyclation reaction [19]. At the temperature above 400 °C, the phosphate esters, which are between the cellulosic units, are removed favoring the formation of the aromatic ring. The oxygen functionality density gradually reduces. Volumetric expansion takes place due to the leaving ester molecules. At the elevated temperatures, secondary pore size contraction takes place due to the formation of the aromatic groups due to continuous cleavage, which leads to bulking of cell wall [19]. Even though a thorough wash is made after activation some of the phosphate molecules are retained in the wood structure [19], hence, the adsorption capacity of the SPAC is comparatively lower to that of SAC.

In case of PAC, the lower concentration of the solution fails to remove the binding lignin and hemicellulosic materials. Further, the temperature in the packed bed is about 400 °C in which the tar formation blocks the pores. The poorer pore development could also be due non-effective heat transfer. In fixed beds, there is a temperature gradient from the periphery to the core because the interstitial spaces between particles act as thermal insulation. The phosphate esters are not completely removed due to the lower temperature. The cleavage of the oxygen groups are inhibited due to the presence of these phosphate esters and the cyclation reaction does not occur. Hence, the oxygen functionalities remain constant and in turn make the carbon more hydrophilic in nature. Since the MG is also a cationic dye, electrostatic repulsion takes place. Water cluster blocks the pore since the PAC is hydrophilic. Hence the adsorption on the PAC is lower compared to that SAC, SPAC and CAC.

3.2. *Effect of contact time and initial dye concentration*

The equilibration time for maximum adsorption was determined by studying the adsorption of the dye of a known concentration at different contact time. Fig. 2 is the plot of percentage removal with time for different carbonaceous adsorbents. The increase in adsorption did not vary much beyond contact time of 1 h for all the samples studied. However, due to the slight increase, the equilibration was fixed to be 3 h for all further experiments. The rate of adsorption on SAC, SPAC, PAC, and CAC were studied by changing the initial dye concentration and keeping all other parameters constant (carbon dosage 0.05 g, temperature (30 ± 2 °C) and natural pH). The initial dye concentration was 50, 100, 150, 200 mg l^{-1}. For SAC the initial dye concentration was taken as 300, 400, 500 mg l^{-1} for the isotherm calculations since there is complete removal of colour within 30 min at lower concentrations. The uptake of the dye was rapid initially and slowed down as time proceeded. On comparing the adsorption capacity of different carbons, 100% removal was achieved in the case of SAC at lower carbon dosages within

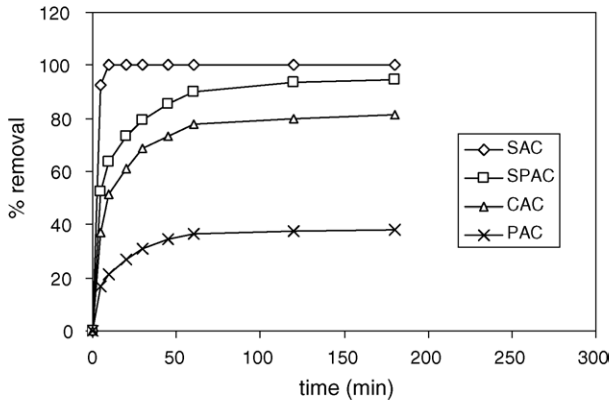

Fig. 2. Effect of initial concentration and contact time of MG on various carbonaceous adsorbents at 30 °C.

15 min and then the adsorption became almost constant. It was observed that in all cases, the increase in initial concentration of the dye decreased the percentage removal. At higher concentrations, the percentage removal decreased however the adsorption capacity increased with increase in concentration. Though the carbonaceous substrate was same, the treatment and the surface modification contribute to the difference in the adsorption capacity. The adsorption capacity of SAC, SPAC, CAC and PAC were found to be 834.93, 355.72, 302.62 and 144.57 mg g^{-1}, respectively at 50 °C. Hence the adsorption of MG was in order of SAC > SPAC > CAC > PAC [cf. Section 3.1].

3.3. *Effect of carbon dosage*

The variation of equilibrium time and adsorption capacity was studied as a function of change in carbon loading. The adsorption characteristics of different carbons were studied. The carbon dosage was varied as 0.05, 0.1, 0.15 and 0.2 g by keeping all other parameters constant (concentration 300 mg l^{-1}, temperature (30 ± 2 °C) and natural pH). A plot of percentage removal with the carbon dosage for all carbons at equilibration time of 3 h is given in Fig. 3. It was observed that 100% removal was achieved at a carbon dosage of 100 mg for SAC and for other carbon complete removal was achieved at higher carbon dosages. The adsorption capacity of PAC was far lower than the CAC, SAC and SPAC because of the hydrophilic nature of PAC [cf. Section 3.1].

3.4. *Effect of temperature*

The uptake of MG increases with the increase in the temperature, which clearly indicates that the adsorption process is endothermic. There is an increase of 10–15% in adsorption process for different adsorbents. The increase in the percentage removal with the increase in temperature for SAC is given in Fig. 4. Increase in temperatures causing the frequency of the intermolecular collisions to increase there by increasing the rate of diffusion into the pores. This causes the amount of material to be adsorbed on the surface to increase. Increase in temperature also decreases the activation energy barrier there by increasing the rate of adsorption [20].

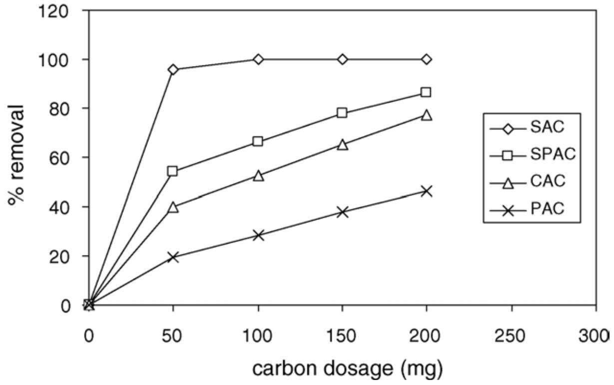

Fig. 3. Effect of carbon dosage of MG on various carbonaceous adsorbents at 30 °C, initial concentration 300 mg l^{-1}.

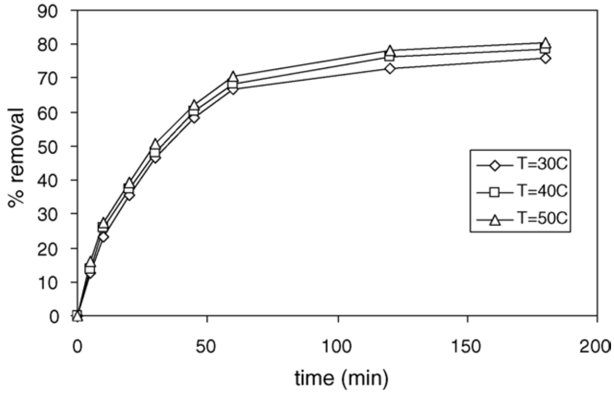

Fig. 4. Effect of temperature of MG on various carbonaceous adsorbents at initial concentration of 300 mg l^{-1}.

3.5. *Adsorption isotherms*

The experimental adsorption data were fitted to the Langmuir, Freundlich and Temkin isotherms. The Langmuir adsorption isotherm is based on the assumption that all adsorption sites are equivalent and adsorption in an active site is independent of whether the adjacent sites is occupied or not. The data of the uptake of MG has been processed in accordance with the Langmuir isotherm equation [21]:

$$\frac{C_e}{q_e} = \frac{1}{bX_m} + \frac{C_e}{X_m} \tag{1}$$

where X_m is the monolayer adsorption capacity in mg g^{-1}, C_e the equilibrium concentration mg l^{-1}, q_e the amount of MG adsorbed per unit mass of adsorbent in mg g^{-1}, b is the Langmuir equilibrium constant in l mg^{-1}.

Freundlich isotherm which is based on multi layer adsorption phenomena, is given in the linearized form as [22]:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \tag{2}$$

where K is the adsorption capacity in mg g^{-1} and N (=1/n) is the adsorption intensity in g l^{-1}.

Temkin isotherm, which relates the heat of adsorption and surface coverage of the dye molecules on the adsorbent is given in the linearized form as [23]:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \tag{3}$$

where R is the gas constant and B (=RT/b) is related to heat of adsorption.

The Langmuir, Freundlich and Temkin isotherm constants at different temperatures are listed in Table 3. It is found that the Langmuir isotherm gives the best representation of the data with the highest correlation coefficient. Of all the adsorbents, SAC had the maximum adsorption capacity and PAC had the least because the surface area and surface charge favored SAC. Hence a large surface area is covered by dye molecules as compared to other carbons.

Table 3
Langmuir, Freundlich and Temkin isotherms for adsorption of dye on carbonaceous adsorbents at different temperatures

Activated carbon	T (°C)	Langmuir isotherm			Freundlich isotherm			Temkin isotherm	
		X_m (mg g^{-1})	b (l mg^{-1})	R^2	K (mg g^{-1})	N	R^2	B	R^2
SAC	30	799.88	0.116	0.9957	404.19	7.80	0.8186	84.24	0.9356
	40	820.36	0.171	0.9955	458.00	8.97	0.8244	78.42	0.9485
	50	834.93	0.280	0.9953	561.28	13.7	0.7964	50.15	0.9025
SPAC	30	305.22	0.278	0.9966	138.57	5.02	0.9782	48.88	0.998
	40	334.79	0.286	0.9975	148.38	5.25	0.982	47.11	0.956
	50	355.72	0.426	0.9935	175.60	5.43	0.9936	44.88	0.948
CAC	30	254.89	0.730	0.9995	82.36	4.49	0.9626	44.32	0.933
	40	281.03	0.751	0.9992	84.35	4.56	0.8215	43.44	0.925
	50	302.62	0.769	0.9936	98.10	4.31	0.745	42.56	0.942
PAC	30	124.47	0.0295	0.9996	22.46	0.922	0.9222	28.25	0.933
	40	133.28	0.0318	0.9985	25.26	3.33	0.9325	27.98	0.925
	50	144.52	0.0335	0.9997	32.16	3.74	0.9736	26.72	0.942

3.6. *Kinetic studies*

The mechanism and the efficiency of the adsorption process can be inferred from their kinetic studies. Kinetics studies were carried out at different temperatures (30, 40 and 50 °C) and the adsorption process was found to increase with increasing temperature. Data are fitted for Lagergren's pseudo-first-order equation and second-order equation of which second-order equation fits better. Lagergren's pseudo-first-order equation [24] is given by

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{4}$$

where q_e is the amount of MG adsorbed per unit mass of adsorbent at equilibrium in mg g^{-1}, q_t the amount of MG adsorbed per unit mass of adsorbent at time in mg g^{-1}, and K_1 is the first-order rate constant in min^{-1}.

The linearised form of the pseudo-second-order equation [25] is:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{t}{q_e}, \quad V_0 = K_2 q_e^2 \tag{5}$$

where K_2 is the second-order rate constant in g mg^{-1} min^{-1}. The experimental and calculated value of the adsorption capacity are compared and given in Table 4. Based on the regression coefficient and calculated values of adsorption capacity, the adsorption process obeys the pseudo-second-order kinetic model.

3.7. *Thermodynamic correlations*

The changes in enthalpy (ΔH°), entropy (ΔS°) and the free energy (ΔG°) were evaluated using the equations given below [3]:

$$\Delta G^\circ = -RT \ln b \tag{6}$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

$$\Delta S^\circ = \left(\frac{\Delta G^\circ - \Delta H^\circ}{T}\right) \tag{8}$$

where b_1, b_2 is the Langmuir constant at temperatures of 40, 50 °C.

Table 4
Kinetic parameters for adsorption of dye on carbonaceous adsorbents at different temperatures

Activated carbon	T (°C)	First-order, K_1 (min^{-1})	q_e (calculated) (mg g^{-1})	R^2	q_e (experimental) (mg g^{-1})	Second-order, K_2 ($\times10^{-4}$ g mg^{-1} min^{-1})	q_e (calculated) (mg g^{-1})	R^2
SAC	30	0.0232	226.46	0.9183	573.72	1.14	591.71	0.9992
	40	0.0242	256.97	0.967	585.2	1.15	690.9996	0.9996
	50	0.0290	240.7	0.931	596.7	1.17	615.76	0.9995
SPAC	30	0.0283	128.66	0.9450	253.32	2.78	266.09	0.9992
	40	0.0284	136.40	0.9710	265.6	2.94	278.24	0.9998
	50	0.0293	138.58	0.9754	274.48	3.11	287.35	0.9990
CAC	30	0.024	97.09	0.9092	194.95	3.70	204.54	0.9997
	40	0.0279	101.48	0.9535	203.26	3.73	215.44	0.9995
	50	0.0295	104.94	0.9725	220.96	3.81	229.51	0.9991
PAC	30	0.0254	59.80	0.9445	76.36	7.5	79.85	0.9998
	40	0.0266	60.29	0.9345	107.7	7.8	114.24	0.9997
	50	0.0325	62.86	0.9648	110.9	8.2	116.82	0.9998

Table 5
Thermodynamic parameters for adsorption of dye on carbonaceous adsorbents at different temperatures

Activated carbon	Temperature (°C)	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
SAC	30	26.721		
	40	28.601	30.228	0.078
	50	30.835	41.339	0.076
SPAC	30	24.09		
	40	25.88	30.157	0.190
	50	28.23	47.616	0.223
CAC	30	25.670		
	40	26.45	12.906	0.126
	50	27.22	24.163	0.168
PAC	30	25.256		
	40	24.216	4.527	0.098
	50	23.568	5.825	0.091

Table 6
Mass transfer coefficient for adsorption of dye on carbonaceous adsorbents at different temperatures

Activated carbon	Temperature (°C)	Mass transfer coefficient (m h^{-1})
SAC	30	20.52
	40	31.08
	50	46.32
SPAC	30	1.32
	40	2.10
	50	3.66
CAC	30	2.40
	40	10.74
	50	19.02
PAC	30	0.87
	40	1.08
	50	1.75

The results are reported in Table 5. The endothermic nature of the process is well explained by the positive value of the enthalpy change. The negative value of the free energy suggests that the adsorption process is spontaneous and the affinity of the adsorbent for the dye is indicated by the positive value of entropy [3].

3.8. Mass transfer coefficient

The mechanism of adsorption form solution consist of three stages: (a) diffusion across the boundary layer surrounding the particle (process controlled by external mass transfer coefficient), (b) diffusion within the particle assuming solid diffusion mechanism and (c) adsorption at a site [23]. Here mass transfer coefficient has been determined for various carbons. The adsorption rate is mainly influenced by initial concentration and temperature. The major sorption takes place within 30 min which indicates the possibility of formation of monolayer on outer side of inner surface of the pore. The mass transfer coefficient was determined using the equation [26]:

$$\ln\left(\frac{C_0}{C_t}-\frac{1}{1+\rho_\mathrm{p}K}\right)=-\left(\left(\frac{1+\rho_\mathrm{p}K}{\rho_\mathrm{p}K}\right)K_\mathrm{L}a\right)t+\ln\left(\frac{1+\rho_\mathrm{p}K}{\rho_\mathrm{p}K}\right) \tag{9}$$

where $K_\mathrm{L}a$ is the mass transfer coefficient in m h^{-1}, ρ_p the density in kg m^{-3} and K is the Langmuir constant in l g^{-1}.

The value of $K_\mathrm{L}a$ is determined by plotting $\ln(C_\mathrm{t}/C_0 - 1/1+\rho_\mathrm{p}K)$ versus time. Table 5 gives the mass transfer coefficient for various carbons at different temperatures. The mass transfer coefficient increases with increase in temperature which confirms that the process is endothermic. Further the mass transfer coefficient is higher in SAC and gradually decreases with other carbons suggest the favorability of adsorption. In case of SPAC the adsorption should overcome the surface charge repulsion due to the retained phosphate molecules in the wood structure. The mass transfer coefficient is least in PAC due to poor pore development as well as surface charge repulsion. Also, after activation the surface area of the particle increases indicating a decrease in the grain size. As the area increases, the mass transfer coefficient also increases since the mass transfer is a process of consequent attachment and the detachment of the molecules. Here as the area increases, the molecules find more activation sites to adsorb and hence the overall value of the coefficient increases. This is evident from the values in Table 6. Mass transfer coefficient increases with increase in area and further the mass transfer coefficient depends upon the active sites available for the adsorption.

4. Conclusion

Rubberwood sawdust was found to be a viable raw material for the preparation of activated carbon. The activated carbon prepared using stem in FBR was found to be superior to the other carbons. In all the cases the kinetics was found to follow the pseudo-second-order reaction model. The kinetic constant as well as the mass transfer coefficient was found to increase with temperature. Thermodynamic analysis of the adsorption suggests the process to be endothermic as well as spontaneous.

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