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Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36

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Abstract

Activated carbons, prepared from low-cost mahogany sawdust and rice husk have been utilized as the adsorbents for the removal of acid dyes from aqueous solution. An acid dye, Acid Yellow 36 has been used as the adsorbate. Results show that a pH value of 3 is favourable for the adsorption of acid dye. The isothermal data could be well described by the Langmuir and Freundlich equations. Kinetic parameters of adsorption such as the Langergren pseudo-first-order constant and the intraparticle diffusion rate constant were determined. For the present adsorption process, intraparticle diffusion of dye molecule within the particle has been identified to be rate limiting. The adsorption capacities of sawdust carbon (SDC) and rice husk carbon (RHC) were found to be 183.8 mg and 86.9 mg per g of the adsorbent respectively. The results indicate that SDC and RHC could be employed as low-cost alternatives to commercial activated carbon in wastewater treatment for the removal of acid dyes.

Keywords: Adsorption; Activated carbon; Isotherms; Acid Yellow 36; Kinetics

1. Introduction

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics etc. to colour their products; these dyes are invariably left in the industrial wastes. Dyes even in low concentrations effect the aquatic life and food web. Since many organic dyes are harmful to human beings, the removal of colour from process or waste effluents becomes environmentally important. Due to the large degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [1,2]. This led to the study of other effective methods.

The adsorption process is one of the efficient methods to remove dyes from effluent [3]. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions. Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbons

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are very expensive [4–7]. This has led to search for cheaper substituents. Nowadays, a number of low-cost, commercially available adsorbents have been tried for dye removal. These include coal fly-ash, wood, silicagel, agricultural wastes and cotton wastes [5–9]. Adsorption studies for dye removal have been carried out using activated carbon made from non-conventional sources as adsorbents [10–12]. However, as the adsorption capacities of the above adsorbents are not large, new adsorbents are still under development. Activated carbon obtained from rubber seed coat, palm seed coat and myrobalan waste were investigated for the removal of wide variety of impurities from water and wastewater. In general, these carbons will be as efficient in the adsorption of both organics and inorganics as the commercial activated carbons [13].

The purpose of this work was to investigate the adsorption capacity of activated carbons, prepared from low-cost mahogany sawdust and rice husk on adsorption of acid dyes from aqueous solution. Acid Yellow 36 was selected for the adsorption experiment due to its presence in wastewaters of several industrial such as textile, tannery, paper, soap, cosmetics, polishes, wax etc. It is a mono-azo dye. Its toxic and carcinogenic nature has been reported. Acute toxicity of Acid Yellow 36 to heteropneustes fossilis has also been reported. Besides mortality, other adverse effects of Acid Yellow 36 to the test fish included loss of body weight, changes in body colours, restlessness, jerky and random movements [14,15]. We investigated the equilibrium and kinetics of adsorption. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The batch contact time method was used to measure the adsorption rate. Kinetic parameters were then evaluated. The results will be useful for further application of SDC and RHC in colour removal from wastewater.

2. Experimental

2.1. Materials

The sawdust and rice husk were collected from local saw-mill and rice-mill respectively. They were separately washed with hot distilled water to remove dust like impurities and dried in sun. The resulting materials were separately carbonised by heating in air. Activation was applied by means of steam. Details of operating condition are given in Table 1. All samples were grounded and dried at (100 ± 5) °C for overnight before the determination of their chemical properties. Before utilisation, the carbons were thoroughly washed with distilled water for several times by decantation and subsequently filtered and then dried in hot air oven at (100 ± 5) °C.

Acid Yellow 36 (C.I. 13065) was obtained from Fluka, USA, in 70% purity. All other chemicals were of AR grade and purchased from E. Merck (India). Double distilled water was used for solution preparation. The solution pH was adjusted by adding a small amount of 0.1 M HCl or NaOH.

A Shimadzu (Japan) UV-VIS spectrophotometer (160 A) was employed for absorbance measurements using silica cells of path length 1 cm.

2.2. Methods

Adsorption experiments were carried out by shaking adsorbents with 50 ml dye solution of

Table 1
Operating conditions for the preparation of activated carbon

Material	Carbonisation condition		Steam-activation condition		
	Temp. (°C)	Duration (h)	Temp. (°C)	Duration (h)	Steam pressure (kg/cm^2)
Sawdust	500	1	800	1	1.5
Rice husk	400	1	600	1	1.5

Table 2
Physicochemical characteristics of SDC and RHC

Characteristics	Values	
	SDC	RHC
Bulk density (g/ml)	0.38	0.73
Solid density (g/ml)	3.6	1.5
Moisture content (%)	0.52	6.62
Ash content (%)	6.5	45.97
Particle size (mesh)	200–60	200–16
Surface area (m^2/g)	516.3	272.5
Surface acidity (meq/gm)	0.02	0.1
Surface basicity (meq/gm)	2.34	0.45

required concentration and pH at 30 °C in a thermostated shaker operated at 150 rpm. The samples were withdrawn from the shaker and the dye solution was separated from the adsorbent by centrifugation. Dye concentration in the supernatant solution was estimated by measuring absorbance at maximum wavelength ($\lambda_{\max} = 414$ nm) and computing concentration from the calibration curve. Kinetics of adsorption was determined by analysing adsorptive uptake of the dye colour from aqueous solution at different time intervals. Isothermal studies were conducted by adding various doses of adsorbent and shaking the reaction mixture for the equilibrium time. Influence of the pH was studied by adjusting the reaction mixture to different initial pH value and analysing the residual colour for equilibrium contact time. The amount of dye adsorbed onto the carbons, q_e (mg/g), was calculated by mass balance relationship [Eq. (1)].

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye, respectively

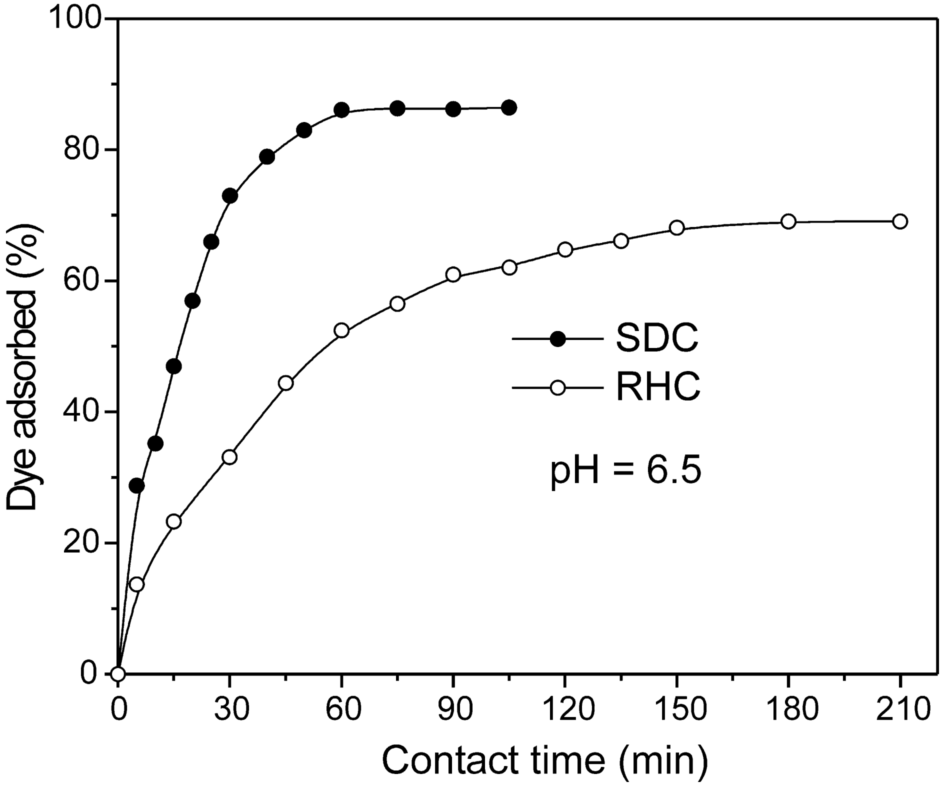

Fig. 1. Effect of contact time for the adsorption of Acid Yellow 36 on RHC and SDC.

(mg/l), *V* the volume of the solution (l), and *W* the weight of the carbon used (g).

3. Results and discussion

The physicochemical characteristics of SDC and RHC are summarised in Table 2. Both surface acidity and surface basicity of SDC and RHC have been determined using titration methods [16].

3.1. Adsorption kinetic studies

The kinetic of adsorption was studied for its possible importance in the treatment of dye containing industrial effluents. The influence of contact time on removal of AY36 by SDC and RHC is shown in Fig. 1. It is evident that both the carbons are efficient to adsorb AY36 with different efficiencies. Sawdust carbon possesses higher adsorption capacity than rice husk carbon at equilibrium. The different adsorption capacity of the said adsorbents with respect to equilibrium time is in conformity with the order of surface basicity (SDC>>RHC) and surface area (SDC>RHC). The dye adsorption process attains equilibrium gradually for both the carbons. To attain equilibrium, it takes 60 min and 180 min for SDC and RHC respectively. This may be due to the fact that the activated carbon is composed of macro and micro pores. In the process of dye colour adsorption, initially dye molecule has to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively long contact time. The adsorption of dye here is mainly due to physisorption even though chemisorption may not be written off. Mohan et al. [17] reported that the of adsorption

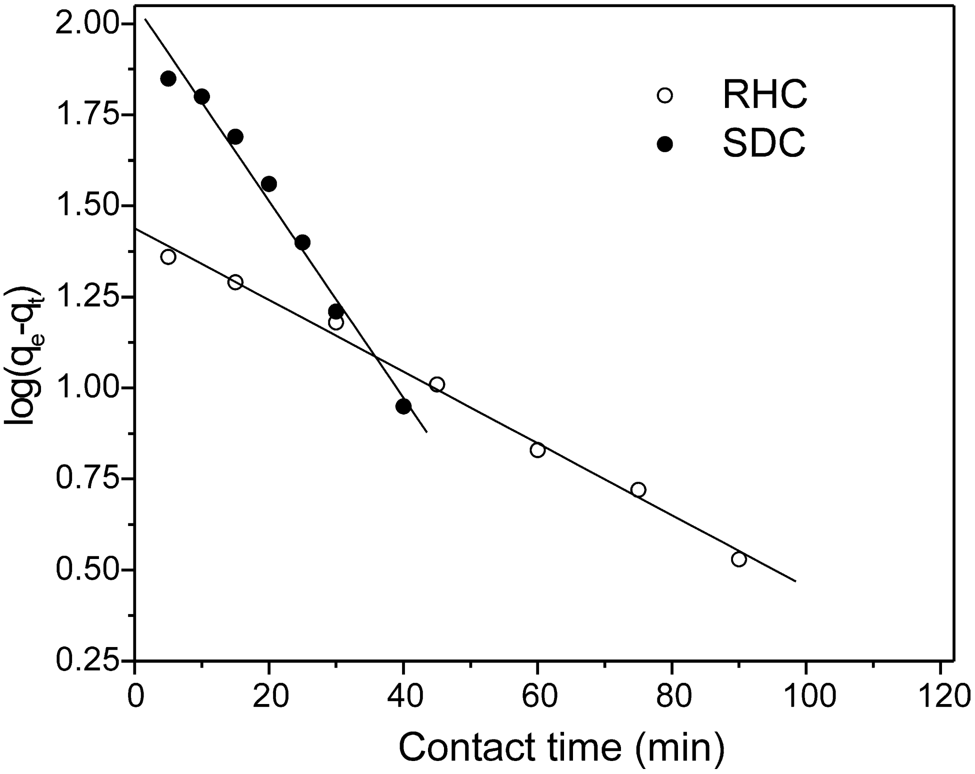

Fig. 2. Langergren plots corresponding to the adsorption of Acid Yellow 36 on RHC and SDC.

of Direct Brown 1:1 from aqueous solution onto commercial activated carbon, Filtrasorb-400 was due to physisorption and the contact time required to attain equilibrium was 400 min. The time profile of dye uptake is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent.

3.2. Adsorption kinetic rate constant

Kinetic data were treated with the following Langergren's pseudo-first-order rate equation [4,18,19]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad}}{2.303}\right)t \qquad (2)$$

where q_e and q_t refer to the amount of adsorption at the equilibrium and at any time t. k_{ad} is the adsorption rate constant. The plot of log $(q_e - q_t)$ versus t shows a straight line correlation coefficient >99), indicating the applicability of pseudo-first-order kinetics (Fig. 2). The pseudo-first-order rate constants for SDC and RHC are calculated to be 0.06 min^{-1} and 0.02 min^{-1} respectively at 30 °C.

The data of solid-phase dye concentrations against time at an initial dye concentration of 1000 mg/l were further processed for testing the role of diffusion (as the rate-controlling step) in the adsorption process. Adsorption process incorporates the transport of adsorbate from bulk solution to the interior surface of the pores [20]. There is a possibility that the transport of dye from the solution into the pores of the adsorbent is rate controlling in batch experiments with rapid stirring. The rate parameters for intraparticle diffusion (k_p) for different dyes are determined using the following equation [21,22].

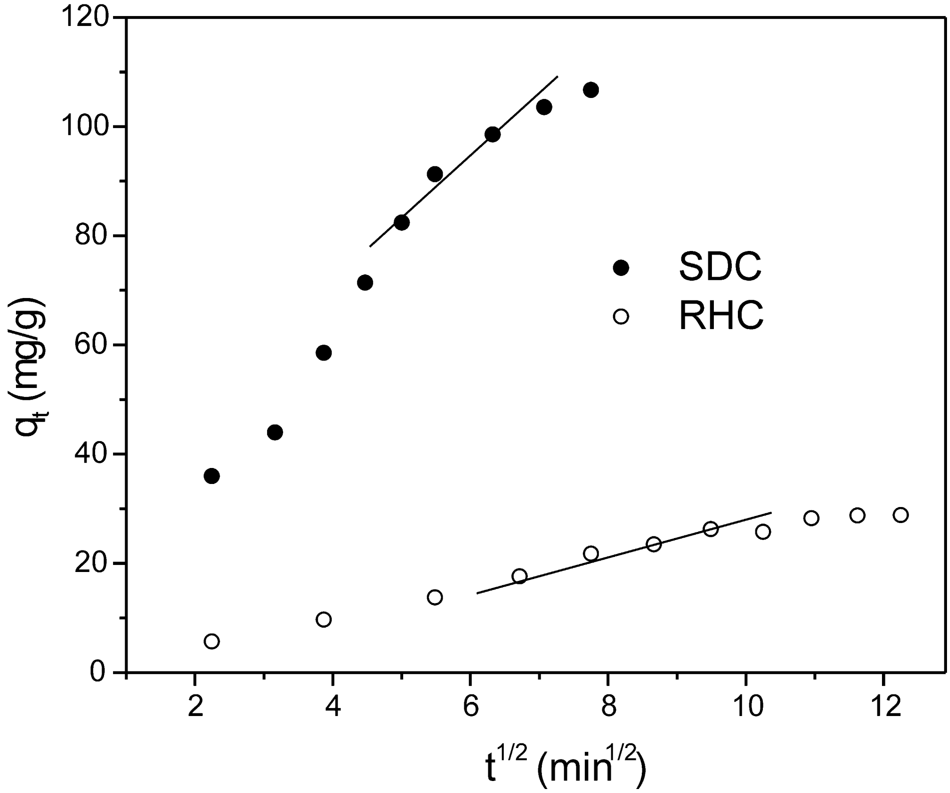

Fig. 3. Intraparticle diffusion plot for the adsorption of Acid Yellow 36 on RHC and SDC.

$$q_r = k_p t^{1/2} \qquad (3)$$

where k_p is the intraparticle diffusion rate constant.

Due to mass transfer effects, the shape of q_t versus $t^{1/2}$ plot is curved at a small time limit [20]. All the plots have the same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intraparticle diffusion. These phenomena have been reported for the adsorption of dye on activated carbon [17]. At a certain time limit (about 25 min), the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process (Fig. 3). The values of k_p are obtained from the slope of the straight lines, and are 2.43 mg/g min$^{1/2}$ (for RHC) and 9.81 mg/g min$^{1/2}$ (for SDC).

3.3. Adsorption isotherm studies

Once the equilibrium time was known, adsorption isotherm studies for SDC and RHC were performed. The respective adsorption isotherms for AY36 at 30 °C are shown in Fig. 4. The isotherms have been classified according to Giles' classification [23]. Giles has classified adsorption isotherms into four main groups: L, S, H and C. According to the above classification both carbons show L-type isotherm (Fig. 4). The data show that the affinity of AY36 to SDC is higher. This is due to having higher effective surface area and basicity of SDC than that of RHC.

3.4. Quantification of the adsorption isotherm data

The isothermal equilibrium data were processed employing Langmuir and Freundlich isotherm

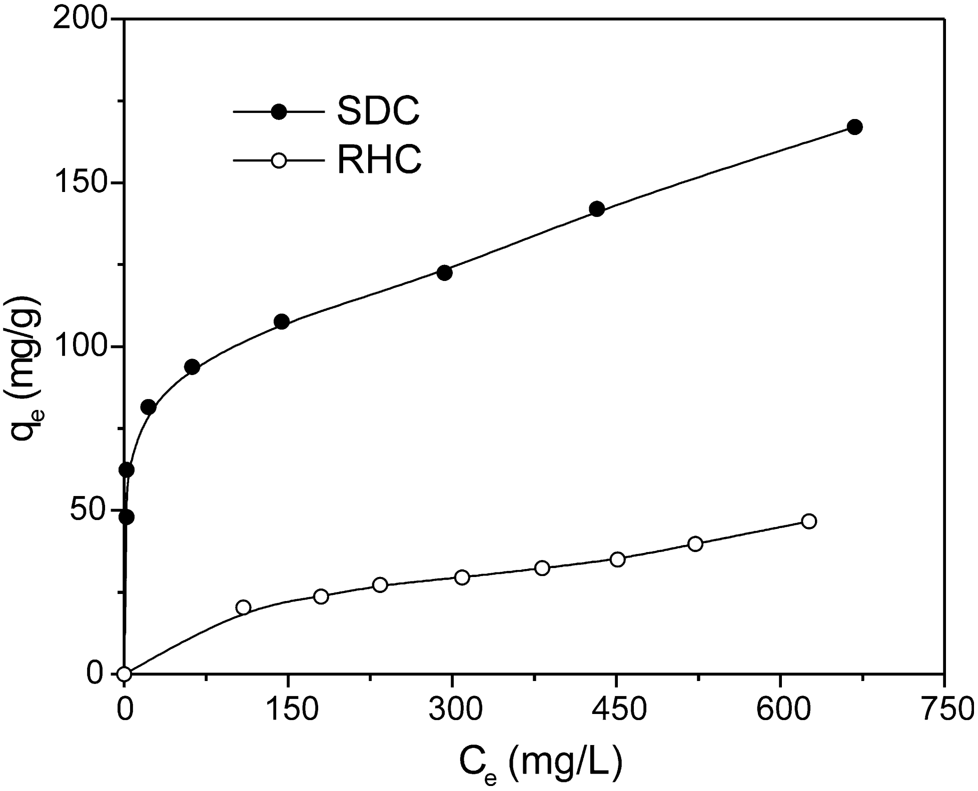

Fig. 4. Adsorption isotherms for Acid Yellow 36 with RHC and SDC.

equations. The Langmuir equation, which has been successfully applied to many adsorption [24–29] is given by

$$q_e = \frac{K_L S_m C_e}{1 + K_L C_e} \tag{4}$$

where S_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg/g), C_e the adsorbate equilibrium concentration (mg/g) and K_L the Langmuir constant (l/mg). S_m represent a practical limiting adsorption capacity when the surface is fully covered with adsorbate molecules and assists in the comparison of adsorption performance. Eq. (4) can be rearranged to a linear form

$$\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \tag{5}$$

A linearised plot of $\frac{C_e}{q_e}$ versus C_e is obtained both for SDC and RHC as shown in Fig. 5. The fits

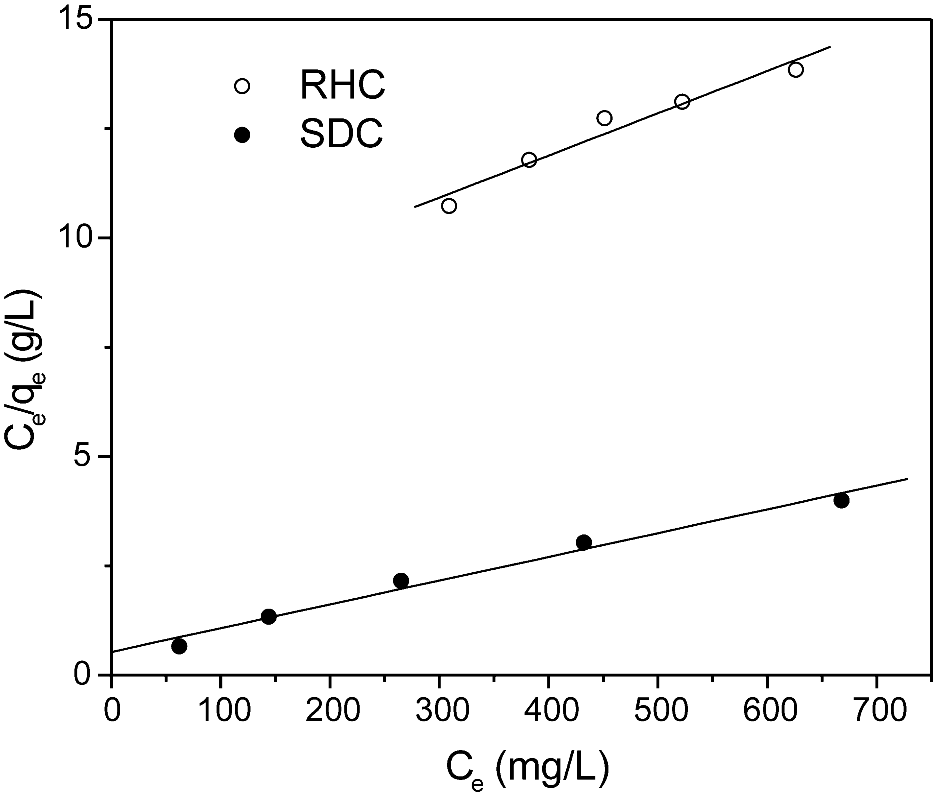

Fig. 5. Langmuir plots for the adsorption of Acid Yellow 36 on RHC and SDC.

Table 3
Langmuir and Freundlich constants for the adsorption of AY36 on SDC and RHC

Carbon	Langmuir isotherm			Freundlich isotherm	
	S_m (mg/g)	K_L (l/mg)	R_L	K_F	n
SDC	183.8	0.01	0.09	41.7	4.9
RHC	86.9	0.002	0.33	2.1	2.3

are quite well for both the carbons (correlation coefficient >0.97). This suggests the applicability of the Langmuir model [Eq. (4)] for the investigated system; the results also demonstrate monolayer coverage of AY36 at the outer surface of the carbons. Similar observations were reported for dye adsorption onto activated carbon [30,31]. K_L and S_m are computed from the slopes and intercepts. Table 3 lists the calculated results. Data show that the SDC have high adsorption capacity than that of RHC. G McKay [11] obtained S_m value of 200 mg/g and 160 mg/l for the adsorption of Telon Blue and Deorlene Yellow respectively on commercial activated carbon. Namasivayam et al [30] reported a S_m value of 6.72 mg/g for adsorption of Congo Red (anionic dye) onto activated carbon prepared from coir pith.

One of the essential characteristics of the Langmuir isotherm could be expressed by dimensionless constant called equilibrium parameter, R_L [32].

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{6}$$

where C_0 is the initial solute concentration (mg/l). The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). It has been seen that the adsorption of AY36 on RHC and SDC are favourable (Table 3) [18,29]. The Freundlich equation, which was also applied for the adsorption of dye [33] is given as:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where K_F is roughly an indicator of the adsorption capacity and $1/n$ the adsorption intensity. In general, as the K_F value increases the adsorption capacity of the adsorbent for a given dye increases. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. Values, $n > 1$

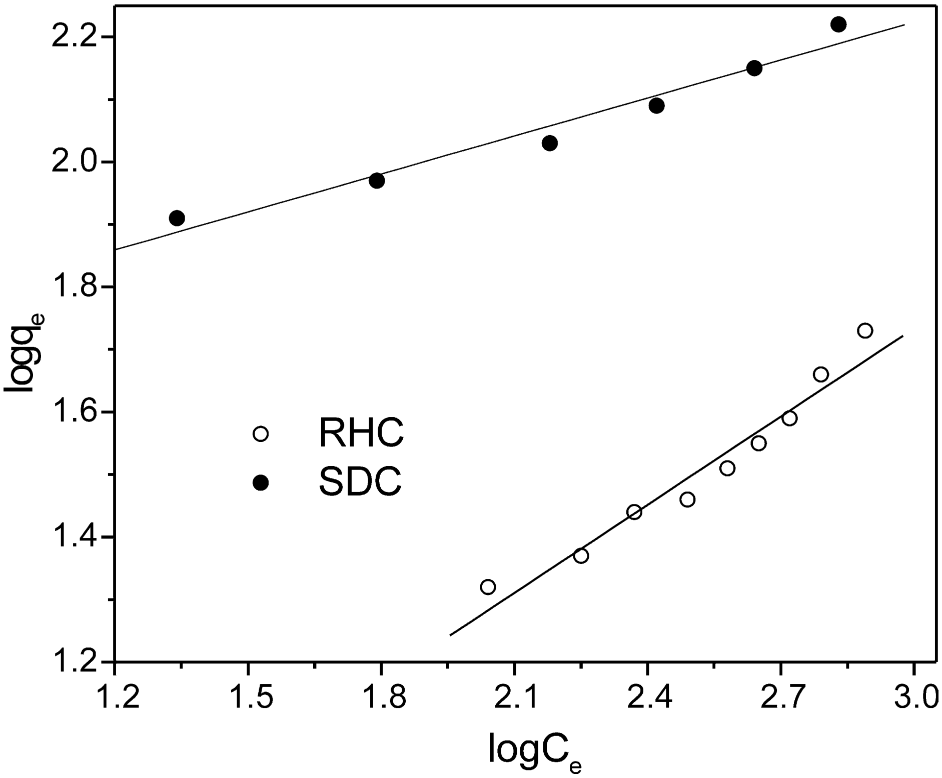

Fig. 6. Freundlich plots corresponding to the adsorption of Acid Yellow 36 on RHC and SDC.

represent favourable adsorption condition [33]. Eq. (7) can be rearranged to linear form

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (8)$$

Linear plots of log q_e vs. log C_e (Fig. 6) (correlation coefficient ~0.98) show that the adsorption of AY36 onto SDC and RHC also follow the Freundlich isotherm. Similar observations were reported for dye adsorption onto activated carbon [30,31]. Values of K_F and n were calculated from the intercepts and slopes of the plots and are listed in Table 3. The results suggest that the Acid Yellow 36 is favourably adsorbed by actvated carbons prepared from sawdust and rice husk.

3.5. Effect of pH

The effect of solution pH on the adsorption of AY36 by SDC and RHC are shown in Fig. 7. For both the carbons, the amount of adsorption decreases when the pH increased. Low pH (3 and below) was found to be favourable for maximum adsorption of AY36. Similar results of pH effect were also reported for the adsorption of Congo Red onto activated carbon [30]. The carbon surfaces acquire a basic character on high temperature (>973 K) heat treatment [16]. Galiatsatou et al. [23] show that the steam activation at 800 °C increases the basic surface groups of activated carbon with increasing activation time. It has been reported that the basic surface properties arise from two types of interactions: (i) electron-donor acceptor (EDA) complex formation that predominates in carbon of low oxygen content and (ii) pyrone-type groups contribution, which prevails in carbons of high oxygen content. Two possible mechanisms of adsorption of AY36 on RHC and SDC may be considered: (a) electrostatic interaction between the protonated groups of carbon and acidic dye and (b) the chemical reaction

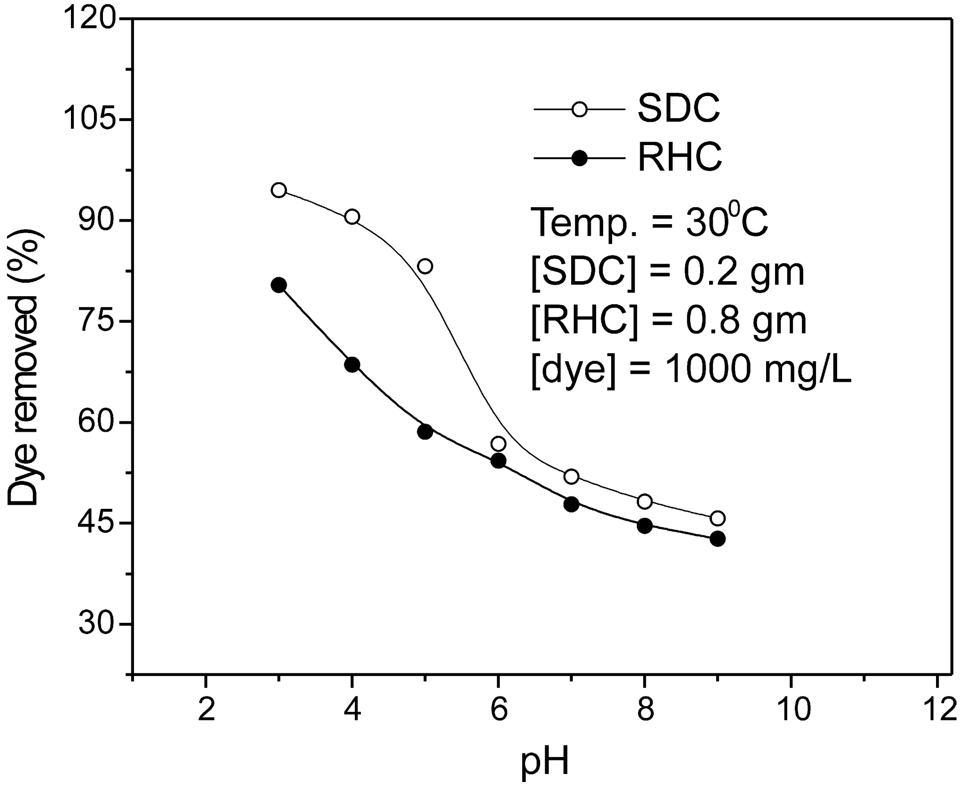

Fig. 7. Effect of pH for the adsorption of Acid Yellow 36 on RHC and SDC.

between the adsorbate and the adsorbent. At low pH (3 and below), a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of AY36 at alkaline pH is due to the presence of excess OH^- ions competing with the dye anions for the adsorption sites. At alkaline pH significant adsorption of the anionic dye on the adsorbent still occurred. This suggests that the second mechanism, i.e., chemisorption, might be operative.

4. Conclusion

The results of present investigation show that activated carbon prepared from low cost materials, mahogany sawdust and rice husk have suitable adsorption capacity with regard to the removal of Acid Yellow 36 from its aqueous solution. Mahogany sawdust carbon has better adsorption capacity than rice husk carbon. The adsorption is highly dependent on contact time, adsorbent dose and pH. The optimal pH for favorable adsorption of Acid Yellow 36 is 3 and below. Adsorption obeys both Freundlich and Langmuir isotherms. Adsorption kinetics follows Lagergren first order kinetic model.

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