

Preparation of activated carbons from bio-waste: effect of surface functional groups on methylene blue adsorption

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Abstract Low-cost activated carbons were prepared by physical activation of bio-waste rice husk. Various physicochemical characterization techniques confirmed the high surface area and oxygen functional groups on the surface. It has been confirmed that activation under humidified carbon dioxide followed by ozonation resulted the highest number of surface functional groups on activated carbon. Nitrogen adsorption–desorption isotherms confirmed the highest surface area ($417 \text{ m}^2/\text{g}$), whereas elemental analysis ensured the increasing oxygen content after activation. Temperature-programmed decomposition quantified these surface oxygen functional groups, and it was concluded that ozonation increased both acidic and basic groups. The developed activated carbons were tested during the removal of a model dye methylene blue from aqueous medium in the concentration range 10–30 mg/L. Typical results indicated that adsorption studies are consistent with the Langmuir isotherm model with maximum monolayer adsorption capacity of 28.5 mg/g, and the dimensionless separation factor (R_L) values between 0.006 and 0.030 confirmed a favorable adsorption. Methylene blue adsorption followed pseudo-second order kinetics indicating MB was adsorbed onto the surface via chemical interaction.

Keywords Carbon dioxide · Isotherm · Kinetics · Ozone · Rice husk · Temperature-programmed decomposition

Introduction

Activated carbon (AC) is a microcrystalline material with a complex heterogeneous surface functionality (Benaddi et al. 2000). Due to its high surface area and surface functional groups, AC has been widely used as an adsorbent for the removal of pollutants from gas streams and water (Gupta et al. 2005; Gupta and Rastogi 2009; Ahmad et al. 2012; Nath et al. 2013). It has been reported that both physical and chemical properties of carbon may significantly alter the adsorption capacity (Al-Degs et al. 2000; Gupta and Rastogi 2009). Agricultural by-products such as rice husk (Gupta et al. 2006; Manoj Kumar Reddy et al. 2013a), bagasse (Gupta et al. 2000), sawdust (Chakraborty et al. 2006), nut shell and other materials (Mohan et al. 2000; Hayashi et al. 2002; Jain et al. 2003, 2004; Hameed and Ahmad 2009; Mittal et al. 2010a, b; Ahmad et al. 2012; Nethaji et al. 2013a, b) were used as precursors to AC.

In general, ACs may be prepared either by physical or by chemical activation of carbon char (Kannan and Sundaram 2001; Kalderis et al. 2008; Ozdemir et al. 2011; Zhang et al. 2011; Manoj Kumar Reddy et al. 2013a). The treatment of agricultural waste under physical activation proceeds via carbonization under inert conditions at high temperatures ($>800 \text{ }^\circ\text{C}$) followed by treatment in the presence of steam, carbon dioxide and air at relatively higher temperatures (800–1,000 $^\circ\text{C}$). In contrast to physical activation, chemical activation is carried out in one stage in the presence of a variety of reagents such as acids, bases and salts (Hayashi et al. 2002; Attia et al. 2008; Kalderis et al. 2008). AC preparation by chemical activation leads low surface area, whereas physical method may lead to high surface area (Ros et al. 2006).

Synthetic organic dyes have been extensively used in textile, paper, printing, food, cosmetics and leather

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industries (Mittal et al. 2008; Hameed and Lee 2009; Ben Mansour et al. 2012; Gupta et al. 2012). Dyes are an important class of organic pollutants in the ecosystem. Some of the dyes as well as their metabolics have been identified as toxic, mutagenic and carcinogenic and may cause serious environmental problems (Manoj Kumar Reddy and Subrahmanyam 2012). As many of the synthetic dyes are non-biodegradable and resistant to oxidative degradation, conventional wastewater treatment methods may not be applicable for their removal (Ghezzer et al. 2008). Hence, adsorption is an attractive alternative, and there is a great demand for development of low-cost ACs (Ros et al. 2006). It has been reported that both the surface chemistry and surface area of AC affect the adsorption capacity during the removal of dyes from wastewater (Al-Degs et al. 2000; Liu et al. 2010). Hence, a better understanding of surface chemistry may advance the proper utilization of ACs.

The objective of this present study is to develop ACs from rice husk by physical activation (CO_2 , steam and ozone). Understanding the surface chemistry and performance estimation during the removal of methylene blue from water will form part of the study. The relationship between the chemical character of carbon surface and its effect on adsorption will be discussed. Influence of various parameters such as the choice of adsorbent, MB concentration and contact time of MB were studied in detail.

This work was carried out in Indian Institute of Technology Hyderabad Hyderabad, Andhra Pradesh, during the period of May 8, 2012–April 3, 2013.

Methods and materials

Preparation of adsorbent

Rice husk was obtained from local rice mills. Prior to physical activation, it was cleaned with deionized water and dried at 373 K for 48 h in an oven followed by carbonization at 1,173 K under N_2 atmosphere for 5 h. At the same temperature, steam/ CO_2 or humidified CO_2 was introduced for 2 h. The sample was cooled in the same atmosphere and named as SRC, CRC and SCAC, respectively. The flow rate of gas and the heating rate were fixed at 100 mL/min and 10 K/min.

Ozone treatment

In ozone activation process, rice husk char was treated with ozone that was produced ($\text{O}_3 = 1,100$ ppmv) in a home-made non-thermal plasma dielectric barrier discharge reactor by passing 500 mL/min zero air, and samples were treated up to 12 h (Karupiah et al. 2013; Manoj Kumar Reddy et al. 2013b) and the resulting samples were named as steam followed by ozone-treated rice husk carbon (OSRC). In a similar way, CO_2 followed by ozone-treated rice husk carbon (OCRC) and humidified CO_2 treatment followed by ozone-treated rice husk carbon (OSCRC) were prepared. During the ozone treatment, it is often reported that ozone decomposes to give nascent oxygen that may be responsible for the surface functional groups shown in Fig. 1a.

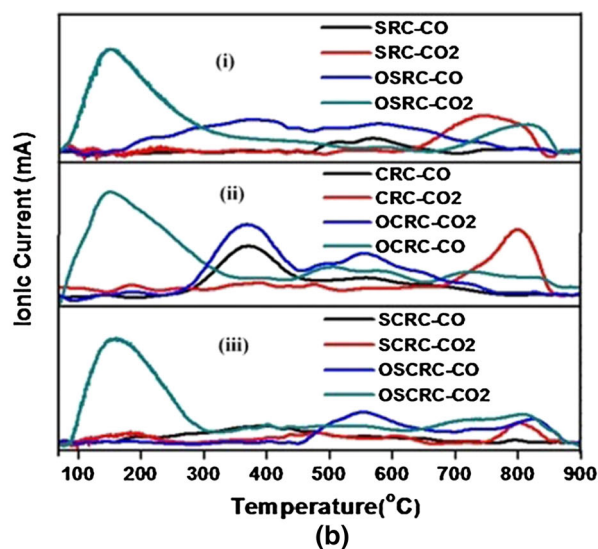
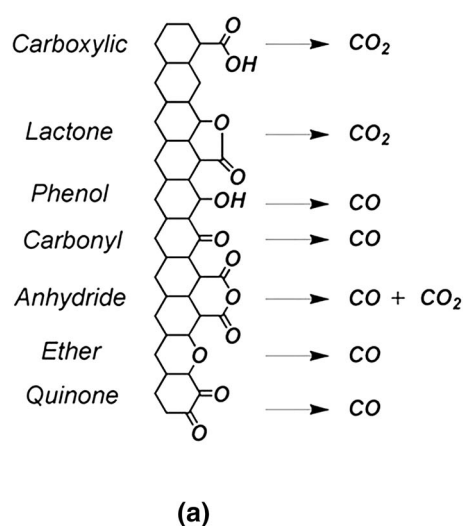
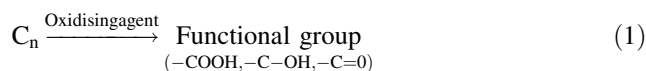


Fig. 1 a Surface oxygen containing groups on activated carbon. b Evolution profiles of CO and CO_2 in TPD of various RC samples before and after different treatments (i) SRC, (ii) CRC and (iii) SCRC

Table 1 Physico-chemical properties of activated carbons

Sample	BET surface area (m ² /g)	Micropore surface area (m ² /g)	External surface area (m ² /g)	Micropore volume (cc/g)	CO (mmol/g)	CO ₂ (mmol/g)	Total (CO + CO ₂) (mmol/g)
SRC	345	270	75	0.33	1.77	2.82	4.59
CRC	388	305	83	0.27	2.65	2.13	4.78
SCRC	372	291	81	0.31	2.61	1.25	3.86
OSRC	368	285	83	0.35	4.62	5.52	10.14
OCRC	411	322	88	0.41	5.13	4.18	9.31
OSCRC	417	325	92	0.37	4.04	6.41	10.45

Adsorbate

Methylene blue is a basic dye with heterocyclic aromatic chemical moiety. The molecular formula is C₁₆H₁₈ClN₃S (3,7-bis(dimethylamino)-phenazathionium chloride) with absorption maxima at 668 nm. The dye stock solution 1,000 mg/L was prepared by dissolving 1 g dye in organic free water. The experimental solutions were obtained by diluting the dye stock solution to the desired initial concentrations (10, 20 and 30 mg/L).

Characterization

Nitrogen adsorption measurements at 77 K were performed on Nova 2200 (Quantachrome Instruments, USA) adsorption apparatus. Before the adsorption, samples were degassed at 573 K for 3 h. The specific surface area was calculated from adsorption–desorption isotherms using BET (Brunauer–Emmett–Teller) method. C, H, N and O analysis was performed using Eurovector EA elemental analyzer. A weighed sample was placed in a tin capsule and combusted at high temperature (1,253 K). Then, the gas passing through the combustion column was introduced into a series of adsorption columns coupled with a thermal conductivity detection system. Mass titration technique was used to determine the PZC. Increasing amounts of sample from 0 to 2 g (0.4 g intervals) was added to 10 mL of 3, 6, and 10.8 pH was maintained using HNO₃ and NaOH. The resulting pH of each suspension was measured after 24 h (Noh and Schwarz 1990).

Temperature-programmed decomposition (TPD) studies were done using 100 mg of the sample loaded on a quartz reactor. The samples were first flushed with He for 1 h at room temperature followed by decomposition in the range 300–1,173 K at a heating rate of 10 °C/min in a Quantachrome gas sorption analyzer. TPD products were analyzed by a mass spectrometer (RGA PRISMA PLUS 200 AMU) calibrated with gas mixtures of known compositions. The intensity of the following peaks with m/e 2, 4, 15, 18, 28, 30, 32 and 44 was monitored simultaneously (Manoj Kumar Reddy et al. 2013a). In a typical adsorption process,

Table 2 Elemental analysis (wt%, dry basis)

Sample	Element (%)			
	C	H	N	O
SRC	69.4 ± 0.29	1.8 ± 0.12	2.7 ± 0.12	3.8 ± 0.21
CRC	71.7 ± 0.32	0.9 ± 0.11	1.1 ± 0.11	4.0 ± 0.11
SCRC	70.9 ± 0.31	1.5 ± 0.14	1.0 ± 0.10	4.3 ± 0.13
OSRC	70.1 ± 0.30	1.5 ± 0.21	1.7 ± 0.15	4.4 ± 0.14
OCRC	71.0 ± 0.27	1.0 ± 0.11	1.1 ± 0.14	4.6 ± 0.11
OSCRC	70.8 ± 0.33	1.3 ± 0.13	0.9 ± 0.11	4.7 ± 0.12

± values represent standard deviation

the residual MB concentration was estimated as a function of time using a double-beam UV spectrophotometer (Shimadzu, Japan) at 668 nm, and the estimation was done using a calibration curve.

Results and discussion

Textural properties of the activated carbons

The surface area, micropore surface area, external surface area and micropore volume of different carbon samples are given in Table 1. As seen in Table 1, for all the samples, surface area increases on ozone treatment, which may be due to the fact that ozone may decompose on the surface and resulting atomic oxygen may oxidize the surface (Valdés et al. 2002). It may be concluded that physical activation followed by ozonation improves the surface area of OSCRC to 417 m²/g when compared to the carbon char that has only 18 m²/g.

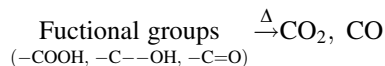
Elemental analysis

As seen from the elemental analysis data presented in Table 2, activation under humidified CO₂ increased the oxygen content to 4.3 % that was further increased to 4.7 % on ozonation. It has been reported that oxygen function groups play an important role during the adsorption process

and also changes the surface chemistry/charge of the ACs. Presence of more oxygen groups may be beneficial, especially for the removal of dyes from water.

Surface chemistry

The chemical structure of some of oxygen surface groups is shown in Fig. 1a (Figueiredo et al. 1999). Oxygen function groups present on AC surface were quantified using temperature-programmed decomposition (TPD) (Manoj Kumar Reddy et al. 2013a). During the thermal treatment under inert atmosphere, various functional groups may decompose and evolve CO₂ and CO.



As reported earlier, these groups are mainly carboxylic groups (that releases CO₂ below 673 K), carboxylic anhydride groups (that release both CO₂ and CO above 873 K), lactone groups (that release CO around 923 K), phenol groups (that release CO around 973 K) and carbonyl groups (that release CO around 1,123 K) (Figueiredo et al. 1999; Pereira et al. 2003; Manoj Kumar Reddy et al. 2013a). The groups that release CO₂ have an acidic character, whereas CO-evolving groups have a basic character. As seen in Table 1, physical activation followed by ozonation gave higher amount of CO₂ and CO when compared to activation only under steam or CO₂. From Fig. 1b, it is clear that after ozone treatment, intensity of the low temperature CO₂ peak (<573 K) increased due to the formation more amount of carboxylic groups. For OSRC, intensity of CO peak also

increased when compared to SRC, probably due to the formation of carboxylic anhydride and lactone groups after ozone treatment. In a similar manner, for OSCRC, the increase of CO peak intensity at >723 K may be due to the formation of carboxylic anhydride, lactone and phenolic groups (Manoj Kumar Reddy et al. 2013a). Hence, it may be concluded that ozone treatment increases the oxygen functional groups on the surface.

Adsorption studies

The developed ACs (SRC, CRC, SCRC, OSRC, OCRC and OSCRC) were tested for batch adsorption studies during the removal of methylene blue (MB) from water. For this purpose, to a 0.1 g AC in a glass flask, 100 mL of the MB solution of varying concentration (10–30 mg/L) was added. The solution was stirred at 298 K for 75 min to achieve the adsorption–desorption equilibrium. The desired pH was maintained using 0.01 M HNO₃ and NaOH. The concentration of MB in the solutions was determined as a function of time using a double-beam UV–Visible spectrophotometer at 668 nm. The amount of adsorption at equilibrium, q_e (g kg⁻¹) and percentage of adsorption was calculated as follows (Manoj Kumar Reddy et al. 2013a):

$$q_e = (C_0 - C_e)V/W \quad (1)$$

$$\text{Adsorption percent (\%)} = C_0 - C/C_0 \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium concentrations, V is the volume of solution, W is the weight of adsorbent and C is the concentration of the dye at the end of adsorption.

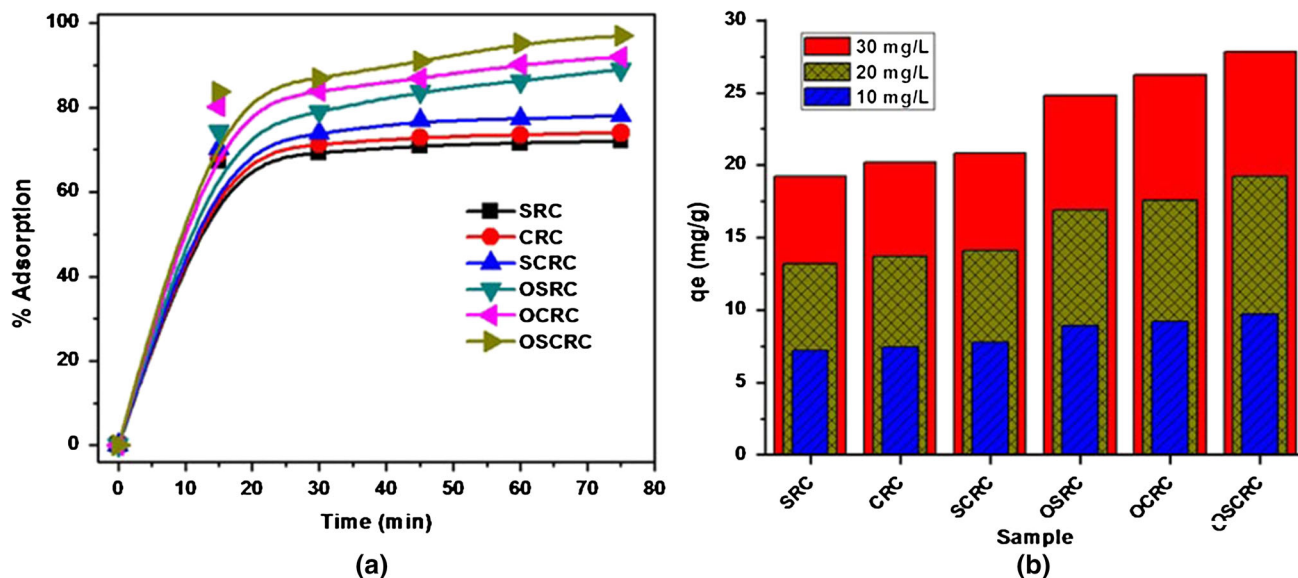


Fig. 2 Equilibrium parameters of activated carbon samples. **a** Percentage adsorption for 10 mg/L MB solution, **b** unit adsorption capacity for different concentrations

Table 3 Equilibrium parameters q_e and percentage of adsorption of dye onto activated carbon

Sample	10 ppm		20 ppm		30 ppm	
	q_e (mg/g)	Percentage adsorption	q_e (mg/g)	Percentage adsorption	q_e (mg/g)	Percentage adsorption
SRC	7.2	72	13.2	66	19.2	64
CRC	7.4	74	13.7	68.5	20.2	67.3
SCRC	7.8	78	14.1	70.5	20.8	69
OSRC	8.9	89	16.9	84.5	24.8	82
OCRC	9.2	92	17.6	88	26.2	87.3
OSCRC	9.7	97	19.2	96	27.8	92

Effect of contact time and MB concentration

As MB is a basic dye, its adsorption on ACs may be influenced by surface acidic groups present on the ACs. The percentage adsorptions as a function of time for different ACs are shown in Fig. 2a, whereas the effect of MB concentration on unit adsorption capacity is shown in Fig. 2b and Table 3. As seen in Fig. 2b, with increasing MB concentration from 10 to 30 mg/L, the unit adsorption capacity of MB increases from 7.2 to 19.2 mg/L for SRC, 7.4 to 20.2 mg/L in CRC, 7.8 to 20.8 mg/L for SCRC, 8.9 to 24.8 mg/L for OSRC, 9.2 to 26.2 mg/L for OCRC and 9.7 to 27.8 mg/L for OSCRC, respectively. Figure 2a indicated that OSCRC showed the best performance among adsorbents, whereas Fig. 2b confirmed the best unit adsorption capacity of OSCRC. As seen from Fig. 2b, for the concentrations tested in the present study (10, 20 and 30 mg/L), OSCRC showed the highest unit adsorption capacity after 75 min. Table 4 compares the unit adsorption capacity of rice husk-derived ACs for various adsorbates. It is concluded that ACs prepared by physical activation has good adsorption properties. From the Figs. 2a, 3a, b, it is clear that the percentage adsorption (Fig. 2a) and unit adsorption capacity (Fig. 3a, b) is almost constant after 60 min. As there is no appreciable adsorption after 60 min, the data at 75 min are taken as the measure of equilibrium attainment. These studies also confirmed that the unit adsorption capacity (q_e) of the adsorbent is influenced by the amount of oxygen groups on the surface. The best activity of ozone-treated samples may be due to high surface area and the presence of more number of acidic functional groups on the surface. Increasing concentration (from 10 to 30 mg/L) leads to higher MB unit adsorption capacity at equilibrium conditions at 300 K. The effect of ozone treatment on unit adsorption capacity for SRC and OSRC as a function of MB initial concentration and contact time is shown in Fig. 3, which confirms increasing q_e on OSRC with increasing concentration from 10 to 30 mg/L.

Table 4 Literature comparison of unit adsorption capacity of adsorbates prepared from rice husk

Adsorbent	Activation	q_e (mg/g)	Adsorbate	References
Rice husk carbon	Steam/900 °C	19.2	Methylene blue	Present study
Rice husk carbon	CO ₂ /900 °C	20.2	Methylene blue	Present study
Rice husk carbon	Steam + CO ₂ /900 °C	20.8	Methylene blue	Present study
Rice husk carbon	Steam/900 °C/O ₃ at RT	24.8	Methylene blue	Present study
Rice husk carbon	CO ₂ /900 °C/O ₃ at RT	26.2	Methylene blue	Present study
Rice husk carbon	Steam + CO ₂ /900 °C/O ₃ at RT	27.8	Methylene blue	Present study
Rice husk carbon	Steam/750 °C/	15	Cu(II)	Zhang et al. 2011
Rice husk carbon	ZnCl ₂ /750 °C	1.22	As	Kalderis et al. 2008
Rice husk carbon	Steam/700 °C	19.89	Methylene blue	Kannan and Sundaram 2001
Rice husk carbon	H ₂ O ₂ /400 °C	26.6	Malachite green	Ramaraju et al. 2013
Rice husk carbon	HNO ₃ /400 °C	18.1	Malachite green	Ramaraju et al. 2013
Rice husk carbon	HNO ₃ /400 °C	14.1	Methylene blue	Manoj Kumar Reddy et al. 2013a, b
Rice husk carbon	H ₂ O ₂ /400 °C	18.7	Methylene blue	Manoj Kumar Reddy et al. 2013a, b
Rice husk carbon	NaOH/70 °C	9.8	Malachite green	Chowdhury et al. 2011
Rice husk carbon	H ₂ O ₂ /110 °C	13.2	Safranin-T	Gupta et al. 2006

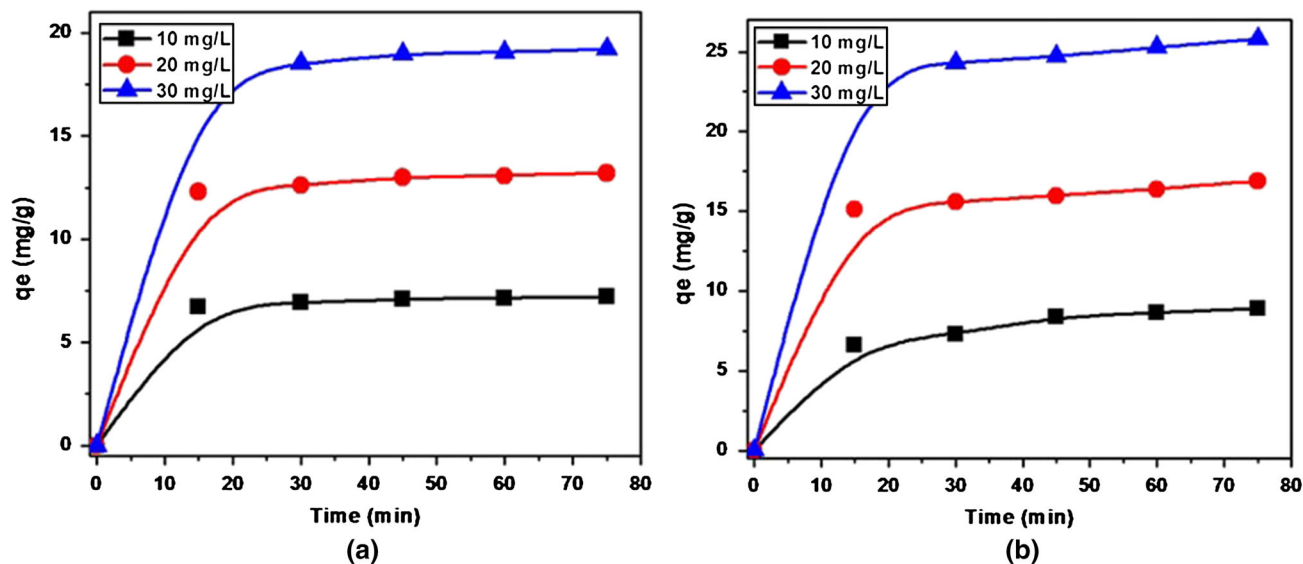


Fig. 3 Unit adsorption capacity of MB (q_e in mg/g) on a SRC, b OSRC

Adsorption isotherms

Adsorption isotherm is important for understanding any adsorption process. The analysis of the isotherm data by fitting into adequate isotherm models is an important step that gives useful information for upscaling the process. It also provides valuable information on the interaction of molecules with adsorbent. The experimental data has fitted well in Langmuir isotherm, and the linear form the isotherm is represented as Eq. (3) (Geethakarathi and Phani Kumar 2011; Manoj Kumar Reddy et al. 2013a; Ramaraju et al. 2013)

$$C_e/q_e = C_e/Q_m + 1/K_L Q_m \quad (3)$$

Where q_e (mg/g) is unit adsorption capacity, C_e (mg/L) is the equilibrium concentration of dye in solution, Q_m (mg/g) is the maximum monolayer sorption capacity and the Langmuir adsorption constant K_L (L/mg). C_e/q_e versus C_e graph is shown in Fig. 4a, b, where the slope and the intercept are equal Q_m and K_L . Table 5 presents Langmuir constants for various reaction conditions.

In a similar manner, Langmuir isotherm in terms of a dimensionless equilibrium parameter (R_L) may be presented as follows (Khattri and Singh 2000; Juang et al. 1997)

$$R_L = 1/(1 + K_L C_0) \quad (4)$$

where K_L is the Langmuir constant and C_0 is the initial dye concentration (mg/L). Typical values of R_L between 0 and 1 indicate a favorable adsorption, whereas $R_L > 1$ indicates an unfavorable adsorption, and it is termed linear when $R_L = 1$. R_L values in the present study (Table 5) were

found be between 0 and 1 for the concentrations 10, 20 and 30 mg/L, confirming a favorable isotherm.

Adsorption kinetics

The kinetics of adsorption describes the rate of solute uptake by the adsorbent. Kinetic models were applied to fit the experimental data for the concentration of the MB in the range 10–30 mg/L. Adsorption results fitted well into the pseudo-second order kinetic model. The linearized form of the pseudo-second order model is written as follows (Manoj Kumar Reddy et al. 2013a; Tsai and Chen 2013) and the corresponding plots are shown in Fig. 4c, d.

$$t/q_t = 1/k_2 q_e + t/q_e \quad (5)$$

where q_t (mg/g) is the amount of adsorbate uptake at time t . The slope and the intercept of plot of t/q against t is used to calculate the adsorption rate constants (k_2), and the amount of adsorption (q_e -mg/g) at equilibrium (Manoj Kumar Reddy et al. 2013a) is shown in Table 6.

Effect of pH

The effect of pH variation (between 2 and 10) on dye adsorption was studied using the best performing OSRC under identical conditions. The required pH was maintained with standard buffers. Typical results presented in Fig. 5 confirms that adsorption of MB is strongly influenced by pH, which is explained based on the point of zero charge (PZC). At $\text{pH} < \text{PZC}$, carbon surface may be positively charged due to H^+ . Carboxylic groups become



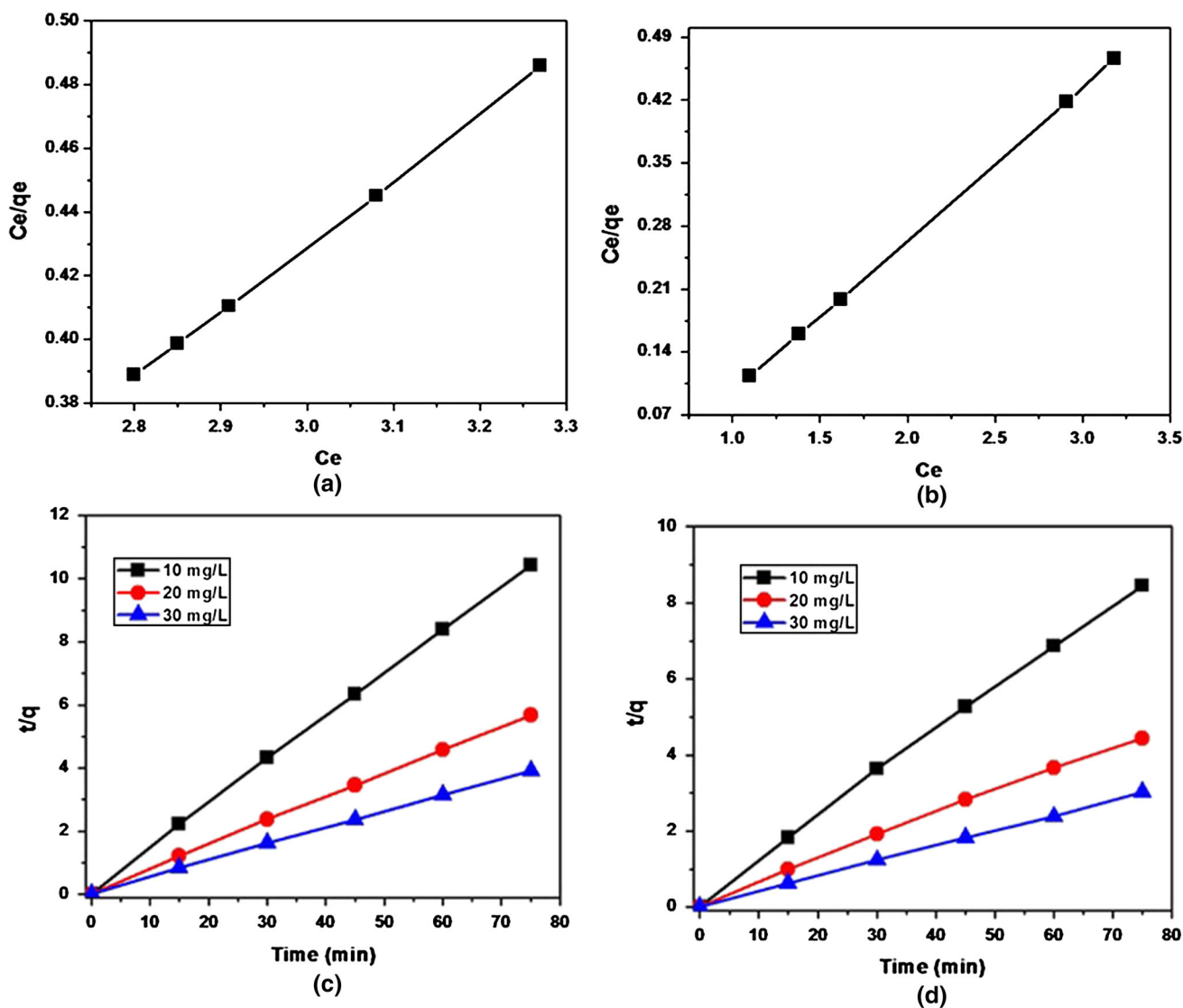


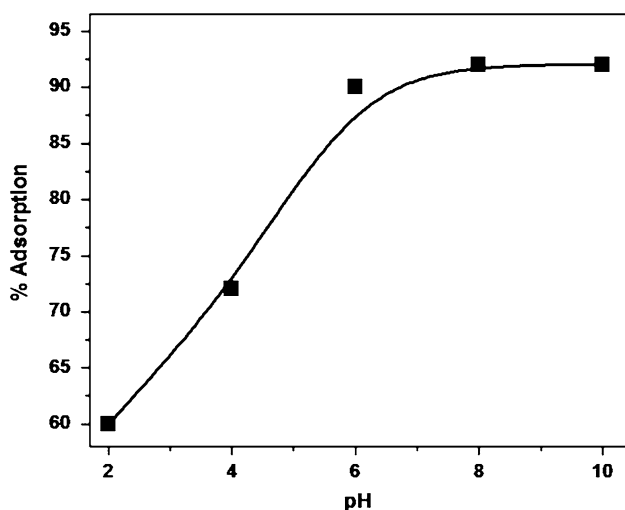
Fig. 4 Langmuir adsorption isotherm of MB at 300 K on a SRC, b OSRC, c pseudo-second order kinetics profile during MB adsorption at 300 K on SRC, d OSRC with 100 mL solution

Table 5 Estimated parameters of Langmuir isotherm for adsorption of MB on adsorbents

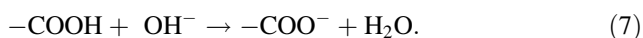
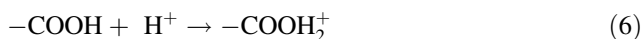
Samples	10 ppm				20 ppm				30 ppm			
	Q_m (mg/g)	K_L (L/mg)	R^2	R_L	Q_m (mg/g)	K_L (l/mg)	R^2	R_L	Q_m (mg/g)	K_L (l/mg)	R^2	R_L
SRC	7.1	4.14	0.999	0.023	13.4	2.31	0.998	0.028	19.6	2.30	0.998	0.021
CRC	7.3	5.61	0.999	0.017	13.3	5.56	0.999	0.011	20.5	4.23	0.998	0.011
SCRC	7.8	3.17	1	0.030	14.2	8.16	0.999	0.008	20.7	7.67	0.999	0.006
OSRC	9.2	4.23	0.999	0.023	17.1	4.13	0.999	0.015	25.6	2.26	0.999	0.021
OCRC	9.3	8.18	0.999	0.012	17.3	6.92	0.999	0.009	26.3	5.62	0.999	0.008
OSCRC	9.7	9.5	0.999	0.010	19.6	8.23	0.999	0.008	28.5	7.74	0.999	0.006

Table 6 Calculated parameters of pseudo-second order kinetics of MB adsorption on adsorbents

Samples	10 mg/L				20 mg/L				30 mg/L			
	q_e (exp) (mg/g)	q_e (mg/g)	K_2 (mg/g/h)	R^2	q_e (exp) (mg/g)	q_e (mg/g)	K_2 (mg/g/h)	R^2	q_e (exp) (mg/g)	q_e (mg/g)	R^2	K_2 (mg/g/h)
SRC	7.2	7.2	1.36	0.999	13.2	13.3	1.26	0.999	19.2	19.6	0.999	1.23
CRC	7.4	7.4	1.37	0.999	13.7	13.8	1.32	0.999	20.2	20.5	0.999	1.27
SCRC	7.8	7.8	1.65	0.999	14.1	14.2	1.51	0.999	20.8	20.8	0.999	1.21
OSRC	8.9	9.1	3.68	0.989	16.9	16.9	2.5	0.998	24.8	25.6	0.999	2.25
OCRC	9.2	9.2	3.52	0.997	17.6	17.1	2.46	0.998	26.2	26.3	0.999	2.16
OSCRC	9.7	9.8	4.15	0.997	19.2	19.6	3.9	0.999	27.8	28.5	0.999	3.78

**Fig. 5** Effect of pH on the percentage adsorption of MB for 30 mg/L initial concentration on OSCRC

protonated at pH below PZC (Eq. 6). Hence, at lower pH, a possible protonation of the carboxyl and other functional groups may take place. Under such conditions, repulsion between dye cations and the adsorbent surface may be expected, hence low adsorption. In addition, at lower pH, H^+ ions may also compete with positively charged MB cations during adsorption. Thus, at low pH, the adsorption is low.



At $\text{pH} > \text{PZC}$ (4.9), the adsorbent surface is negatively charged that facilitates more electrostatic attraction between positively charged adsorbate species and negatively charged adsorbent, and these interactions facilitate higher adsorption capacity (Karagöz et al. 2008; Franca et al. 2009).

Conclusion

Physical activation of bio-waste material rice husk was carried out for the preparation of ACs. Elemental analysis indicated the increasing oxygen content on activation under humidified steam that increased further on ozone treatment. Temperature-programmed decomposition was used to quantify the oxygen groups, which confirmed the highest amount for humidified steam followed by ozone treatment. Among the ACs, ozone-treated SCRC (OSCRC) has the highest surface area $\sim 420 \text{ m}^2/\text{g}$ and showed good performance during the adsorption of methylene blue. The equilibrium data for methylene blue adsorption fitted well into Langmuir equation, and the best monolayer adsorption capacity calculated for OSCRC was 28.5 mg/g, which is close to the experimental value (27.8 mg/g).

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