Int. J. Environ. Sci. Technol. (2015) 12:1363–1372
DOI 10.1007/s13762-014-0506-2

ORIGINAL PAPER

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

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Received: 18 July 2013 / Revised: 28 November 2013 / Accepted: 11 January 2014 / Published online: 30 January 2014

**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 $m^2/g$), 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 steams 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 °C) followed by treatment in the presence of steam, carbon dioxide and air at relatively higher temperatures (800–1,000 °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 (Ghezzar 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 ($O_3 = 1{,}100$ 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 (Karuppiah 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.

$$C_n \xrightarrow{\text{Oxidisingagent}} \underset{(-COOH,-C-OH,-C=0)}{\text{Functional group}} \qquad (1)$$

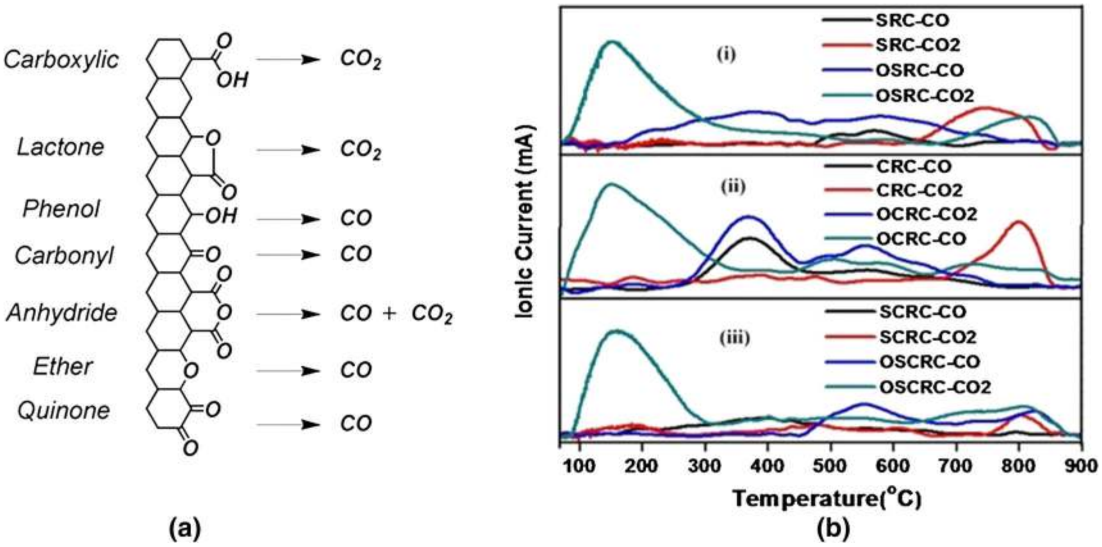

**Fig. 1** **a** Surface oxygen containing groups on activated carbon. **b** Evolution profiles of CO and CO2 in TPD of various RC samples before and after different treatments (*i*) *SRC*, (*ii*) *CRC* and (*iii*) *SCRC*

**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 $C_{16}H_{18}ClN_3S$ (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 $HNO_3$ 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, 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.

**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

## 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 $m^2/g$ when compared to the carbon char that has only 18 $m^2/g$.

### Elemental analysis

As seen from the elemental analysis data presented in Table 2, activation under humidified $CO_2$ 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 $CO_2$ and CO.

$$\underset{(-\mathrm{COOH},\ -\mathrm{C}--\mathrm{OH},\ -\mathrm{C{=}O})}{\text{Fuctional groups}} \overset{\Delta}{\rightarrow} \mathrm{CO_2},\ \mathrm{CO}$$

As reported earlier, these groups are mainly carboxylic groups (that releases $CO_2$ below 673 K), carboxylic anhydride groups (that release both $CO_2$ 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 $CO_2$ 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 $CO_2$ and CO when compared to activation only under steam or $CO_2$. From Fig. 1b, it is clear that after ozone treatment, intensity of the low temperature $CO_2$ 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 $HNO_3$ 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):

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

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

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.

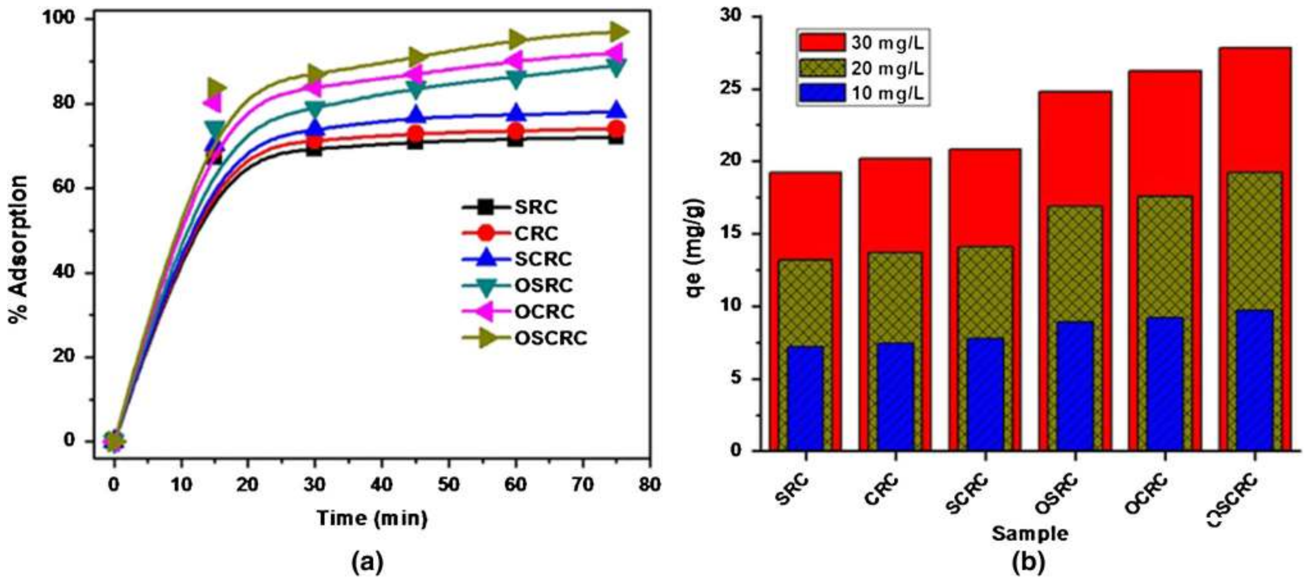

**Fig. 2** Equilibrium parameters of activated carbon samples. **a** Percentage adsorption for 10 mg/L MB solution, **b** unit adsorption capacity for different concentrations

**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 qe 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 | $H_2O_2$/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 | $H_2O_2$/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 | $H_2O_2$/110 °C | 13.2 | Safranin-T | Gupta et al. 2006 |

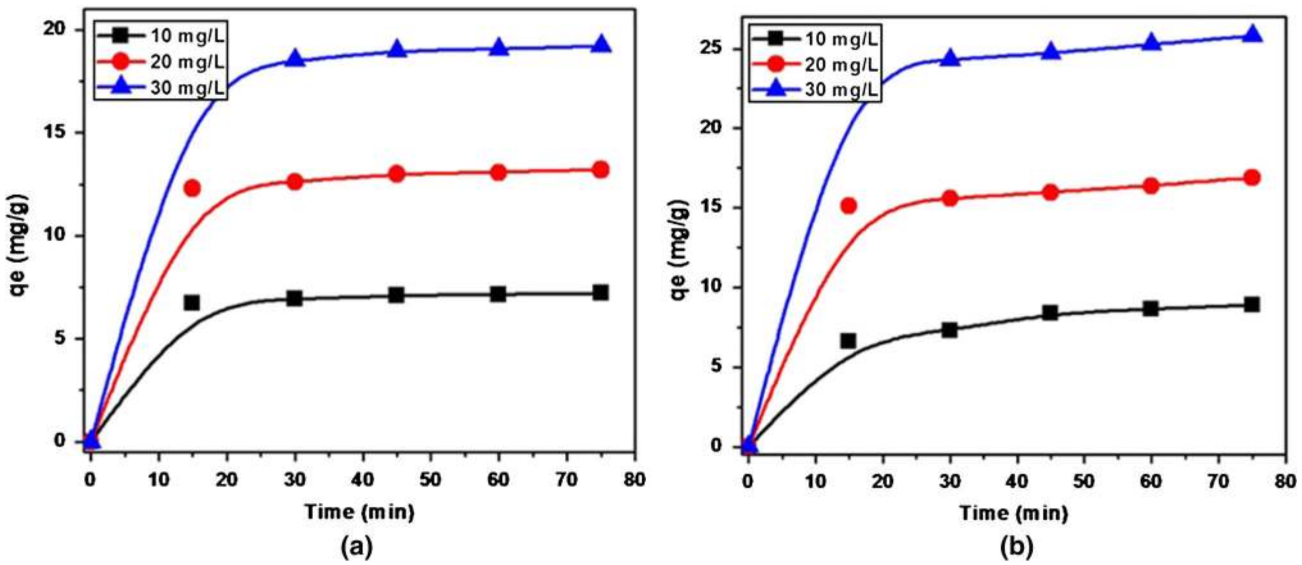

**Fig. 3** Unit adsorption capacity of MB (qe in mg/g) on **a** SRC, **b** OSRC

### *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) (Geethakarthi and Phanikumar 2011; Manoj Kumar Reddy et al. 2013a; Ramaraju et al. 2013)

$$C_e/q_e = C_e/Q_m + 1/K_L Q_m \tag{3}$$

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)

$$R_L = 1/(1 + K_L C_0) \tag{4}$$

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.

$$t/q_t = 1/k_2 q_e + t/q_e \tag{5}$$

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 OSCRC 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 pH < PZC, carbon surface may be positively charged due to $H^+$. Carboxylic groups become

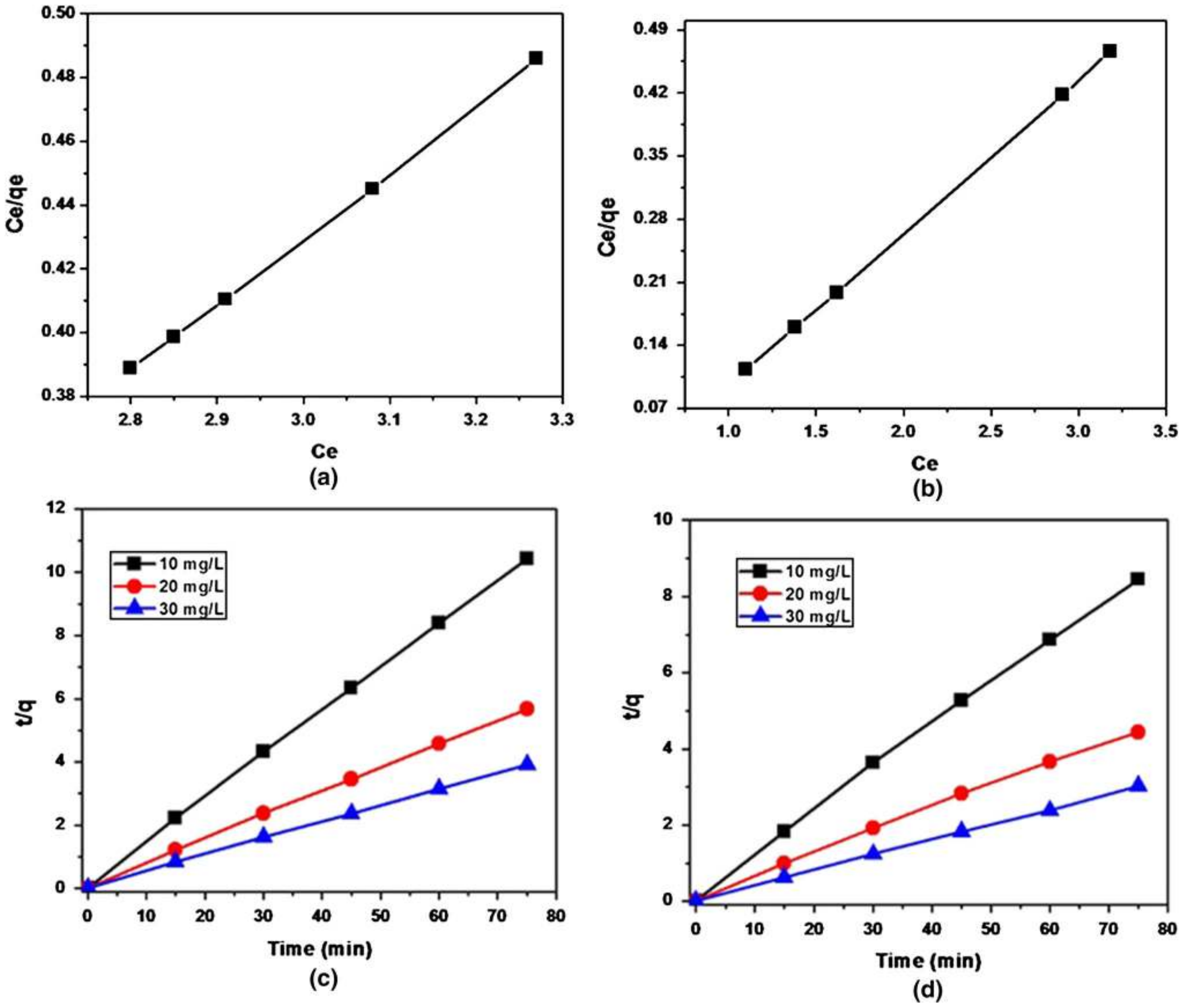

**Fig. 4** Langmuir adsorption isotherm of MB at 300 K on **a** SRC, **b** OSRC, **c** pseudo-second order kinetics profile during MB adsorption at 300 K on SRC, **d** OSRC with 100 mL solution

**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 |

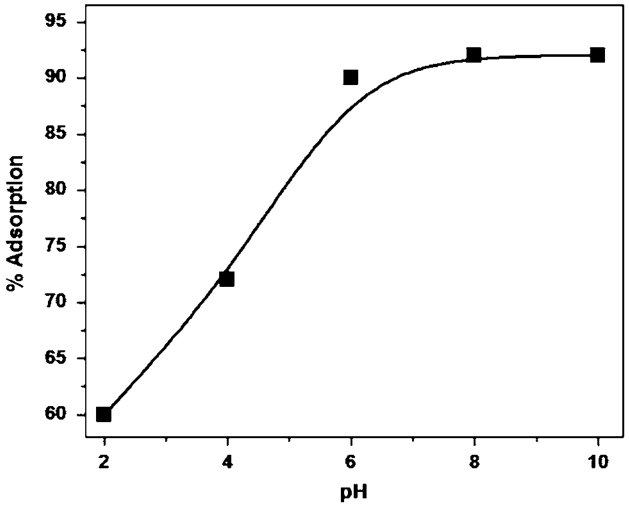

**Fig. 5** Effect of pH on the percentage adsorption of MB for 30 mg/L initial concentration on OSCRC

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.

$$-\mathrm{COOH} + \mathrm{H}^+ \rightarrow -\mathrm{COOH}_2^+ \qquad (6)$$

$$-\mathrm{COOH} + \mathrm{OH}^- \rightarrow -\mathrm{COO}^- + \mathrm{H_2O}. \qquad (7)$$

At pH > 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 ~420 $m^2/g$ 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).

**Acknowledgments** The authors are grateful for the financial support provided by the Ministry of Environment and Forest (Ref: No. 19-37/2008-RE), India, for this research.

## References

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim M (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19(5):1464–1484

Al-Degs Y, Khraisheh MAM, Allen SJ, Ahmad MN (2000) Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Res 34(3):927–935

Attia AA, Girgis BS, Fathy NA (2008) Removal of methylene blue by carbons derived from peach stones by 'H3PO4 activation: batch and column studies. Dyes Pigments 76:282–289

Ben Mansour H, Houas I, Montassar F, Ghedira K, Barillier D, Mosrati R, Chekir-Ghedira L (2012) Alteration of in vitro and acute in vivo toxicity of textile dyeing wastewater after chemical and biological remediation. Environ Sci Pollut Res 19(7):2634–2643

Benaddi H, Bandosz TJ, Jagiello J, Schwarz JA, Rouzaud JN, Legras D, Béguin F (2000) Surface functionality and porosity of activated carbons obtained from chemical activation of wood. Carbon 38(5):669–674

Chakraborty S, Basu JK, De S, DasGupta S (2006) Adsorption of reactive dyes from a textile effluent using sawdust as the adsorbent. Ind Eng Chem Res 45:7363

Chowdhury S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Desalination 265:159–168

Figueiredo JL, Pereira MFR, Freitas MMA, Orfao JJM (1999) Modification of the surface chemistry of activated carbons. Carbon 37:1379–1389

Franca AS, Oliveira LS, Ferreira ME (2009) Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. Desalination 249:267–272

Geethakarthi A, Phanikumar BR (2011) Adsorption of reactive dyes from aqueous solutions by tannery sludge developed activated carbon: kinetic and equilibrium studies. Int J Environ Sci Technol 8(3):561–570

Ghezzar MR, Belhadj M, Abdelmalek F, Rais A, Addou A (2008) Non-thermal plasma degradation of wastewater in presence of titanium oxide by gliding arc discharge. Int J Environ Waste Manag 2:458–470

Gupta VK, Rastogi A (2009) Biosorption of hexavalent chromium by raw and acid-treated green alga Oedogonium hatei from aqueous solutions. J Hazard Mater 163(1):396–402

Gupta VK, Mohan D, Sharma S, Sharma M (2000) Removal of basic dyes (rhodamine B and methylene blue) from aqueous solutions using bagasse fly ash. Sep Sci Technol 35(13):2097–2113

Gupta VK, Mittal A, Gajbe V (2005) Adsorption and desorption studies of a water soluble dye, Quinoline Yellow, using waste materials. J Colloid Interface Sci 284(1):89–98

Gupta VK, Mittal A, Jain R, Mathur M, Sikarwar S (2006) Adsorption of Safranin-T from wastewater using waste materials—activated carbon and activated rice husks. J Colloid Interface Sci 303(1):80–86

Gupta VK, Jain R, Mittal A, Saleh TA, Nayak A, Agarwal S, Sikarwar S (2012) Photo-catalytic degradation of toxic dye amaranth on TiO2/UV in aqueous suspensions. Mater Sci Eng C 32(1):12–17

Hameed BH, Ahmad AA (2009) Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. J Hazard Mater 164(3):870–875

Hameed BH, Lee TW (2009) Degradation of malachite green in aqueous solution by Fenton process. J Hazard Mater 164(2–3):468–472

Jain AK, Gupta VK, Bhatnagar A, Suhas (2003) A comparative study of adsorbents prepared from industrial wastes for removal of dyes. Sep Sci Technol 38:120016585

Jain AK, Gupta VK, Jain S, Suhas (2004) Removal of chlorophenols using industrial wastes. Environ Sci Technol 38(4):1195–1200

Hayashi JI, Horikawa T, Takeda I, Muroyama K, Nasir AF (2002) Preparing activated carbon from various nutshells by chemical activation with K2CO3. Carbon 40:2381–2386

Juang RS, Wu FC, Tseng RL (1997) The ability of activated clay for the adsorption of dyes from aqueous solutions. Environ Technol 18:525–531

Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos E (2008) Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. Bioresour Technol 99(15):6809–6816

Kannan N, Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons: a comparative study. Dyes Pigments 51:25–40

Karagöz S, Tay T, Ucar S, Erdem M (2008) Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Bioresour Technol 99:6214–6222

Karuppiah J, Linga Reddy E, Manoj Kumar Reddy P, Ramaraju B, Subrahmanyam C (2013) Catalytic nonthermal plasma reactor for the abatement of low concentrations of benzene. Int J Environ Sci Technol 1–8. doi:10.1007/s13762-013-0218-z

Khattri SD, Singh MK (2000) Colour removal from synthetic dye wastewater using a bioadsorbent. Water Air Soil Pollut 120:283–294

Liu Q-S, Zheng T, Li N, Wang P, Abulikemu G (2010) Modification of bamboo-based activated carbon using microwave radiation and its effects on the adsorption of methylene blue. Appl Surf Sci 256:3309–3315

Manoj Kumar Reddy P, Subrahmanyam C (2012) Green approach for wastewater treatment: degradation and mineralization of aqueous organic pollutants by discharge plasma. Ind Eng Chem Res 51(34):11097–11103

Manoj Kumar Reddy P, Mahammadunnisa S, Ramaraju B, Sreedhar B, Subrahmanyam C (2013a) Low-cost adsorbents from bio-waste for the removal of dyes from aqueous solution. Environ Sci Pollut Res 20(6):4111–4124

Manoj Kumar Reddy P, Rama Raju B, Karuppiah J, Linga Reddy E, Subrahmanyam C (2013b) Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor. Chem Eng J 217:41–47

Mittal A, Gupta VK, Malviya A, Mittal J (2008) Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials. J Hazard Mater 151(2–3):821–832

Mittal A, Mittal J, Malviya A, Kaur D, Gupta VK (2010a) Adsorption of hazardous dye crystal violet from wastewater by waste materials. J Colloid Interface Sci 343(2):463–473

Mittal A, Mittal J, Malviya A, Kaur D, Gupta VK (2010b) Decoloration treatment of a hazardous triarylmethane dye, Light Green SF (Yellowish) by waste material adsorbents. J Colloid Interface Sci 342(2):518–527

Mohan D, Gupta VK, Srivastava SK, Chander S (2000) Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste. Colloids Surf A 177(2–3):169–181

Nath K, Panchani S, Bhakhar MS, Chatrola S (2013) Preparation of activated carbon from dried pods of *Prosopis cineraria* with zinc chloride activation for the removal of phenol. Environ Sci Pollut Res 20(6):4030–4045

Nethaji S, Sivasamy A, Kumar RV, Mandal AB (2013a) Preparation of char from lotus seed biomass and the exploration of its dye removal capacity through batch and column adsorption studies. Environ Sci Pollut Res 20(6):3670–3678

Nethaji S, Sivasamy A, Mandal AB (2013b) Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass. Int J Environ Sci Technol 10(2):231–242

Noh J, Schwarz JA (1990) Effect of $HNO_3$ treatment on the surface acidity of activated carbons. Carbon 28:675–682

Ozdemir M, Bolgaz T, Saka C, Sahin O (2011) Preparation and characterization of activated carbon from cotton stalks in a two-stage process. J Anal Appl Pyrolysis 92:171–175

Pereira MFR, Soares SF, Órfão JJM, Figueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon 41(4):811–821

Ramaraju B, Manoj Kumar Reddy P, Subrahmanyam C (2013) Low cost adsorbents from agricultural waste for removal of dyes. Environ Prog Sustain Energy. doi:10.1002/ep.11742

Ros A, Lillo-Ródenas MA, Fuente E, Montes-Morán MA, Martín MJ, Linares-Solano A (2006) High surface area materials prepared from sewage sludge-based precursors. Chemosphere 65(1):132–140

Tsai W-T, Chen HR (2013) Adsorption kinetics of herbicide paraquat in aqueous solution onto a low-cost adsorbent, swine-manure-derived biochar. Int J Environ Sci Technol 10(6):1349–1356

Valdés H, Sánchez-Polo M, Rivera-Utrilla J, Zaror CA (2002) Effect of ozone treatment on surface properties of activated carbon. Langmuir 18:2111–2116

Zhang J, Fu H, Lv X, Tang J, Xu X (2011) Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process. Biomass Bioenergy 35:464–472