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Removal of 3-chlorophenol from water using rice-straw-based carbon

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Abstract

The removal of 3-chlorophenol (CP) from water by carbon derived from burning of rice straw was evaluated in this study. Rice straw was burned at 300 °C in the air to obtain rice carbon (RC). Scanning electron micrographs showed a highly porous structure of RC. NMR and FTIR spectroscopy suggested an enhanced aromaticity of RC and the presence of oxygen-containing functional groups. Adsorption of CP by RC was characterized by L-shaped nonlinear isotherms, suggesting surface adsorption rather than partitioning. The adsorption occurred most strongly when CP existed as a neutral species. The adsorption decreased with increasing pH due to increased deprotonation of surface functional groups of RC and dissociation of CP. The adsorption capacity determined by data-fitting to the Langmuir model was 14.2, 12.9, 11.4 and 4.9 mg g^{-1} at pH 4, 6, 8 and 10, respectively. These results suggest that rice-straw-based carbon may be effectively used as a low-cost substitute for activated carbon for removal of chlorophenols from water.
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1. Introduction

Chlorophenols are a group of phenolic compounds that have been widely used in paper, biocide, cosmetic and public health industries [1,2]. They can be also formed in water as a result of chlorination [3]. These compounds have been discharged into the environment and hence frequently found in wastewaters, and surface and ground waters [2]. Because of high toxicity, carcinogenicity, yet poor biodegradability, chlorophenols are among the priority contaminants of major environmental concern. Effective removal of chlorophenols for water reclamation has been a constant task.

Various techniques including ozonation, membrane filtration, ion exchange, adsorption, electrochemical degradation and photocatalytic degradation have been developed for removing phenolic compounds from waters [4–7]. The adsorption method has the advantage over other techniques in chlorophenol removal effectiveness, cost and equipment handling, and hence is the most frequently used. Tested adsorbents include both inorganic and organic materials and their hybrids such as organoclays [8,9], biosolids [10,11], industrial wastes [12,13] and activated carbons [14–18]. Activated carbons have been shown to be the most effective adsorbents for chlorophenols, due apparently to their high surface areas, high porosities, and other favorable surface properties. There is thus a growing need to produce carbon-based adsorbents that are comparable to activated carbons in adsorption capacity yet more cost-effective. This is especially significant when treating waters on a large scale.

Selected agricultural wastes such as fruit stones, coconut shells, and corn cobs are excellent raw materials for activated carbon manufacturing [19–22]. Others such as rice and wheat straws are often burned directly in the field for the purpose of quick disposal of these wastes and land clearing [23,24]. Recent studies have shown, however, that the carbons derived from rice and wheat straws were highly effective adsorbents for pesticides. When adsorbing the pesticide diuron, these adsorbents were >50 times more effective than their precursors. Mixing wheat carbon with soils resulted in increased adsorption of diuron by the soils [25,26]. Rice and wheat straws may thus be alternatives to or additional precursors for activated carbon.

Rice straw is a by-product of rice production, which plays a prominent role in world food supply [24]. In Taiwan, annual production of rice straw is estimated to be 2 million tonnes, which would yield a large quantity of carbon materials. If the carbon derived from rice straw is proved to be an effective adsorbent for chlorophenols, it may be used as a low-cost substitute for activated carbon in the remediation of chlorophenol contamination. The objective of this study was thus to evaluate the adsorptivity of a rice-straw-based carbon for a model chlorophenol, 3-chlorophenol (CP), from water. The carbon was prepared by burning rice straw in the air without additional activation processes, which may reduce the cost of the product.

2. Materials and methods

2.1. Sample preparation

CP with a purity of 99% was purchased from Acros Organics and used as received. Its stock solution of $1000\,\text{mg L}^{-1}$ was prepared by dissolving 0.1 g of CP in 100 mL of 0.01 M $CaCl_2$ solution, and stored in the dark at $4\,^\circ\text{C}$. The stock solution, prepared weekly, was subsequently used to prepare all the CP solutions for the adsorption experiments.

Rice straw was collected from the Agricultural Research Institute experimental field in Taichung County, Taiwan. The straw was dried at room temperature and burned at $300\,^\circ\text{C}$ in a furnace for 10 min with supply of air (flow rate $= 100\,\text{mL min}^{-1}$). The resulting residue was collected, and rice carbon (RC) was obtained by washing with de-ionized water to remove soluble salts. RC was air-dried, ground, passed through a 20-mesh sieve, and stored in a plastic bottle prior to use.

2.2. Sample characterization

Elemental analyses of rice straw and RC samples were conducted using a Heraeus Elemental Analyzer and Jobin-Yvon Ultima ICP-AES. Scanning electron micrographs were obtained on a Jeol JSM 6500F scanning electron microscope. Transmission FTIR spectra were acquired for the samples randomly distributed in a KBr pellet, using a ThermoNicolet Nexus FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and a KBr beamsplitter. Spectra in the range of 4400–$400\,\text{cm}^{-1}$ were obtained by co-addition of 64 individual scans with an optical resolution of $4\,\text{cm}^{-1}$. ^{13}C CP-MAS NMR spectra of the samples were collected on a Bruker DSX400WB NMR spectrometer. The magic angle spinning (MAS) rate was 6.5 kHz. For each scan, a pulse with a carrier frequency of 100 MHz was applied and the recycle time was 1.5 s. The number of scans was 2168 for each spectrum. The BET surface area and total pore volume of the sample were obtained using Micrometritics ASAP 2000 surface area analyzer and nitrogen adsorption at 77 K. With the nitrogen adsorption data, average pore sizes were determined using the *t*-plot and BJH methods [27]. Real density (σ_R) of the sample was determined by the water-displacement method with a picnometer. Point of zero charge (PZC) was measured by potentiometric titration with the RC suspensions in 0.001, 0.01 and 0.1 M KCl solutions [28].

2.3. Analysis of CP

CP in all the samples was analyzed using a high-performance liquid chromatograph (Varian ProStar) equipped with a UV–vis detector and a C18 column (Supelco 516). The wavelength of detection was set at 274 nm. The mobile phase was a mixture of 65% methanol and 35% water at a flow rate of $1\,\text{mL min}^{-1}$.

2.4. Kinetic study

The batch method was used to determine the kinetic adsorption of CP on RC. RC (0.05 g) and 10 mL of 0.01 M $CaCl_2$ solution were initially mixed in each of a series of amber glass centrifuge tubes for 1 h. To each tube was then added 10 mL of 0.01 M $CaCl_2$ solution of CP to make the initial concentration of CP to be $30\,\text{mg L}^{-1}$. The centrifuge tubes were mechanically agitated at 150 rpm. At given time intervals, the tubes were centrifuged and the supernatants were filtered using a 0.2-μm (pore size) PTFE syringe filter pre-treated with isopropanol to be hydrophilic. The concentrations of residual CP in the filtrates were analyzed.

2.5. Adsorption isotherms

CP adsorption by RC was conducted using the batch method. RC (0.05 g) and 20 mL of 0.01 M $CaCl_2$ solution were placed in each of a series of 50-mL amber glass centrifuge tubes with Teflon-lined caps. The tubes were shaken for 1 h to homogenize the suspensions. Various volumes of the CP stock solution were then added into the tubes. Additional 0.01 M $CaCl_2$ solution was further added to bring the final volume of suspension in each tube to 50 mL. The initial CP concentrations in the tubes were 3, 5, 10, 15, 20, 25, 30, 40 and $50\,\text{mg L}^{-1}$. The tubes for each CP concentration were in triplicate. To evaluate the pH effect, the suspensions in the tubes were adjusted for their pH values to 4, 6, 8, or 10. The tubes were shaken for 24 h, and the pH was constantly adjusted to desired values. The tubes were then centrifuged at 5000 rpm for 30 min, and the supernatants were filtered for CP analysis as described earlier. The amount of CP adsorbed by RC was calculated as the difference between the initial and final concentrations of CP in the filtrate.

2.6. Adsorption models

Adsorption data of CP on RC were analyzed by use of the Freundlich and Langmuir models. The Freundlich equation can be written in the following linear form:

$$\log \frac{x}{m} = \frac{1}{n} \log C_\text{e} + \log K_\text{F}$$

where x/m and C_e are the equilibrium concentrations of CP in the adsorbed and liquid phases in mg g^{-1} and mg L^{-1}, respectively; K_F and n are the Freudlinch coefficients related to the adsorption capacity and intensity, respectively, and can be calculated from the slope and intercept of the linear plot with $\log(x/m)$ versus $\log C_\text{e}$. The Langmuir equation can be rearranged in the

following linear form:

$$\frac{C_e}{x/m} = \frac{C_e}{S_m} + \frac{1}{K_L S_m}$$

where K_L and S_m are the Langmuir constants related to the adsorption energy and adsorption capacity, respectively, and can be calculated from the slope and intercept of the linear plot with $C_e/(x/m)$ versus C_e.

3. Results and discussion

3.1. Characterization of RC

Chemical compositions of rice straw and rice carbon are listed in Table 1. The C, O, H, and N contents for rice straw accounted for 87% of the total weight (w/w). Other minor components (not listed) included Si (4.6%), K (2.5%), P (0.5%), Ca (0.3%) and Mg (0.3%). Burning in the air resulted in a significant loss of C, O, and H. The C, O, and H for RC accounted for only 44%. Yang and Sheng [25,26] reported that the residue of rice straw burning contained 33% elemental Si and 21% K. The remainder of RC in this study is thus assumed to consist mainly of silica, as metal ions including K were washed off. The decreases in the H/C and O/C molar ratios of RC as compared to rice straw indicated that RC was more unsaturated and aromatic [29], suggesting burning-induced carbonization of rice straw. Polyaromatic frame is the essential structure of activated carbon highly effective for adsorption. The H and O of RC may be largely attached to aromatic matrixes and possibly to silica as functional groups (e.g., –OH and –COOH). It has been reported that an abundance of oxygen-containing functional groups were present in crop-residue-derived carbon samples [30].

The density, BET surface area and porosity of RC are listed in Table 2. The density of RC was measured to be 2.11 g cm^{-3}. The BET surface area and total pore volume were determined to be 5.24 m^2/g and 0.024 cm^3/g, respectively, using N$_2$ adsorption at 77 K. The average pore diameter was estimated to be 18.7 nm; the volume of micropores measured by t-plot analysis was negligible. As seen in the scanning electron micrographs (SEM) shown in Fig. 1, burning of rice straw resulted in the creation of pores in RC. This suggests that the surface area of RC may be much higher than that of rice straw, although we did
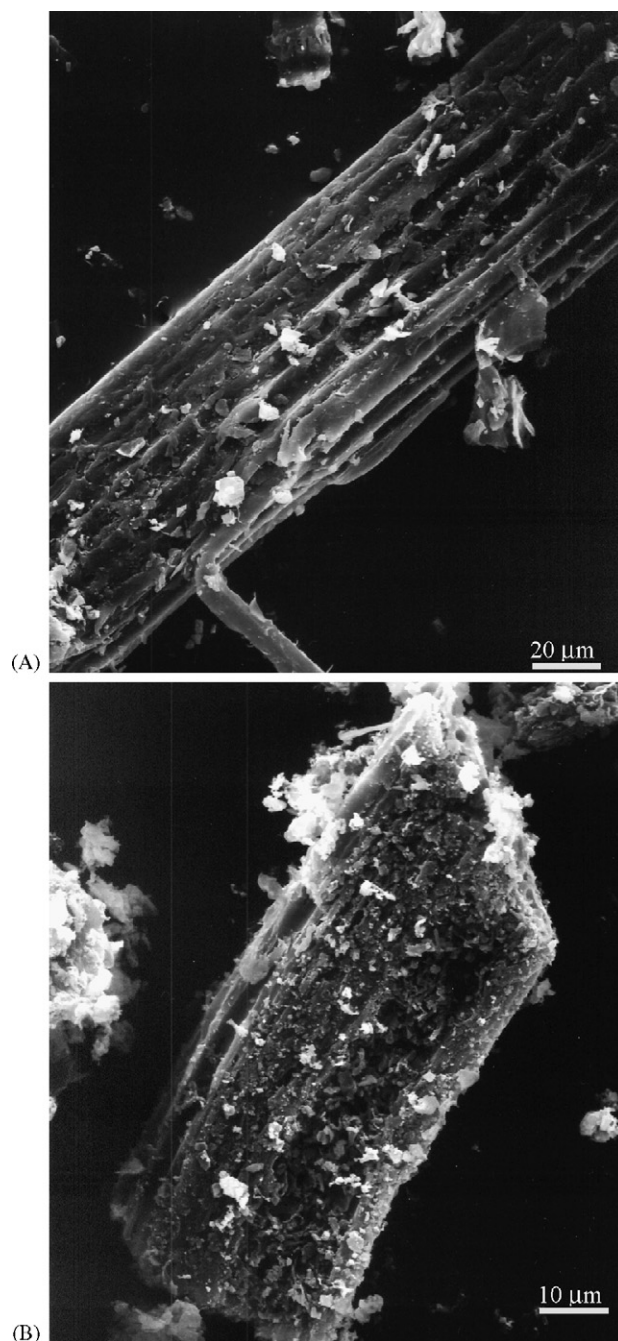

Fig. 1. Scanning electron micrographs of (A) rice straw and (B) rice carbon.

not make such a measurement for original rice straw. The high surface area and porous structure are a requisite for an effective adsorbent.

The ^{13}C NMR spectrum of rice straw exhibited the major peaks between 57 and 105 ppm, which are assigned to O-alkyl C atoms in cellulose (Fig. 2A) [31–33]. The peak at 105 ppm may arise from aromatic C in the lignin structure. The minor peaks at 21, 153 and 173 ppm are assigned to alkyl C in lignin and hemicellulose, aromatic C in lignin, and carboxyl C in hemicellulose, respectively, [32,33]. In the FTIR spectrum of rice straw, a broad OH stretching band (ν(OH)) at ~3400 cm^{-1} is attributed to water and the OH bonds in the oxygen-containing functional

Table 1
The elemental compositions of rice straw and carbon

Sample	O (%)	C (%)	H (%)	N (%)	Molar ratio	
					H/C	O/C
Rice straw	41.0	37.8	5.4	2.3	1.6	0.8
Rice carbon	16.4	26.2	1.8	0.7	0.8	0.5

Table 2
Density, surface area and porosity of rice carbon

Density (g cm^{-3})	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
2.11	5.4	0.024	18.7

groups (Fig. 2B). The positions of the C−H, aliphatic C−C and aromatic C=C, and carboxyl/carbonyl vibrations, contributed by those in the structures of cellulose, hemicellulose and lignin, are indicated by the spectrum of Fig. 2B [34]. These bands partially overlap and thus may not be assigned definitely. Both the NMR and FTIR spectra of rice straw consistently indicate the predominance of carbohydrates in the straw.

Burning resulted in fundamental changes in the nature of rice straw, as observed in both NMR and FTIR spectra (Fig. 2). The intensities of the peaks in the aliphatic C region (0–108 ppm) in the ^{13}C NMR spectrum of RC decreased significantly as compared to rice straw (Fig. 2A). The corresponding changes were also observed in the region of C−H and C−C vibrations in the FTIR spectrum of RC (Fig. 2B). The significant reductions in the intensities of these peaks and vibrations indicate the loss of aliphaticity in the structure of RC. In contrast, new peaks appeared at 68 and 192 ppm in the ^{13}C NMR spectrum of RC, attributable to O-alkyl C and aromatic carboxyl/carbonyl C, respectively, [33,35]. In particular, the peak at 127 ppm, absent for rice straw, indicate the strong aromatic nature of RC [35]. The FTIR spectrum of RC also showed that the C−C and C=C bonds and the oxygen-containing functional groups (e.g., car-
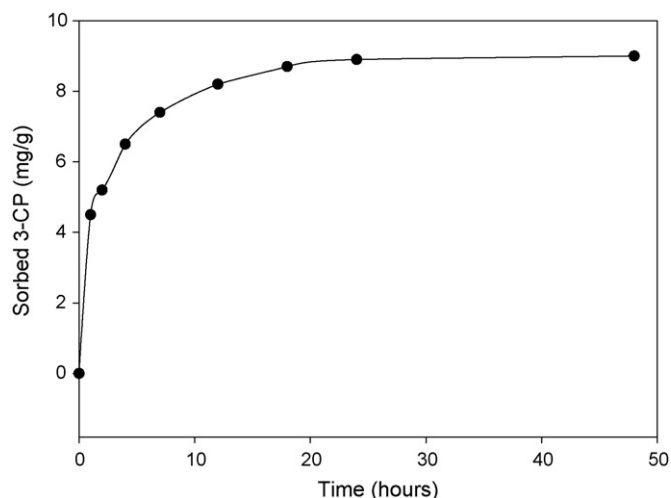

Fig. 3. Adsorption of 3-CP on RC as a function of time.

boxyl, carbonyl, and phenolic OH) were predominant in the structure of RC. These spectroscopic results suggest that burning may effectively convert rice straw to highly adsorbing carbon materials with much enhanced aromaticity.

3.2. Effect of agitation time on CP adsorption

Fig. 3 shows the effect of agitation time on the removal of CP by RC at pH 6. The test was carried out with an initial CP concentration of 30 mg L^{-1} and the solid concentration of 2.5 g L^{-1}. The amount of adsorbed CP initially increased rapidly with time. The adsorption gradually slowed down and leveled off within 24 h. A 79% removal at the selected initial CP concentration and RC concentration was obtained, indicating that RC was a highly effective adsorbent for CP. It also suggests that RC may be used to effectively remove CP and similar contaminants from wastewaters. As the adsorption equilibrium was established within 24 h under the selected conditions, the adsorption under other conditions was presumed to also reach equilibrium within the similar period of time. The 24-h agitation time was therefore chosen when obtaining adsorption isotherms.

3.3. Adsorption isotherms at various pHs

Fig. 4 shows the adsorption isotherms of CP on RC at various pH values at 25 °C. All the isotherms exhibited the L-shape, suggesting surface adsorption that limited sites on the RC surface were available for CP adsorption. As more sites were occupied by CP, the RC surface became increasingly difficult for CP adsorption. With these characteristics, the adsorption isotherms were analyzed by the Freundlich and Langmuir models; the resulting constants with regression coefficients are listed in Table 3. Both models describe the adsorption well.

The $1/n$ values from the Freundlich model ranged from 0.28 to 0.36, indicating that the isotherms were highly nonlinear and that the adsorption may have occurred via a surface mechanism rather than partitioning. The adsorption was presumed to occur primarily on the surface of the carbon fraction of RC, as silica was expected to be highly hydrophilic [36]. Partitioning was not
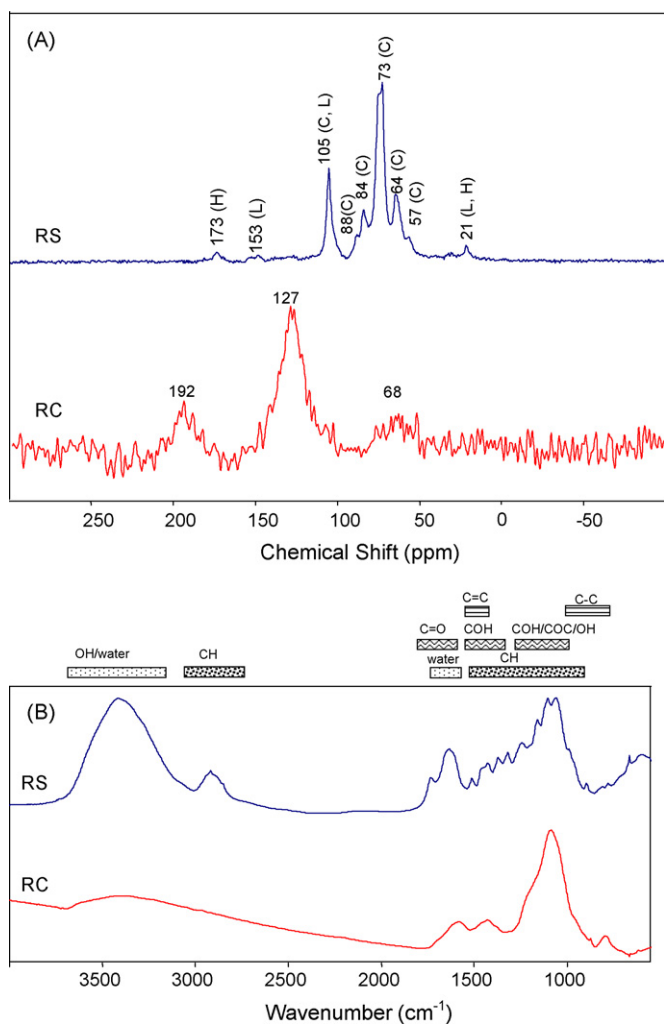

Fig. 2. (A) ^{13}C NMR and (B) FTIR spectra of rice straw and rice carbon.
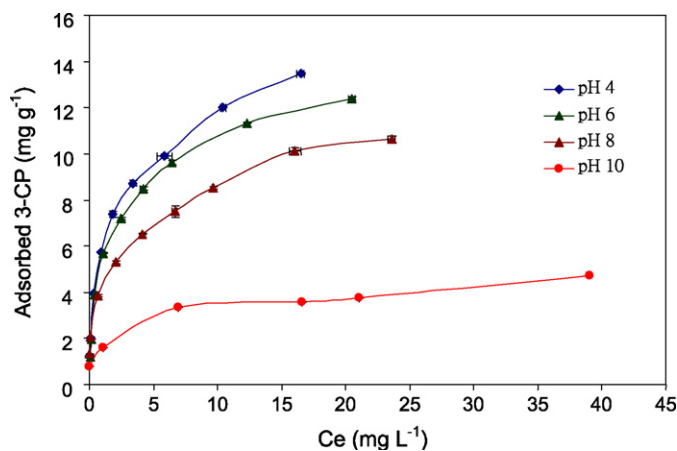
Fig. 4. Adsorption isotherms of 3-CP on RC at various pHs.

expected to occur because burning resulted in RC non-organic in nature. Finally, as the pH was increased from 4 to 10, the K_F value from the Freundlich model and the S_m and K_L values from the Langmuir model decreased (Table 3), indicating a decreasing affinity of RC for CP with increasing pH. Depending on pH, the maximum adsorption (S_m) derived from the Langmuir model ranged from 14.2 to 4.9 mg g^{-1}. The adsorption was less than those in previous studies, in which the reported maximum adsorption of 3-CP on activated carbons ranged from 16.7 to 415 mg g^{-1} [16–18]. This is probably due to the relative low surface area of RC compared with those of activated carbons. Even so, RC may be used as a highly cost-effective substitute for activated carbon for removal of CP from wastewater. Calculated based on the maximum adsorption of RC, 0.7–2 g of RC is needed for treating one litter of wastewater containing 10 mg 3-chlorophenol. It is estimated that rice straw annually produced in Taiwan, if properly managed, may be utilized to produce over 100,000 tonnes of RC. This would provide wastewater industries with an abundant source of carbon-based adsorbents for effective treatment and remediation.

The effect of pH on CP adsorption arose apparently from the charge properties of both CP and RC. It is recognized that oxygen-containing functional groups are present on the surface of RC. These functional groups are subject to protonation/deprotonation, depending on pH. An increase in pH usually

results in surface functional groups partially (or fully) deprotonated and thus a loss of positive charge and/or buildup of negative charge. The influence of the surface functionality is described by the point of zero charge (PZC), the pH value at which the positive charge is equal to the negative charge leading to a net zero charge. Compared to the high PZC of activated carbon (often >7), carbon samples derived from burning usually have a lower PZC, due apparently to a much higher density of surface functional groups. The PZC of RC in this study was determined to be 5.5, similar to that of a wheat-straw-derived carbon [30]. On the other hand, CP is a weak acid with a pK_a of 8.98. CP is present in its neutral form at low pH values (e.g., pH < 8) and its anionic form prevails at high pH values (e.g., pH > 10). Examination of Fig. 4 reveals that an increase in pH from 4 to 8 slightly reduced the CP adsorption by RC. As the predominant species of CP at these pH values, i.e., the neutral form, remained unchanged, the adsorptive reduction resulted clearly from the deprotonation of the functional groups on the surface of RC. The deprotonation resulted in an increased blockage of RC surface by water molecules associated with negative charge. It is thus inferred that CP was primarily adsorbed on the neutral surface of RC. When pH was increased from 8 to 10, the CP adsorption was substantially reduced. Since the surface functional groups were fully deprotonated at these pH values as indicated by the PZC of RC, the dissociation of the phenolic group of CP leading to an enhanced electric repulsion between CP and the carbon surface was clearly responsible for the dramatic reduction in CP adsorption.

4. Conclusions

Burning in the air effectively converts rice straw to rice carbon (RC) with enhanced porosity and aromaticity. This material is effective in adsorbing 3-chlorophenol and may be used as a low-cost substitute for activated carbon for treating wastewater containing chlorophenols. Neutral chlorophenols appear to be strongly adsorbed by RC. Deprotonation of the functional groups on the surface of RC and dissociation of the phenolic group of chlorophenols reduce the chlorophenol adsorption. It is thus recommended that rice-straw-based carbon be used at low-to-neutral pH as an adsorbent for chlorophenols. The removal of chlorophenols by such carbon adsorbents from alkaline wastewaters may be significantly enhanced via pre-acidification of the waters.

Table 3
Coefficients of Freundlich and Langmuir models for 3-CP adsorption on rice carbon

	pH			
	4	6	8	10
Freundlich				
K_F	5.68	4.88	4.50	1.68
$1/n$	0.33	0.36	0.28	0.28
R^2	0.993	0.969	0.996	0.976
Langmuir				
S_m (mg g^{-1})	14.2	12.9	11.4	4.9
K_L	0.69	0.64	0.47	0.25
R^2	0.977	0.992	0.981	0.978

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