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ORIGINAL PAPER

Pentachlorophenol (PCP) adsorption from aqueous solution by activated carbons prepared from corn wastes

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Abstract Corn wastes generated from starch and glucose production industry were used for the preparation of activated carbons. The prepared activated carbons and a commercial activated carbon were evaluated for their capability of adsorbing pentachlorophenol (PCP) from aqueous solution. Batch adsorption experiments were performed under different operating conditions including pH (2–8), adsorbent dosage (0.5–4.0 g/l), initial PCP concentration (10–100 mg/l), contact time (30–300 min), and temperature (25–45 °C). The kinetics and equilibrium models describing the adsorption of PCP by the prepared adsorbents were obtained. The adsorption of PCP by corn waste-based adsorbents was found to follow the second-order kinetics and the Freundlich equilibrium models. The intraparticle diffusion mechanism was successfully fitted to the obtained experimental data. Thermodynamic studies indicated that the adsorption process was exothermic. The adsorbents surface characterization revealed the presence of many functional groups capable of binding the adsorbate molecules. The study results suggest the possible use of corn wastes as a starting material for the production of activated carbon, thus lowering the costs of wastewater treatment processes.

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Introduction

Pentachlorophenol (PCP) is one of the seven chlorophenols with industrial production (Estevinho et al. 2006). Although PCP does not belong to the primarily elaborated list of 12 persistent organic pollutants (POPs), it is considered a persistent compound in the environment (Brás et al. 2005). The United States Environmental Protection Agency (US-EPA) fixed 1 μg/l as the maximum limit of PCP in drinking water, while the European Union limited the maximum PCP discharge concentration in industrial effluents to 1–2 mg/l (Estevinho et al. 2006).

Aqueous effluents from industrial operations such as polymeric resin production, oil refining, iron–steel, petroleum, pesticide, paint, solvent, pharmaceutics, wood-preserving chemicals, coke-oven, and paper and pulp industries contain chlorophenolic compounds (Jianlong et al. 2000). PCP has been widely used as biocide mainly in wood preservation industries and other pesticide applications (Mathialagan and Viraraghavan 2009).

Pentachlorophenol is acutely toxic to a variety of microorganisms and mammals; as it is an inhibitor of oxidative phosphorylation, it appears to accumulate within the food chain and is thought to be mutagenic or at least comutagenic (Mollah and Robinson 1996). PCP acts by uncoupling oxidative phosphorylation via making cell membranes permeable to protons, resulting in dissipation of transmembrane proton gradients and consequential electrical potentials (Law et al. 2003).

It is thus necessary to remove PCP from contaminated water, and several methods have been used for this purpose. These methods include oxidation, biological degradation, membrane filtration, ion exchange, reverse osmosis, photocatalytical degradation, and adsorption (Domínguez-Vargas et al. 2009). The water treatment costs of these technologies range from 10 to 450 US$ per cubic meter of treated water, except adsorption technology. The cost of water treatment using adsorption is 5.0–200 US$ per cubic meter of water (Gupta et al. 2012). Moreover, ability of adsorption to remove toxic chemicals without disturbing the quality of water or leaving behind any toxic degraded products has augmented its usage in comparison with some other treatment methods (Mittal 2006). Thus, among various water purification and recycling technologies, adsorption is a fast, inexpensive, and universal method (Ali and Gupta 2007).

Adsorption as a cost-effective technique has been widely applied for the removal of PCP from aqueous solutions. Various adsorbents were successfully used for PCP removal, e.g., peat–bentonite mixture (Viraraghavan and Slough 1999), activated sludge biomass (Jianlong et al. 2000), spent mushroom compost (Law et al. 2003), pine bark (Brás et al. 2005), almond shell residues (Estevinho et al. 2006), coal fly ash (Estevinho et al. 2007), and fungal biomass (Mathialagan and Viraraghavan 2009).

According to Gupta et al. (2009), activated carbon is considered as an effective adsorbent but the high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper waste materials as potential adsorbents. Recently, activated carbons prepared from natural materials have captured the interest of many researchers for their high adsorption capacities and low cost compared to commercial activated carbons (CAC). In the adsorption technique, the major concern is the selection of adsorbent material (Mittal et al. 2009). In this respect, the production of activated carbon from agricultural by-products has potential economic and environmental impacts as it converts unwanted, low-value agricultural waste to a useful high-value adsorbent (Ekpete and Harcourt 2011).

Generally, two types of activation methods are employed in the production of activated carbon, namely physical and chemical activation (Olorundare et al. 2012). However, chemical activation is now widely applied for the activation because of its lower activation temperature and higher product yield compared with the physical one (Tongpoothorn et al. 2011). According to Tongpoothorn et al. (2011), it was found that alkaline hydroxides such as KOH and NaOH can be used to prepare activated carbons with high specific surface area. Although NaOH and KOH are related compounds, the reaction mechanisms of these two hydroxides are known to be different. KOH intercalates between carbon layers while NaOH reacts with the most energetic sites of the surface, thus presenting a reactivity that strongly depends on both rank and crystallinity of the carbonaceous precursor (Perrin et al. 2004), and sodium hydroxide activation was shown to be particularly interesting because of its low cost, simple handling, and low corroding action (Perrin et al. 2004).

The aims of this work were to utilize corn wastes for the preparation of activated carbons and to investigate the potential use of the prepared carbons for PCP adsorption from aqueous solution at different optimizing conditions. The present research was carried out during 2012–2013 in the laboratories of the *Holding Company for water and Wastewater, Greater Cairo Water Company,* Cairo, Egypt.

Materials and methods

Pentachlorophenol (PCP)

Pentachlorophenol used as an adsorbate in this study was supplied by Supelco Park, Bellefonte, chemical reagents Co. (USA), and was used without any further purification. The molecular weight of PCP is 197.45 g/mol and it has a chemical formula of $C_6H_3Cl_3O$. Corn cobs and corn nodes were obtained from the Egyptian Starch & Glucose Manufacturing Company (ESGC); the company generates corn waste of 247.042 tone/year. The CAC used in the present study is coconut shell-based activated carbon with the following specifications: ash (3 %), moisture (10 %), and bulk density (0.4 g/cm^3).

Activated carbon preparation and characterization

The activated carbons were prepared according to the procedure described by Tongpoothorn et al. (2011) with some modification. The starting materials (either corn nodes or corn cobs) were cleaned with water and dried at 110 °C for 48 h. The dried samples were crushed with a blender and sieved before they were carbonized at 400 °C for 1 h in a muffle furnace in order to produce charcoal. The charcoals obtained were then subjected to impregnation in NaOH solution by weight ratio (1 g charcoal/4 g NaOH) at 70 °C for 24 h. The resulting samples were further activated in a muffle furnace at 800 °C for 2 h. After cooling, the activated carbons were washed successively several times with 1 M HCl followed by hot water until the pH became neutral (= 7). Finally, the washed samples were dried at 110 °C. The obtained activated carbons prepared from corn cobs and corn nodes were abbreviated as CCAC and CNAC, respectively.

The prepared activated carbons were characterized by Fourier transformation infrared technique (FTIR) over the range of 500–4,000 cm^{-1} using Thermo Nicolet Avatar 370 FTIR Spectrometer, Thermo scientific co. The surface characteristics of the adsorbents were also investigated by scanning electron microscope (SEM) using JEOL, JSM-6490LA SEM–JEOL USA, Inc.

The pH point of zero charge (pH_{pzc}) was carried out by taking 50 ml of 0.1 M NaCl solutions in different closed Erlenmeyer flasks. The pH of the solution (pH_o) in each flask was adjusted to values of 2, 4, 6, 8, 10, and 12 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then, 0.2 g of each of the adsorbents was added and agitated in a shaker for 1 h and allowed to stay for 48 h to reach equilibrium with intermittent manual shaking. Then, the final pH value (pH_f) of the supernatant liquid was noted (Abdel Ghani et al. 2013). The value of pH_{pzc} is the pH at which $pH_o = pH_f$.

Pentachlorophenol (PCP) adsorption experiments

The effects of operation parameters on the adsorption of PCP onto corn waste-derived activated carbons such as pH (2–8), adsorbent dosage (0.5–4.0 g/l), initial PCP concentration (10–100 mg/l), contact time (30–300 min), and temperature (25–45 °C) were studied in a batch mode of operation. The solution pH was adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. In each batch experiment, a 250-ml stopper conical flask containing 50 ml PCP of certain concentration was mixed with a certain weight of each of the adsorbents and agitated mechanically at the controlled temperature in a shaking water bath at 200 rpm until equilibrium was reached. The mixture was then filtered and the remaining PCP concentration was determined at wavelength 305 nm using a spectrophotometer Jenway 6715 UV/Vis spectrophotometer, Bibby–Barloworld Scientific Ltd.

The amount of PCP adsorbed at equilibrium (adsorption capacity), q_e (mg/g) was calculated by the following equation:

$$q_e = \left[\frac{c_i - c_e}{w}\right] * v$$

whereas the PCP removal percentage (R %) was calculated by the following equation:

$$R\% = \left[\frac{c_i - c_e}{c_i}\right] * 100$$

where C_i and C_e are the PCP concentrations at the initial time and at equilibrium (mg/l), respectively. V is the volume of the solution (l) and W is the mass of adsorbent used (g).

Results and discussion

Determination of equilibrium time

Equilibrium time is one of the most important parameters for selecting a wastewater treatment system (Abdel Ghani and El-Chaghaby 2007). The equilibrium time for the adsorption of PCP onto (CNAC), (CCAC), and (CAC) was determined over a period from 30 to 300 min. The experiments were performed using an adsorbent dose of (2 g/l), initial solution pH (6), PCP concentration (10–100 mg/l), at room temperature (25 ± 2 °C), and 200 rpm shaking speed. The results are presented in Fig. 1a–c for CNAC, CCAC, and CAC, respectively. It can be observed that the adsorption of PCP onto the studied adsorbents generally increased by increasing the contact time until equilibrium was reached after 210, 240, and 180 min. for CNAC, CCAC, and CAC, respectively. The difference in the equilibrium time between the studied adsorbents might be due to the differences in the surface properties of the adsorbents (Gupta et al. 2011a). This result is interesting because equilibrium time is one of the important considerations for economical wastewater treatment applications (Mbadcam et al. 2011).

Thus, further experiments were conducted at 270 min to ensure maximum PCP adsorption by the studied adsorbents. Figure 1 also indicate that the total adsorption capacities increased with increasing the initial PCP concentrations from 10 to 100 mg/l, which may be attributed to the finding that the initial sorbate concentration provides an important driving force to overcome all mass transfer resistance (Cherifi et al. 2009).

pHpzc and effect of solution pH on PCP adsorption

The solution pH is largely related to the surface chemistry of the adsorbent and on the chemistry of the adsorbate in solution. The surface chemistry of the three investigated adsorbents (CNAC, CCAC, and CAC) has been studied by determining their point of zero charge pH (pH_{pzc}). The point of zero charge pH is the pH at which the surface charge of the solid phase is zero (Mubarik et al. 2012). Figure 2 shows the final against initial pH plots for the studied activated carbons. The intersection of each of these plots with the $y = x$ function is considered to be the pHpzc. The pHpzc was found to be around 3, 6, and 7 for the CAC, corn nodes activated carbon, and corn cobs activated carbons, respectively.

The higher pH_{pzc} values obtained for CCAC and CNAC as compared to the highly acidic pH_{pzc} value of CAC could be attributed to the preparation method of both CCAC and CNAC, which involved an alkali activation step. The acidic or basic pretreatments of the adsorbents caused a change in their surface acidity. According to Kang et al. (2008), acidic pretreatment produces many acidic surface groups, which increased the acidic value. In contrast, basic pretreatment of ACF and GAC decreases the number of acidic groups and increases the number of basic groups on the surface.

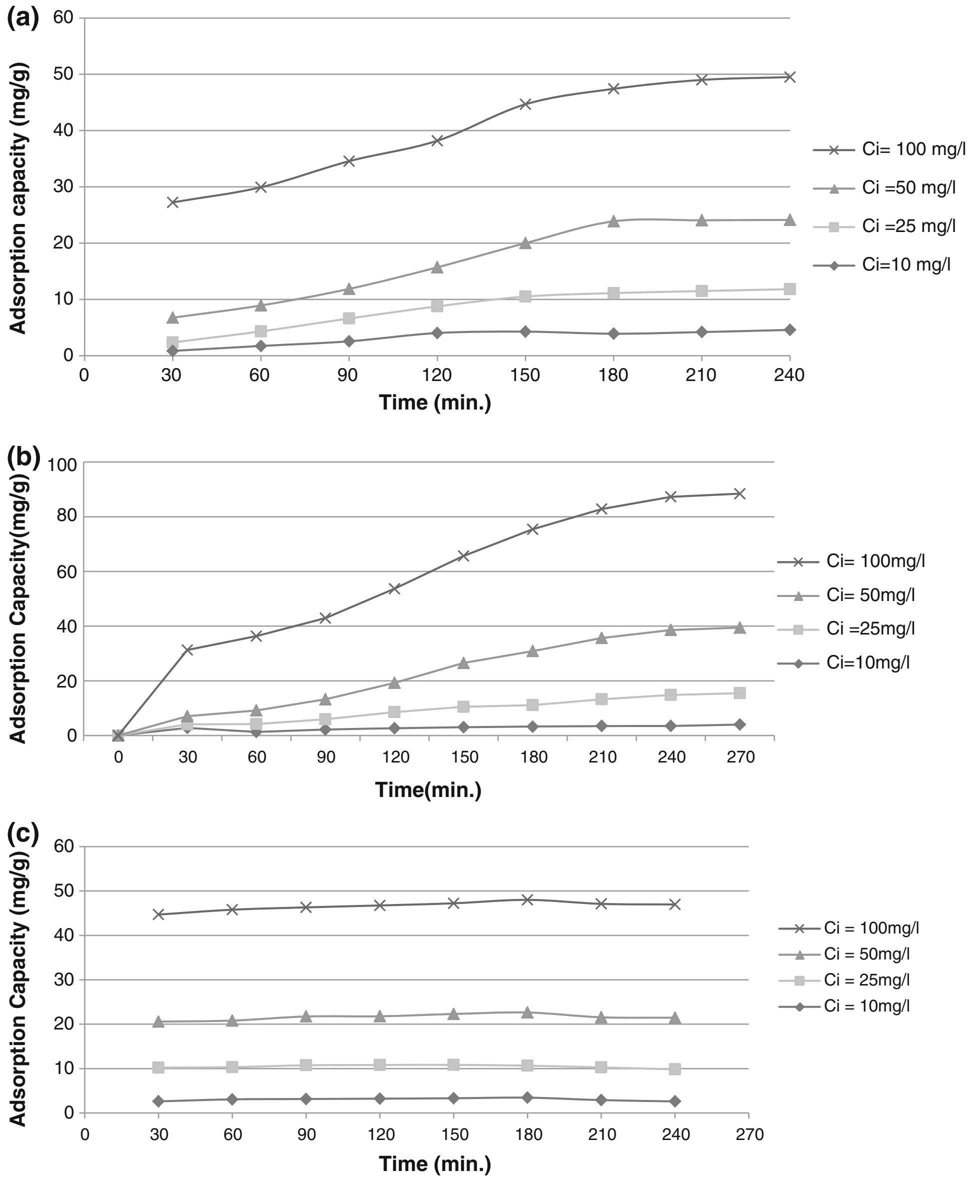

Fig. 1 Effect of contact time on PCP adsorption by **a** CNAC, **b** CCAC, and **c** CAC, adsorbent dosage = 2 g/l, pH:6.0, shaking speed: 200 rpm, Temp = 25 ± 2 °C

In order to find the optimum pH for maximum PCP removal onto CNAC, CCAC, and CAC, batch experiments were performed in the pH range from 2 to 8 using an adsorbent dose of 2 g/l and PCP solutions of 25 mg/l at room temperature. The results are presented graphically in Fig. 3.

The effect of pH on PCP removal by the three studied adsorbents can be explained as previously mentioned in terms of both the surface chemistry of the adsorbents and the chemistry of PCP in solution. The carbon surface is positively charged at pH < pHpzc and negatively charged at pH > pHpzc (Liu et al. 2010). It is also important to mention the chemical characteristics of PCP while discussing the effect of solution pH on biosorption. PCP, the strongest acid of the phenol family, has a pKa value of 4.75 (Schellenberg et al. 1984). Thus, PCP will be mainly in protonated form at pH < pKa and in deprotonated form at pH > pKa (Liu et al. 2010).

As can be seen from Fig. 3, the maximum uptake of PCP by CNAC and CCAC was achieved at pH = 6. At this pH value, the surface of CNAC will be neutral (pH = pHpzc) and the surface of CCAC will be positively charged (pH < pHpzc). It has also to be noted that at pH = 6, the PCP is mainly in its deprotonated form. Thus, attraction between PCP ions and the adsorbent's surface will take place. According to (Ould-Idriss et al. 2011) at pH values in the vicinity of neutrality, the adsorbents will tend to adsorb preferably cations, due to the cooperative effect of the net negative surface charge.

At pH values lower than the adsorbents pHpzc, the removal of PCP by CNAC and CCAC was minimal because of the repulsive forces existing between the

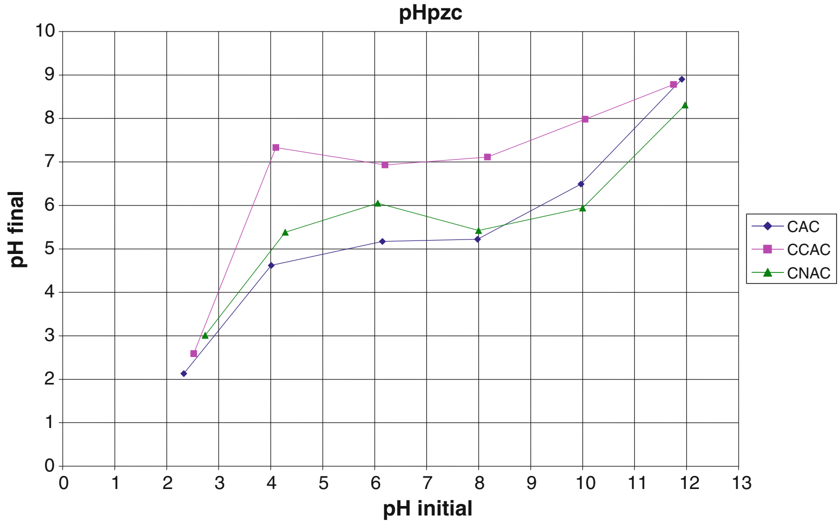

Fig. 2 The final against initial pH plots for the studied activated carbons

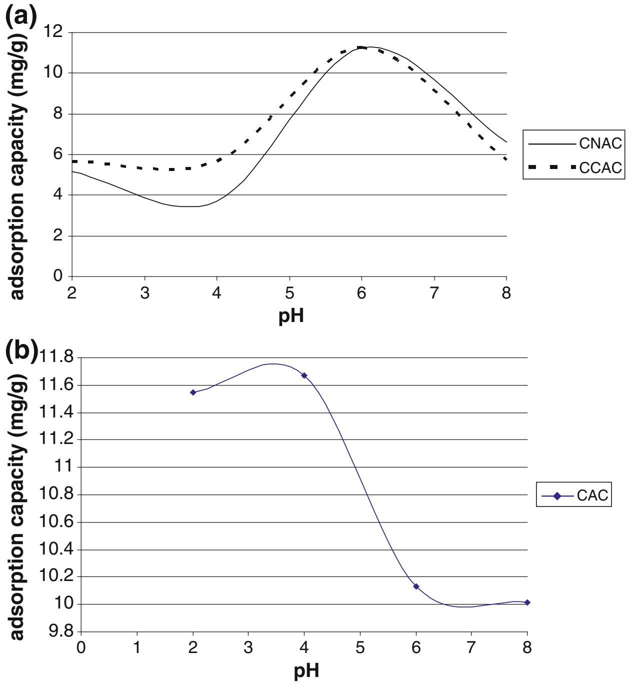

Fig. 3 Effect of pH on the adsorption of PCP by **a** CNAC, CCAC, and **b** CAC at PCP initial concentration = 25 mg/l, adsorbent dosage = 0.1 g/50 ml, contact time 270 min

positively charged activated carbon surface and the PCP present in its protonated form.

The removal of PCP by CNAC and CCAC decreased sharply after pH 6. This observation was attributed to the fact that at pH values higher than pHpzc, the adsorbent surface will be negatively charged. At the same time, PCP exists entirely in the anionic form at neutral and basic pH (Mathialagan and Viraraghavan 2009). Therefore, electrostatic repulsion between the negatively charged adsorbent surface and the anionic PCP will take place leading to lower adsorption.

Regarding the effect of pH on the removal of PCP by CAC, it can be seen from Fig. 3 that the percentage removal of PCP was maximum at pH = 4 and declined by increasing the pH above this value with a sharp decrease at pH > 8. Similar results were obtained by (Lü et al. 2011) for the adsorption of phenol by lignite activated carbon. According to these authors, at very low pH values, there are many positive charges on the surface of activated carbon, which gives a large static repulsion force. As pH increases, the static repulsion force decreases and the phenol adsorption increases. At pH > 8, the decrease in phenol adsorption may be resulted from three reasons. First, the negative charges on the surface of activated carbon increases with pH and phenol changes from molecular state to ionic state, which makes the repulsion force between phenol ions and the activated carbon significant. Second, the phenol ions adsorbed by the activated carbon also have a repulsion force between themselves. Third, the negative charges on the surface of activated carbon are repulsive that represses the disgregation of phenol ions and phenol adsorption.

Kinetic studies

Kinetic studies were conducted at the optimum pH predetermined for each of the investigated adsorbents using an adsorbent dose of 0.1 g; with 50 ml of PCP solution at different concentrations (10, 25, 50, and 100 mg/l). The pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data in order to predict the adsorption kinetics.

The pseudo-first-order equation can be written as follows (Lagergren, 1898): $\ln(q_e - q_t) = \ln q_e - k_1 t$, where

q_e and q_t (mg/g) are the amounts of PCP adsorbed at equilibrium and at time t, respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant. A straight line of $\ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model, and q_e and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model is in the following form: $t/q_t = 1/k_2q_e^2 + t/q_e$, where k_2 (g/mg min) is the rate constant of the second-order equation (Ho and McKay 1998). The plot of t/q_t versus t should give a straight line if pseudo-second-order kinetic model is applicable and q_e and k_2 can be determined from slope and intercept of the plot, respectively.

The constants calculated from the models are given in Table 1. As seen from Table 1, the determination coefficient (R^2) values of the pseudo-second-order kinetic model were higher than their corresponding (R^2) values of the pseudo-first-order kinetic model for the three studied adsorbents. Comparing the q_e values calculated from the kinetic models with the experimental q_e values, it can be noted that the q_e values calculated from the pseudo-second-order model are in good agreement with the experimental ones in contrary to those calculated from the pseudo-first-order model.

The obtained results thus are suggesting that the adsorption of PCP onto CNAC, CCAC, and CAC follows the pseudo-second-order kinetic model. These results indicate that the rate-limiting step for the adsorption of PCP onto the three studied carbons may be chemisorption (El-Naas et al. 2010). According to El-Naas et al. (2010), this may indicate that the adsorption takes place via surface exchange reactions until the surface functional sites are fully occupied; thereafter, phenol molecules diffuse into the activated carbon network for further interactions (such as inclusion complex, hydrogen bonding, and hydrogen phobic interactions (Bulut et al. 2008).

Adsorption mechanism study

It has been previously reported that usually intraparticle diffusion is the rate-limiting step in the adsorption of phenols from water on activated carbons (Lorenc-Grabowska et al. 2012).

The intraparticle diffusion equation, suggested by Weber and Morris (1963), can be expressed as follows: $q_t = K_t^{0.5} + C_{b.}$

Where q_t is the adsorbed quantity of PCP, K is the intraparticle diffusion parameter, and C_b is the thickness of the boundary layer.

The plot of q_t versus $t^{0.5}$ would give a straight line, when the adsorption (or sorption) process is controlled by intraparticle diffusion only, and if it exhibits multilinear plots, then there are two or more steps affecting the

Table 1 Pseudo-first- and second-order kinetic models' constants for the adsorption of PCP onto CNAC, CCAC, and CAC

Conc. (mg/l)	Corn nodes							Corn cobs							Commercial						
	$Q_{exp.}$ (mg/g)	First order			Second order			Q_{exp} (mg/g)	First order			Second order			$Q_{exp.}$ (mg/g)	First order			Second order		
		Qe calc. (mg/g)	K_1 (min^{-1})	R^2	Qe calc. (mg/g)	K_2 (g/mg. min)	R^2		Qe calc. (mg/g)	K_1 (min^{-1})	R^2	Qe calc. (mg/g)	K_2 (g/mg. min)	R^2		Qe calc. (mg/g)	K_1 (min^{-1})	R^2	Qe calc. (mg/g)	K_2 (g/mg. min)	R^2
10	4.57	5.20	0.013	0.781	4.25	8.291×10^{-3}	0.942	3.50	6.52	0.011	0.939	3.25	3.16×10^{-3}	0.984	3.4	2.04	0.012	0.314	3.18	31.85×10^{-3}	0.984
25	11.82	23.08	0.019	0.971	11.11	1.30×10^{-3}	0.971	11.00	17.06	0.015	0.909	9.90	0.89×10^{-3}	0.918	10.8	1.15	0.017	0.966	10.0	19.23×10^{-3}	0.994
50	24.11	122.24	0.031	0.816	22.73	0.43×10^{-3}	0.913	24.00	53.30	0.012	0.887	22.22	0.34×10^{-3}	0.946	22.6	3.76	0.015	0.905	22.22	56.26×10^{-3}	0.997
100	49.50	59.26	0.018	0.921	45.45	0.91×10^{-3}	0.984	48.98	51.11	0.012	0.907	45.46	0.53×10^{-3}	0.928	48	4.67	0.011	0.988	47.62	10.50×10^{-3}	0.999

Table 2 Intraparticle model's constants for the adsorption of PCP onto CNAC, CCAC, and CAC

Conc. (mg/l)	Corn nodes						Corn cobs						Commercial					
	K_1 (mg/g $min^{-0.5}$)	$C_{b\ (1)}$ (mg/g)	R^2	K_2 (mg/g $min^{-0.5}$)	$C_{b\ (2)}$ (mg/g)	R^2	K_1 (mg/g $min^{-0.5}$)	$C_{b\ (1)}$ (mg/g)	R^2	K_2 (mg/g $min^{-0.5}$)	$C_{b\ (2)}$ (mg/g)	R^2	K_1 (mg/g $min^{-0.5}$)	$C_{b\ (1)}$ (mg/g)	R^2	K_2 (mg/g $min^{-0.5}$)	$C_{b\ (2)}$ (mg/g)	R^2
10	0.541	2.287	0.965	0.326	0.496	0.990	0.429	1.959	0.987	0.155	1.171	0.913	0.134	1.927	0.909	0.091	41.110	0.975
25	1.224	4.736	0.989	0.338	6.570	1.000	0.791	3.217	0.953	1.237	8.097	0.934	0.126	9.473	0.835	0.059	17.980	0.990
50	1.932	5.098	0.942	0.119	22.280	0.937	1.372	5.067	0.953	2.403	12.95	0.971	0.279	18.930	0.843	0.348	**11.500**	0.585
100	2.506	11.91	0.939	1.006	33.930	0.998	1.787	13.810	0.948	2.927	4.149	0.943	0.406	42.510	0.984	0.509	2.221	0.979

adsorption process (Abdel Salam 2012). The experimental data for each of the three studied adsorbents show two distinct linear parts indicating that two steps are involved in the adsorption process. The first step is attributed to diffusion through the solution toward the external surface of the adsorbent or the boundary layer diffusion of solute molecules, whereas the second step corresponds to the gradual adsorption stage, where intraparticle diffusion is the rate-limiting step (Lorenc-Grabowska et al. 2012).

The values of the different parameters calculated from the plots of q_t versus $t^{0.5}$ for the intraparticle diffusion model are summarized in Table 2.

Adsorption equilibrium study

The analysis of the adsorption data is important for developing an equation that accurately represents the results and that could be used for design purposes (Gupta et al. 2010). Many equilibrium models have been used to describe adsorption process. In the present work, three of the most widely used equilibrium models such as Langmuir [Eq. (1)], Freundlich [Eq. (2)] and Temkin [Eq. (3)] were applied to fit the experimental data.

$$q_e = q_{max} b C_e / (1 + b C_e) \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

$$q_e = a_t + b_t \ln C_e \tag{3}$$

In these equations, q_e and C_e represent the adsorbent capacity at equilibrium (mg/g) and the concentration of PCP at equilibrium (mg/l). In the Langmuir equation, q_{max} is considered the maximum sorption capacity related to the total cover of the surface and b is associated with sorption energy. From the Freundlich model, K_F represents the sorption capacity and $1/n$ is related to the energy distribution of the sorption sites. The Temkin model constants a_t and b_t are related to the maximum binding energy and heat of adsorption.

The values corresponding to the Langmuir, Freundlich, and Temkin equation parameters are presented in Table 3. Comparing the R^2 values of the three models, it can be noticed that the Freundlich equation showed the best fit to the experimental data for the three studied adsorbents with ($R^2 > 0.99$). It can be also seen that the value of constant (n) is greater than unity indicating a favorable adsorption for the three studied activated carbons (Prakash Kumar et al. 2005).

In the present study, the maximum adsorption capacities (q_m) obtained from the Langmuir model for PCP removal onto CNAC, CCAC, and CAC were found to be 7.143, 5.260, and 9.090 mg/g, respectively. The maximum adsorption capacities for PCP removal onto various adsorbents as previously reported in the literature could be

Table 3 Adsorption isotherms' calculated parameters for the adsorption of PCP onto CNAC, CCAC, and CAC

Model	Equation	Parameters	Adsorbent		
			CNAC	CCAC	CAC
Langmuir	$q_e = q_{max}\, b\, C_e/(1 + bC_e)$	q_{max} (mg/g)	7.143	5.260	9.090
		b (l/mg)	0.667	0.323	0.105
		R^2	0.985	0.964	0.904
Freundlich	$q_e = K_F C_e^{1/n}$	K_f	16.07	1.245	3.56
		n	2.251	3.504	1.357
		R^2	0.990	0.995	0.995
Temkin	$q_e = a_t + b_t \ln C_e$	a_t	16.99	25.62	0.251
		b_t	24.16	64.51	0.029
		R^2	0.819	0.866	0.758

summarized as follows: 15.5 mg/g for spent mushroom compost (Law et al. 2003), 1.7 mg/g for pine bark (Brás et al. 2005), 2.5 mg/g for coal fly ash (Estevinho et al. 2007), 12.9 and 8.18 mg/g for activated charcoal and multiwall carbon nanotubes, respectively (Abdel Salam and Burk 2009).

Effect of temperature and adsorption thermodynamics

The experimental results obtained from PCP adsorption by CNAC, CCAC, and CAC at different temperatures (25, 35, and 45 °C showed that the removal percentage of PCP decreased with an increase in temperature, implying an exothermic nature of the adsorption process (El-Naas et al. 2010). According to Senturk et al. (2009), the decrease in adsorption with the rise in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the vicinal molecules of the adsorbed phase.

In order to gain an insight about the feasibility of the adsorption process, the thermodynamic parameters including free energy change ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated based on equations (IV-VI). In these equations, R is the universal gas constant (8.314 J mol/K) and T is the temperature (K). K_d is the distribution coefficient ($K_d = q_e/C_e$) where q_e and C_e are the equilibrium concentration of PCP on adsorbent (mg/g) and in the solution (mg/l), respectively.

Table 4 Thermodynamic parameters for the adsorption of PCP onto CNAC, CCAC, and CAC

		CNAC	CCAC	CAC
ΔG (J/mol)	(25 °C)	−9,778.625	−8,496.331	−7,312.008
	(35 °C)	−8,054.104	−6,935.52	−8,953.996
	(45 °C)	−4,596.857	−3,628.754	−4,749.212
ΔH (KJ/mol)		−84.821	−78.981	−43.557
ΔS (J mol/K)		−251.584	−236.211	−119.163

$$\Delta G° = -RT \ln K_d \tag{4}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{5}$$

$$\ln K_d = (\Delta S°/R) - \Delta H°/RT \tag{6}$$

The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$, respectively (Fig. 4). The values of the thermodynamic parameters evaluated in the present study are presented in Table 4. Negative $\Delta G°$ values were obtained for the adsorption of PCP on the three studied adsorbents indicating spontaneous nature of the adsorption (Ahmed and Theydan 2012) and the feasibility of the process (Mittal et al. 2008, 2010).

In accordance with the experimental results, negative values were obtained for the enthalpy of adsorption $\Delta H°$, which gives a further confirmation on the exothermic nature of the adsorption process. The negative $\Delta S°$ values suggest according to (Ahmed and Theydan 2012) a decrease in the randomness at sorbate/solution interface during the adsorption process.

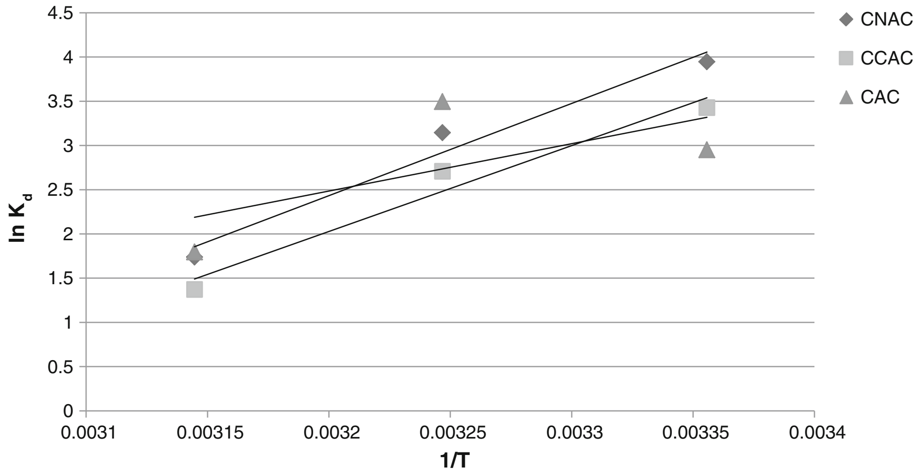

Fig. 4 Plots of 1/T versus $\ln K_d$ for the adsorption of PCP by CNAC, CCAC, and CAC

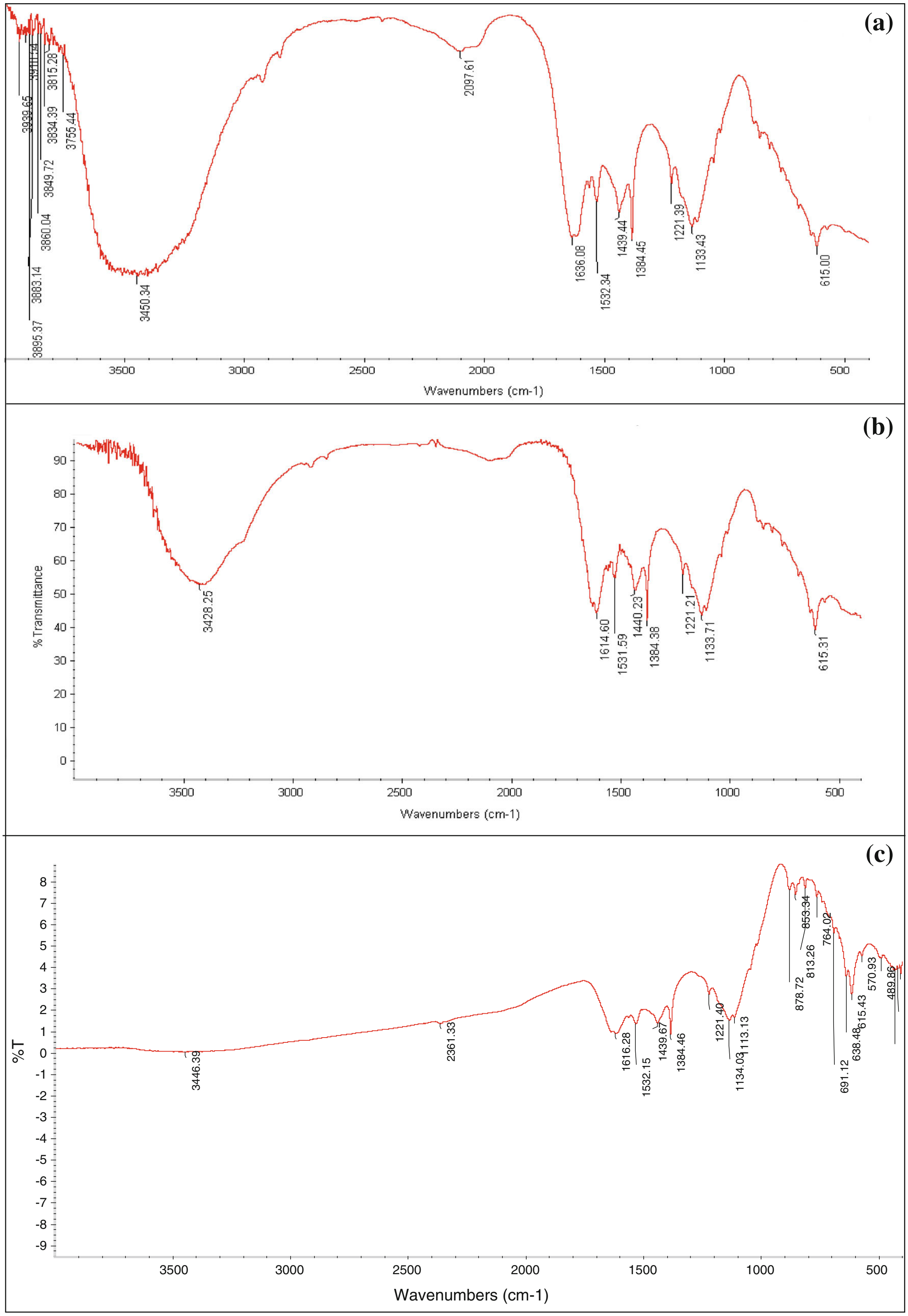

Fig. 5 FTIR spectrum of y **a** CNAC, **b** CCAC, and **c** CAC

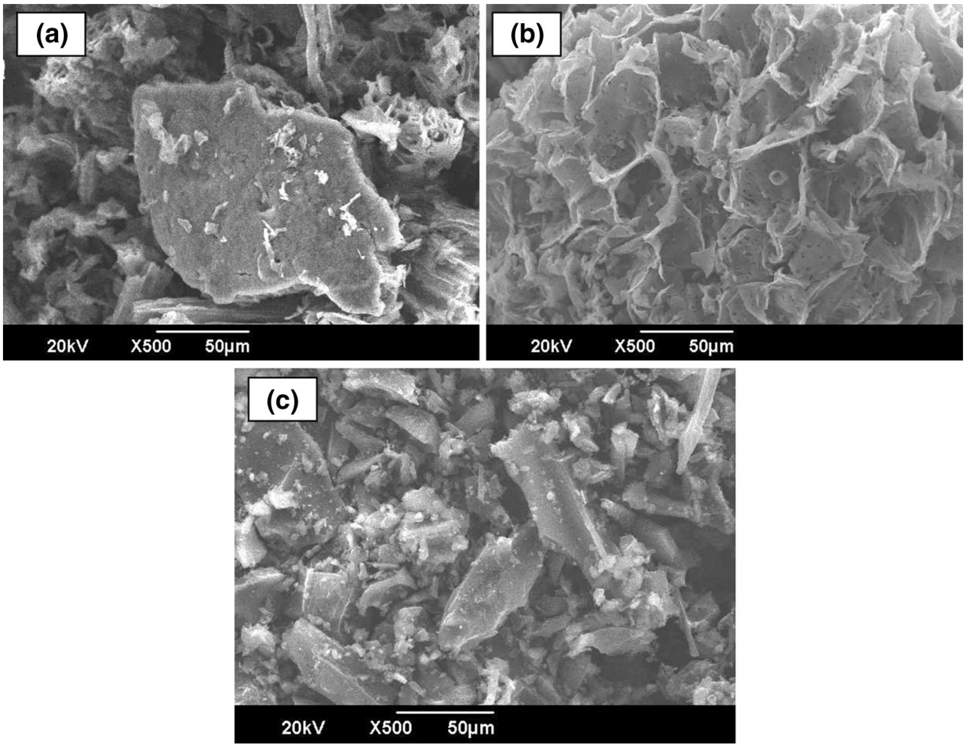

Fig. 6 SEM micrographs of **a** CNAC, **b** CCAC, and **c** CAC

Adsorbents characterization

The FTIR spectra of the activated carbons prepared from corn nodes and corn cobs as well as CAC are shown in Fig. 5. It can be observed that the spectra of the activated carbons prepared from corn wastes are quite similar, whereas these spectrum varied by some deviations when compared to the CAC spectrum.

The spectrum of CNAC (Fig. 5a) depicts a strong peak at 3,450.34 cm^{-1} and a similar band but with smaller intensity was observed in the CCAC spectrum (Fig. 5b) at 3,428.25 cm^{-1} these bands are characteristic of the stretching vibration of hydrogen bonded to the hydroxyl group (from alcohol, phenol, or carboxyl) and water adsorbed by the activated carbon (Olorundare et al. 2012) or adsorption of some atmospheric water during FTIR measurements (Gupta et al. 2011b). On the other hand, the spectrum of CAC (Fig. 5c) displayed very weak and broad band at 3,446.39, which is due to either moisture, O–H, or carboxylic groups. Another band was observed at 2,361.33 cm^{-1}, which may be attributed to C–H interaction with the surface of the carbon. The bands around 1,384 and 1,440 cm^{-1} displayed in all spectra are assigned to C–H vibration for –CH$_3$– and –CH$_2$ = (El-Hendawy 2009). The FTIR bands in the region between 1,430 and 1,660 cm^{-1} are generally ascribed to the skeletal C = C vibrations in the aromatic rings (El-Hendawy 2009). The band around 1,220 cm^{-1} in Fig. 5 was assigned to C–O–C asymmetrical axial deformation of ethers or C–C (= O)–C axial and angular deformation of ketones (Vargas et al. 2011). The FTIR analysis of the adsorbents revealed the presence of many functional groups such as hydroxyl groups, carbonyl group, ethers, and aromatic compounds capable of binding the adsorbate molecules present in solution.

Figure 6 displays the SEM micrographs of CNAC, CCAC, and CAC. The surface morphology of corn nodes activated carbon (Fig. 6a) reveals a cracked surface with irregular holes. The SEM micrograph of corn cobs activated carbon (Fig. 6b) shows a rough texture with heterogeneous surface and a variety of randomly distributed pore size. The CAC (Fig. 6c) has a rough and heterogeneous surface with some cracks. The texture of the studied adsorbents as observed from their SEM micrographs indicates relatively high surface area (Tongpoothorn et al. 2011).

Conclusion

Activated carbons prepared from corn wastes have been successfully used as adsorbents for the removal of PCP from aqueous solution. The adsorption of PCP onto the studied adsorbents reached its equilibrium in a short time (180–240 min.). The adsorption was found to follow the pseudo-second-order kinetic model with intraparticle diffusion as the rate-limiting step. The Freundlich equilibrium model showed the best fit to the experimental data. The maximum adsorption capacities calculated from the Langmuir equation were found to be 7.143 and 5.260 for the activated carbons prepared from corn nodes and corn cobs, respectively. Compared to CAC, the cost of the suggested corn waste-based activated carbons is extremely low and their use for wastewater treatment is suggested to be better from economical and environmental points of view.

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