

Removal of Phenol from Paint Wastewater by Adsorption onto Phosphoric Acid Activated Carbon Produced from Coconut Shell: Isothermal and Kinetic Modelling Studies

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Abstract

The feasibility of using phosphoric acid activated carbon produced from coconut shell to remove phenol from paint wastewater under batch mode was investigated. The results showed that adsorption of phenol was contact time, adsorbent particle size and adsorbent dosage dependent. The batch equilibrium adsorption data were analyzed by two-parameter adsorption isotherm models of Langmuir and Freundlich using the linear regression method. Both isotherm models fitted very well to the equilibrium adsorption data, however, the Freundlich isotherm equation provided the best model to describe the adsorption of phenol onto coconut shell activated carbon. Adsorption capacity (K_f) of 2.01 mg/g and adsorption intensity (n) of 1.07 was obtained for granular coconut shell activated carbon and corresponding 3.63 mg/g and 1.55 for powdered coconut shell activated carbon at 30 °C. The adsorption kinetic data were fitted to three adsorption kinetic models (pseudo first-order, pseudo second-order and intra-particle diffusion) using the linear regression method. The three kinetic models fitted well to the adsorption kinetic data; however, the pseudo second-order kinetic model gave the best fit and the adsorption mechanism was controlled by film diffusion. Thus, phosphoric acid activated carbon produced from coconut shell has the potential for application as an effective adsorbent for phenol removal from wastewater.

Keywords: Activated carbon; Adsorption isotherms; Adsorption kinetics; coconut shell; paint wastewaters.

1. Introduction

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of waste waters (Annadurai et al., 2000). More than two thousand chemical contaminants have been found in waste waters and over 600 are of organic origin (Annadurai et al., 2000). Effluents of paint manufacturing company (PMW) contain highly toxic compounds and organic biorefractory compounds such as phenol (Akyol, 2012). Phenol is a listed priority pollutant by the U.S. Environmental Protection Agency (EPA, 1979) and is considered to be a toxic compound by the Agency for Toxic substances and Disease Registry (ATSDR, 2003). The adverse effects of phenol on health are well documented (Calabrese and Kenyon, 1991) and death among adults has been reported with ingestion of phenol ranging from 1 to 32g (Prpich and Daugulis, 2005). The low volatility of phenol and its affinity for water make oral consumption of contaminated water the greatest risk to humans (Prpich and Daugulis, 2005). Generally, paint wastewaters have adverse effects on human health. If used in closed areas, its chemical components can irritate eyes, skin and lungs and causes headaches and nausea. It can also contribute to respiratory problems; muscle weakness, liver and kidney damage (Akyol, 2012).

Therefore, removing phenols from wastewaters is important prior to discharging wastewater into the environment. Consequently, many treatment processes have been applied for the removal of phenols from waste waters. Some of these processes include: adsorption (Tan et al., 2009; Hamad et al., 2011), photo-fenton degradation (Poulopoulos et al., 2008), catalytic wet oxidation (Chaliha and Bhattacharyya, 2008), photocatalytic degradation (Laoufy et al., 2008; Devipriya and Yesodharan, 2010), and biodegradation (Agarry et al., 2008; ElKarmi et al., 2009). Liquid-phase adsorption has been shown to be an effective way for removing suspended solids, odors, organic matter, and oil from aqueous solutions (Annadurai et al., 2002). Activated carbon is most widely used as adsorbent in the removal of heavy metals, hydrocarbons and other hazardous chemicals (Hameed, 2009) which may be found in waste waters because of its high adsorptive capacity, but its high cost and difficulty in regeneration limits its commercial application in large-scale waste water treatment (Popuri et al., 2007).

Most of the active carbon is black powder or granular amorphous carbon. In addition to its main component carbon, it also contains oxygen, hydrogen and other elements. Activated carbon has large specific surface area and good adsorption characteristics (Zhang et al., 2012). Adsorption on activated carbon is one of

the most efficient techniques used in water treatment process for the removal of organics and micro pollutants from wastes and drinking waters (Abassi and Stree, 1999). Activated carbon has been reported to have high and fast adsorption capacities (Chaiwattananont et al., 1998) due to its well developed porous structure, high surface area and high degree of surface reactivity (Ozcan and Ozcan, 2005). However, because of high cost of commercial activated carbon, its use in the field is sometimes restricted on economical considerations especially in developing countries like Nigeria. As such, attempts have been made by different researchers in recent years to develop activated carbons from preferably low cost materials such as industrial wastes as well as natural agricultural by-products (bagasse, palm date pits, palm shell, coconut husk, rubber seed pericarp, acanthaceae, periwinkle shell, bamboo) which are ubiquitous green waste in the environment for the removal of pollutants from waste waters (Sirichote et al., 2002; Vinod and Anirudhan, 2002; Mohammed et al., 2005; Badmus et al., 2007; Hamad et al., 2011; Hussain et al., 2012; Agarry and Owabor, 2012). The characteristics of agricultural plant materials, such as polar and aromatic components, impose a significant influence on their sorptive behavior (Chen and Schnoor, 2009). More and more interests are focused on developing these agricultural wastes as adsorbent for wastewater treatment due to their relative high sorption affinity, ubiquitous presence in the environment, and the ease of being modified to materials with higher efficiency (Li et al., 2010; Chen et al., 2011; Agarry and Aremu, 2012). Therefore, efforts are still needed to produce activated carbon from low cost adsorbents that have high adsorption capacity.

Coconut palm (*Cocos nucifera*) is a member of the Arecaceae family (palm family). The coconut palm is grown throughout the tropics. It sustains the livelihood of millions of people in coastal regions of the tropical world (Hameed et al., 2008). It is one of the most important crops in Nigeria and thus, a large amount of coconut shells are generated annually which has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Therefore, any attempt to reutilize this waste will be useful as it will help in reducing environmental wastage. However, there is a dearth of information on the use of coconut shell activated carbon in the removal of phenol as organic pollutant from raw paint wastewater using the adsorption technology. Most of the information in literature reported the removal of phenol from simulated or synthetic phenol aqueous solution (Namasivayam and Kavitha, 2004; Sathishkumar et al., 2009; Ma et al., 2010; Hamad et al., 2011). Thus, this study was undertaken to prepare activated carbon from coconut shell using phosphoric acid as the activating agent to remove phenol from raw paint wastewaters. The adsorption isotherms and kinetics of phenol removal onto the coconut shell-derived activated carbon was obtained.

2. Materials and Methods

2.1 Sample Collection

Paint wastewaters were obtained from two different paint industries located in Lagos of Nigeria. Coconut shells were obtained from Ogbomoso market in Nigeria.

2.2 Carbonization of Coconut Shell and Its Chemical Activation

The starting raw material, coconut shell (agricultural by-product) was sun dried and crushed into small chips (< 1 mm and > 1 mm particle sizes) prior to carbonization process. It was then placed in a stainless steel container with a cover and put in a furnace. The sample was heated at 400°C for a period of 3 h. After the pyrolysis, the pyrolysed sample (residual char) was allowed to cool and washed with deionized water to remove any left impurities. The washed residual char was dried in an oven at 110°C for 1 h. The next step was the chemical activation. This was done by mixing 100 g of the residual charcoal with 200 ml of phosphoric acid (H₃PO₄) and left for 48 h. After decantation, the sample was pyrolysed at 500°C for 3 h in a furnace. The obtained activated carbon was allowed to cool and then washed with potassium hydroxide (KOH) and deionized water. It was then dried in an oven at 110°C for 3 h. Chemical activation of the carbonized coconut shell was repeated at activation temperature of 600, 700, 800, 900 and 1000 °C, respectively. The activated carbons thus obtained were finally smoothed, stored in well-fitted airtight corked bottles and properly labeled before being characterized.

2.3 Characterization of Coconut Shell-Derived Activated Carbon

The coconut shell-derived activated carbon was characterized for specific surface area, iodine number and functional groups. The specific surface area of the adsorbent was determined using methylene blue (MB) sorption method (Unnithan et al., 2002; Agarry et al., 2013a). Methylene blue aqueous solutions, in the concentration range of 10 to 50 mg/l, were allowed to agitate with 2 g of adsorbent till the attainment of equilibrium. The concentration of MB solutions was determined at 664 nm. The adsorption isotherm data that were obtained was used to calculate specific surface area using Eq. (1):

$$A_s = (M_f \frac{N}{10^5}) A_m 10^{-20} \quad (1)$$

Where A_s is the specific surface area (m^2/g); M_f is the amount of MB (in μmol) adsorbed per 100 g of the biosorbent when the surface is completely covered with a monolayer of MB; N is the Avogadro number, and A_m is the cross-sectional area per molecule on the surface (130 \AA^2). The value of M_f was obtained by extrapolating the isotherm to the q_e and thus taken as point of monolayer coverage. The coconut shell-derived activated carbon was characterized for surface functional groups by Fourier Transform Infra Red Spectroscopy (FT-IR) method using a Perkin-Elmer 2000 infrared spectrometer. The spectrum of the biosorbent was recorded in $400\text{--}4000 \text{ cm}^{-1}$.

The carbonaceous adsorbents were characterized for iodine number in accordance with ASTM (1995). The iodine number gives an indication of the adsorption capacity of activated carbon in microspores (that is, an indication of porosity) (Rengaraj et al., 2002). For the determination of iodine number, 0.1 g of the sample was taken into a 250 ml conical flask. About 10 ml 0.05 M iodine solution in aqueous potassium iodide was added into the flask. After 1 h, the solid mass was separated by centrifuging the mixture and the residual iodine in solution was titrated using 0.1 M sodium thiosulphate solution. The iodine number was calculated as mg of iodine adsorbed by one gram of activated carbon. The samples of carbonaceous adsorbent were tested for pH by stirring with deionized water for 2 h and left for 24 h after which the pH of the water was taken.

2.4 Batch Adsorption Equilibrium Studies

The batch adsorption tests were carried out in a glass-stoppered 250 ml Erlenmeyer conical flask with 100 ml of working volume and an initial phenol concentration of 35 mg/l present in the paint wastewater having a pH of 6. A weighed amount (0.5 g) of granular adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 180 min in a temperature controlled water bath shaker at 30°C . Samples were collected from the flasks at predetermined time intervals for analyzing the residual phenol concentration in the wastewater. Prior to analysis, samples were centrifuged to separate adsorbent from the adsorbate and minimize interferences. The residual phenol concentrations were determined using UV-spectrophotometer at an absorbance wavelength of 340 nm. The procedure was repeated for granular adsorbent dose of 1.0, 2.5, 5.0, 10 g and powdered adsorbent dose of 0.5, 1.0, 2.5, 5.0 and 10 g, respectively. The amount of adsorption at equilibrium, q_e (mg/g) was calculated according to Eq. (2) (Crisafulli et al., 2008):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where C_o and C_e (mg/l) are the initial and final (equilibrium) concentrations of phenol in waste water. V (ml) is the volume of the waste water and W (g) is the mass of dry adsorbent used.

2.5 Batch Kinetic Studies

The procedures for kinetic studies were basically identical to those of batch equilibrium studies. The amount of phenol adsorbed at time t , q_t was calculated according to Eq. (3) (Xun et al., 2007):

$$q_t = \frac{(C_o - C_t)V}{W} \quad (3)$$

Where C_t is the concentration of phenol in waste water at time, t . Where the percentage of phenol removal was calculated using Eq. (4) (Hamad et al., 2011):

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (4)$$

2.6 Adsorption Isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir and Freundlich models were used to describe the equilibrium data.

The Langmuir isotherm model (Langmuir, 1918) is given in Eq. (5):

$$q_e = \frac{Q_{\max} a C_e}{1 + a C_e} \quad (5)$$

Where Q_{\max} and a are isotherm constants. Langmuir constant (Q_{\max}) is a measure of the amount of adsorbate sorbed per unit weight of adsorbent, when saturation is attained. Langmuir constant (a) is related to energy of adsorption (i.e. affinity of the binding sites). Where Q_{\max} and a can be determined from the linear plot of $1/q_e$ vs. $1/C_e$. Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface (Popuri et al., 2007). The basic assumption of Langmuir model is that sorption takes place at specific sites within the adsorbent. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place.

The Freundlich isotherm model (Freundlich, 1906) is given in Eq. (6):

$$q_e = K_f C_e^{1/n} \quad (6)$$

Where K_f and n are Freundlich constants. K_f is roughly an indicator of the adsorption capacity (mg/g) and n is the adsorption intensity. The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surface energy systems (Annadurai et al., 2000). It suggests that binding sites are not equivalent and/or independent. Where, K_f and $1/n$ can be determined from the linear plot of $\log q_e$ vs. $\log C_e$.

2.7 Adsorption Kinetics Modelling

In order to analyze the rate of adsorption and possible adsorption mechanism of phenol onto granular and powdered coconut shell-derived activated carbon, the Lagergren pseudo first- order (Lagergren, 1898), pseudo second-order (Ho and Mckay, 2000) and intraparticle diffusion (Weber and Morris, 1963) were applied to adsorption data.

The Lagergren pseudo first-order kinetic model equation (Lagergren, 1898; Mckay and Ho, 1999) is represented in an integral form as given in Eq. (7):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

Where, q_e is the calculated maximum equilibrium adsorption capacity (mg/g) and k_1 is the adsorption rate constant (min^{-1}). The values of q_e and k_1 were calculated from the slope and intercept of the linear plots of $\ln(q_e - q_t)$ vs t .

The pseudo-second- order kinetic model which is based on the assumption that chemisorption is the rate-determining step and can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where k_2 is the rate constant of second order biosorption (g/mg/min). The initial adsorption rate, h ($\text{mg g}^{-1} \text{min}^{-1}$) is represented as in Eq. (9) (Sari et al., 2010):

$$h = k_{ad2} q_e^2 \quad (9)$$

Values of k_2 and q_e were calculated from the plots of t/q_t vs. t for granular and powdered coconut shell-derived activated carbon.

The Weber and Morris (1963) intra particle diffusion kinetic model can be written as presented in Eq. (10):

$$q_t = K_p t^{1/2} + C \quad (10)$$

Where K_p is the intra particle diffusion rate constant ($\text{mg/g min}^{-1/2}$) and C is the intercept.

The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. Intra particle diffusion is the sole rate-limiting step if the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin (Weber and Morris, 1963; Agarry et al., 2013a, 2013b).

3. Results

3.1 Characterization of Coconut Shell Activated Carbon

FT-IR spectrum of coconut shell activated carbons were obtained in order to identify the functional groups like -OH, -CO, -CHO, N-H, - CONH, -C=C- and -COOH present in them that can be involved in bonding with phenol during adsorption. The FTIR Analysis result (Table 1) shows the transmittance spectra of the coconut shell, granular coconut shell activated carbon, and powdered coconut shell activated carbon.

Table 1. FTIR spectrum elucidation of coconut shell (CS), granular coconut shell activated carbon (GCSAC) and powdered coconut shell activated carbon (PCSAC)

| Wavelength Range (cm ⁻¹) | Absorption peak number (cm ⁻¹) for CS | Absorption peak number (cm ⁻¹) for GCSAC | Absorption peak number (cm ⁻¹) for PCSAC | Suspected functional groups |
|--------------------------------------|---|--|--|--|
| 3700-3200 | 3625-3210 | 3528 | 3520 | OH groups |
| 3000-2800 | 2904-2862 | 2895 | 2893 | CH stretching |
| 1750-1700 | 1739-1710 | 1724.7 | 1725 | C=O stretch |
| 1670-1500 | 1658.7-1525.2 | 1598.4 | 1598 | COOH and C=C stretch (alkenes), NH ₂ deformation, NH deformation |
| 1450-1250 | 1450 -1260 | 1368.6 | 1368.3 | C-H bend, C-O, C-N, and OH, COOH) and amide group (N-H bending), CH ₂ deformation |
| 1150-1050 | - | 1108 | 1107 | C-O (alcohol), C-N stretch (nitriles), C-H bending (alkanes), PO ₄ ³⁻ stretching |

The values of the specific surface area, iodine number, bulk density, ash content and moisture content obtained for the granular and powdered coconut shell activated carbons are presented in Table 2.

Table 2: Characterization of coconut shell carbon activated at 900 and 1000°C

| Particle size | Activation temperature (°C) | Bulk density (g/cm ³) | Ash content (%) | Iodine number (m ² /g) | Specific surface area (m ² /g) |
|-------------------------------|-----------------------------|-----------------------------------|-----------------|-----------------------------------|---|
| Granular coconut shell carbon | 900 | 0.311 | 2.65 | 487 | 1076.09 |
| Powdered coconut shell carbon | 900 | 0.265 | 2.63 | 679 | 1344.83 |
| Granular coconut shell carbon | 1000 | 0.295 | 2.64 | 568 | 2148.27 |
| Powdered coconut shell carbon | 1000 | 0.254 | 2.62 | 700 | 2406.52 |

3.2 Effect of Temperature on Carbon Yield

Fig. 1 shows the effect of activation temperature on the yield of carbon from coconut shell of different particle size (> 1 mm and < 1 mm).

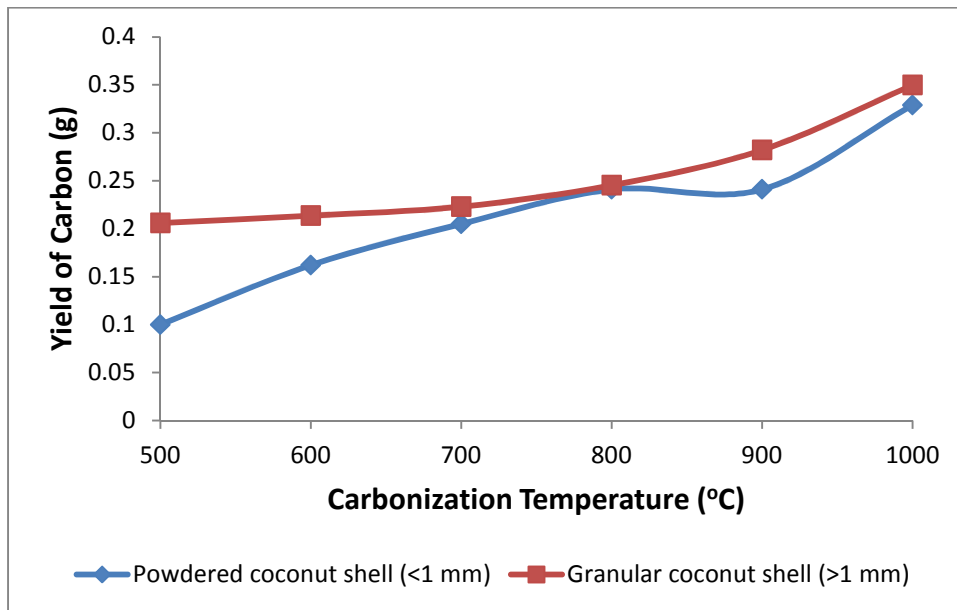


Fig. 1: Effect of temperature on the yield of carbon from coconut shell

3.3 Effect of Adsorbent Particle Size

Result for the effect of adsorbent particle size on the adsorption of phenol by coconut shell-derived activated carbon is as shown in Fig. 2.

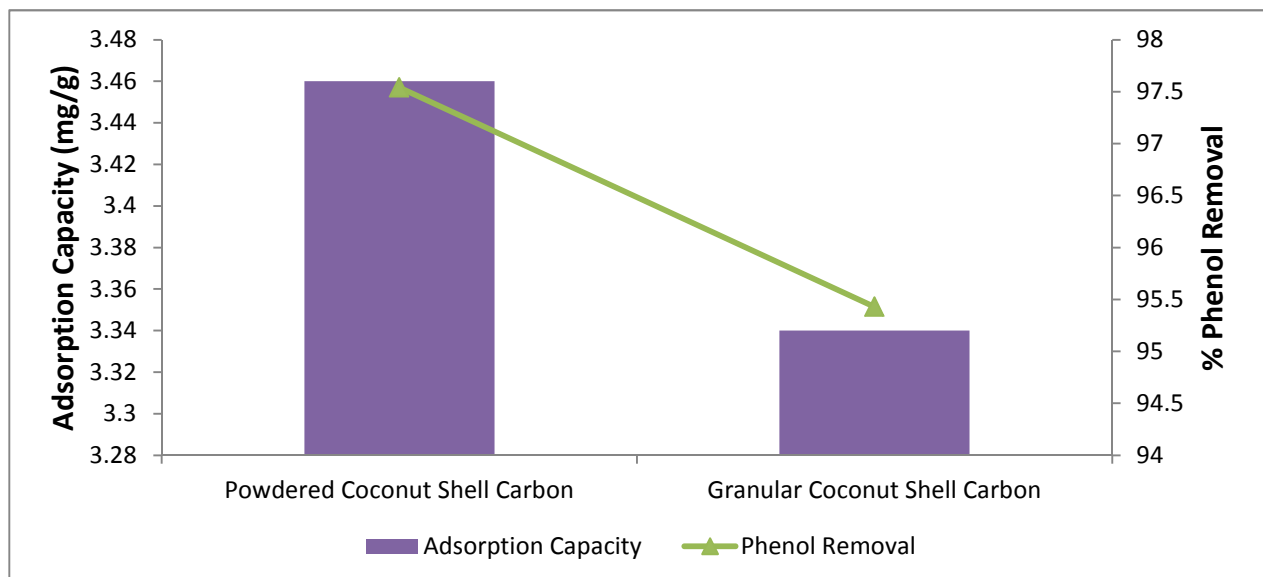


Fig. 2: Effect of adsorbent particle size (granular and powdered coconut shell activated carbon) on phenol adsorption

3.4 Effect of Adsorbent Dosage

In this study, five different adsorbent dosages were selected ranging from 0.5 to 10 g while the phenol concentrations present in the paint wastewater is 35 mg/l. The results are presented in Fig. 3.

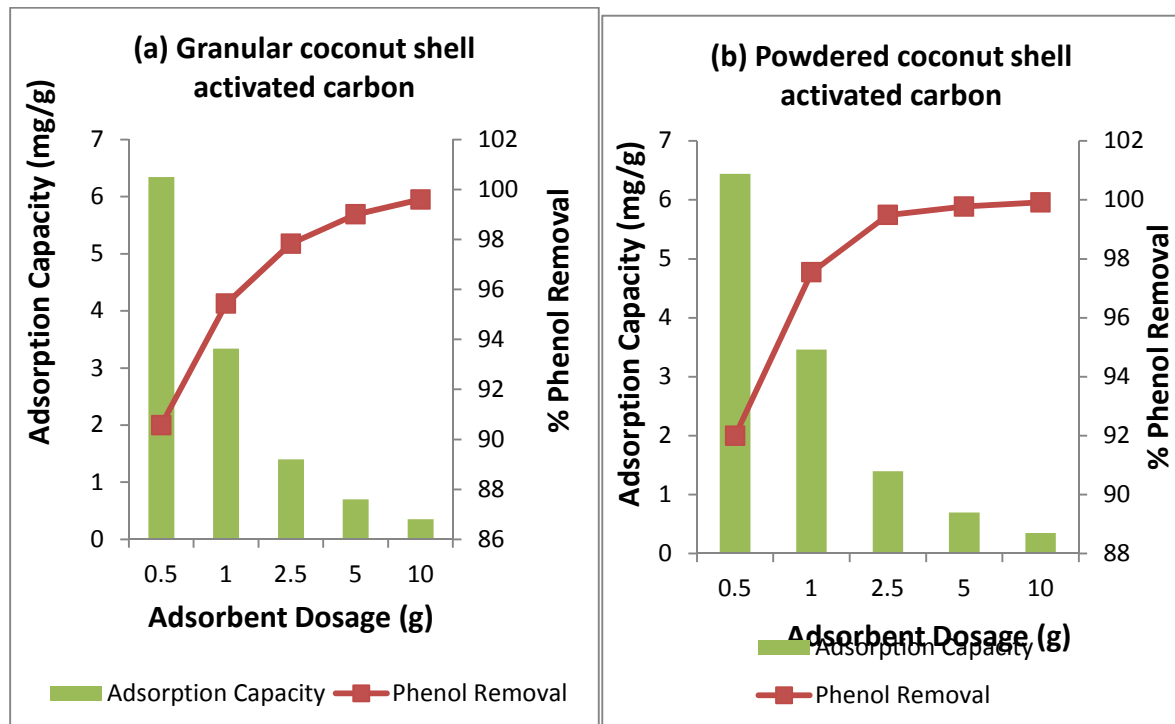
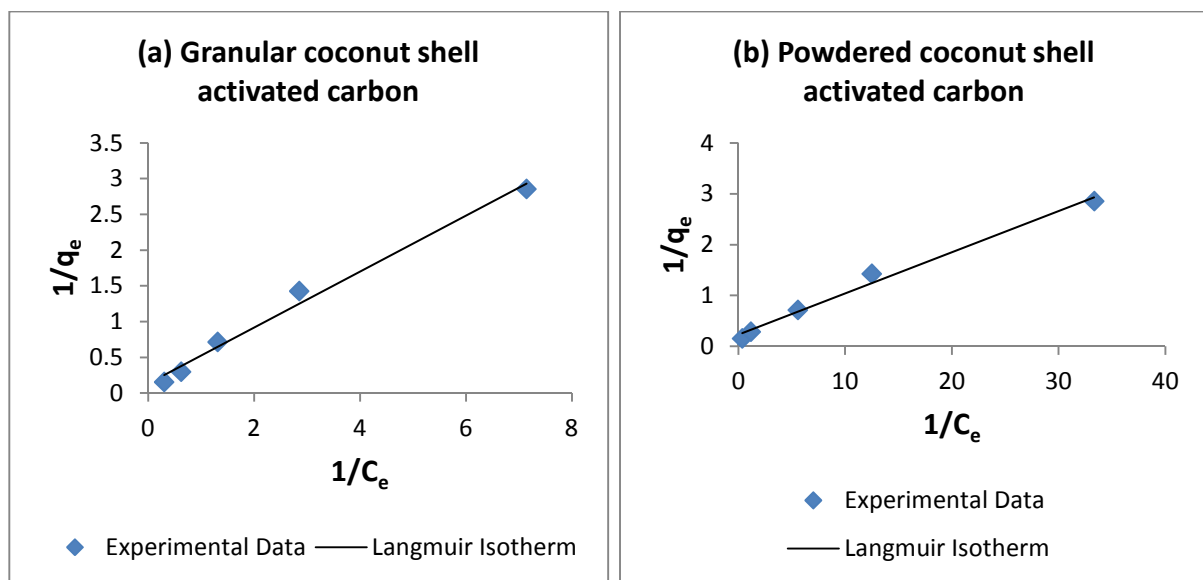


Fig. 3: Effect of adsorbent dosage on phenol adsorption by (a) granular coconut shell activated carbon, (b) powdered coconut shell activated carbon

3.5 Adsorption Isotherms

The isotherm plots of Langmuir and Freundlich for granular and powdered coconut shell activated carbon are presented in Fig. 4 and the estimated isotherm constants from the plot are presented in Table 3.



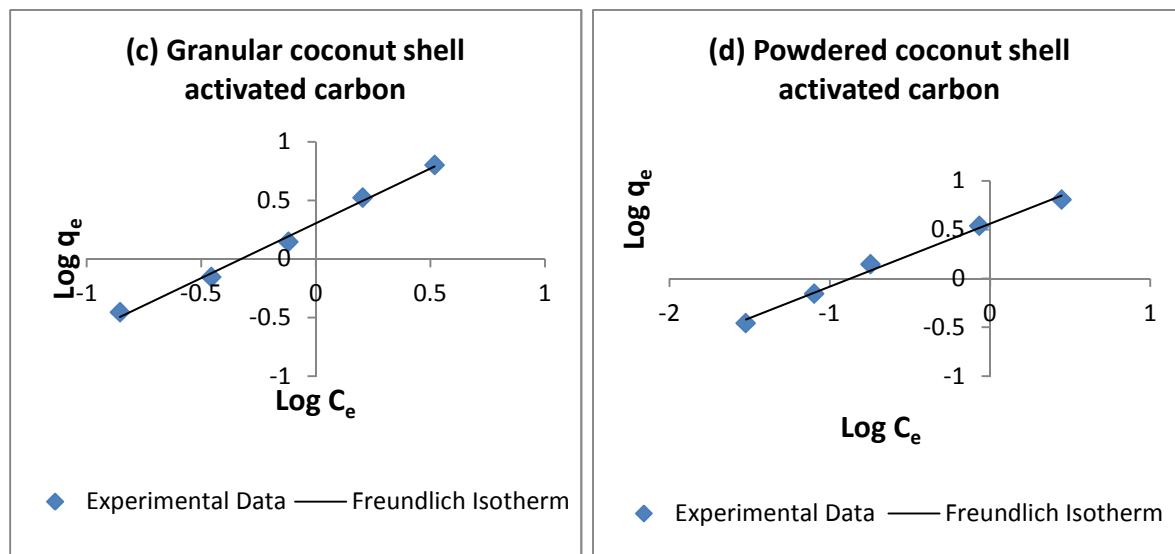


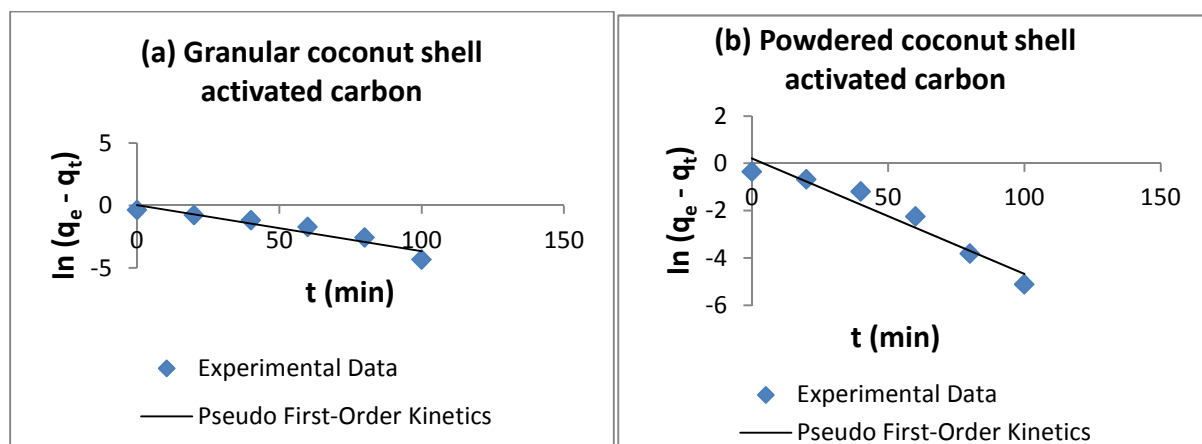
Fig. 4: Langmuir isotherm model fitted to the phenol equilibrium adsorption data for (a) granular coconut shell-derived activated carbon, (b) powdered coconut shell-derived activated carbon. Freundlich isotherm model fitted to the phenol equilibrium adsorption data for (c) granular coconut shell activated carbon, (d) powdered coconut shell activated carbon.

Table 3. Adsorption isotherm parameters and correlation coefficients obtained for phenol adsorption by coconut shell activated carbon

| Isotherm models | Granular coconut shell activated carbon | Powdered coconut shell activated carbon |
|--------------------|---|---|
| Langmuir | | |
| q_{max} (mg/g) | 7.58 | 4.31 |
| a (L/mg) | 0.3376 | 12.5 |
| R^2 | 0.9880 | 0.9890 |
| Freundlich | | |
| K_f (mg/g)(L/mg) | 2.01 | 3.63 |
| n | 1.07 | 1.55 |
| R^2 | 0.9940 | 0.9920 |

3.6 Adsorption Kinetics Modelling

The plots of fitted pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models to the adsorption kinetic data are presented in Fig. 5 while the estimated constants of these models are given Table 4.



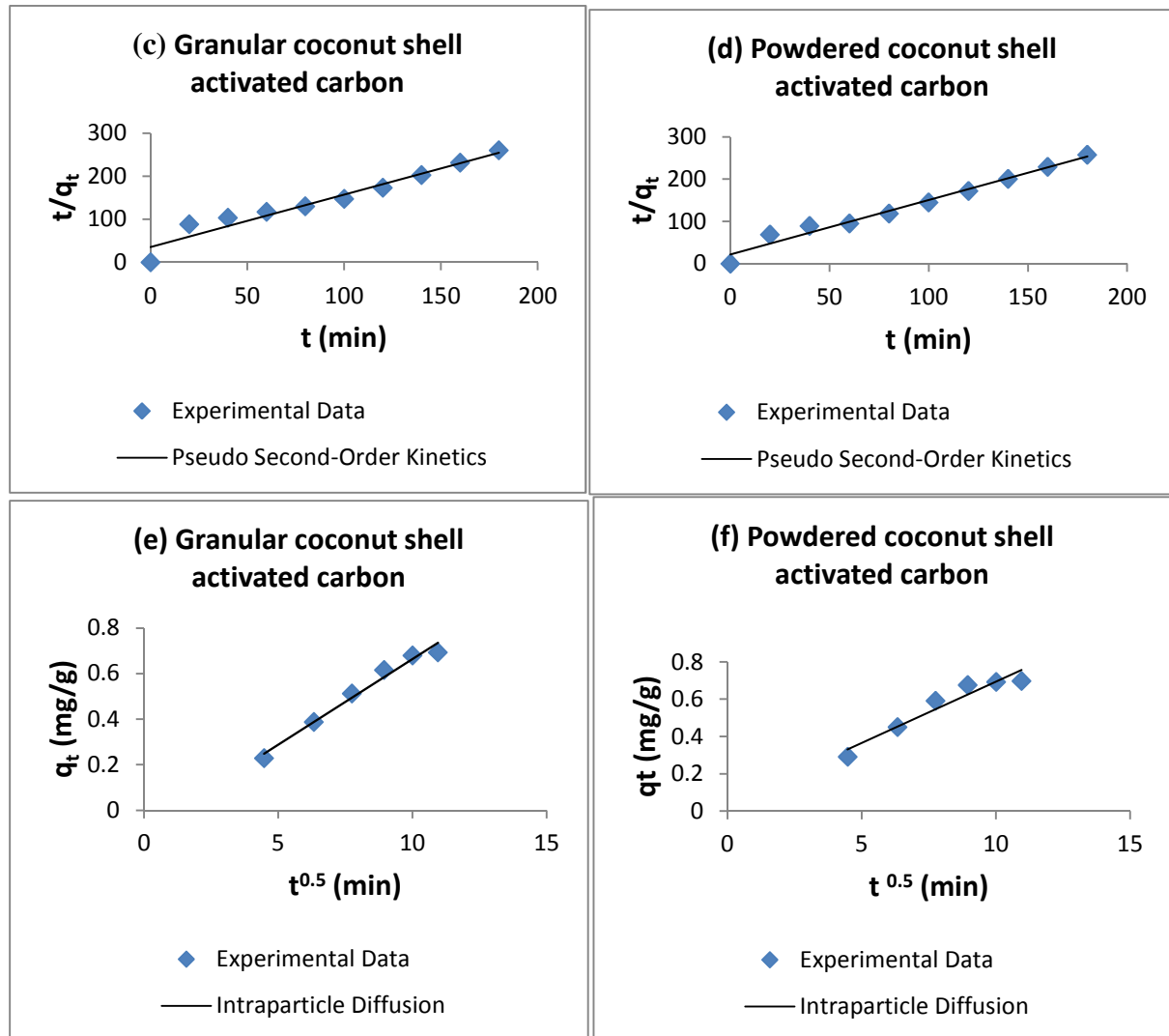


Fig. 5: Pseudo first-order kinetics fitted to phenol adsorption kinetic data of (a) granular coconut shell-derived activated carbon, (b) powdered coconut shell-derived activated carbon. Pseudo second-order kinetics fitted to phenol adsorption kinetic data of (c) granular coconut shell-derived activated carbon, (d) powdered coconut shell-derived activated carbon. Intra-particle diffusion model fitted to phenol adsorption kinetic data of (e) granular coconut shell-derived activated carbon; (f) powdered coconut shell-derived activated carbon.

Table 4. Pseudo first-order, pseudo second-order and intra-particle diffusion kinetic constants and correlation coefficients obtained for phenol adsorption by coconut shell activated carbon

| Kinetic models | GCSAC | PCSAC |
|---|--------|--------|
| Pseudo first-order | | |
| k_1 (min^{-1}) | 0.036 | 0.048 |
| q_e (theo.) (mg/g) | 1.020 | 1.231 |
| q_e (exp) (mg/g) | 0.693 | 0.698 |
| R^2 | 0.9030 | 0.9480 |
| Pseudo second-order | | |
| k_2 ($\text{g}/(\text{mg}\cdot\text{min})$) | 0.043 | 0.078 |
| q_e (theo.) (mg/g) | 0.821 | 0.775 |
| h ($\text{mg g}^{-1}\text{min}^{-1}$) | 0.0289 | 0.0469 |
| R^2 | 0.9470 | 0.9770 |
| Intra-particle diffusion | | |
| K_p ($\text{mg}/(\text{g min}^{0.5})$) | 0.075 | 0.065 |
| C | -0.088 | 0.036 |
| R^2 | 0.9770 | 0.9270 |

4. Discussion

From Table 1, coconut shell spectra's vibrations shows that it may have the presence of phenols or monomeric alcohols due to the wave numbers corresponding to $3625\text{-}3210\text{ cm}^{-1}$. It also has peaks around the range of 1260 cm^{-1} to 1658.7 cm^{-1} , which might lead to the existence of alkenes, alkanes, amines and nitro compounds. Strong stretching vibrations at 1739 cm^{-1} may correspond to the C-H bonds of the Phenyl ring substitution overtones. The presence of N-H bonds of the amines and O-H bonds of the carboxylic acids are also suspected however from Table 1, it can be observed that the spectra of the coconut shell and the activated carbon vary by large deviations. But the granular and powder activated carbon spectra are the same. The spectra's vibration of the granular activated carbon are stretched from 2895 cm^{-1} to 3528 cm^{-1} thus giving a clue for the presence of O-H bonds of carboxylic acids, monomeric alcohols and phenols, along with the presence of C-H bonds of aromatic rings and N-H of the amines. In addition, it has peaks at 1108 cm^{-1} which may indicate the existence of alcohols, ethers and nitriles. Furthermore, the spectra also imply a composition of alkanes, alkenes and CN amines present in the activated carbon.

Bulk density is an important parameter of powdered solids. The American Water Work Association has set a lower limit on bulk density at 0.25 g/ml for activated carbon to be of practical use. The bulk density values of the prepared coconut shell activated carbon at different size and temperature as presented in Table 2 satisfies this condition. The bulk densities values are in agreement with the values reported in literature (Gueu et al., 2003; Veena Devi et al., 2012). From Table 2, it can be seen that the ash content in the coconut shell activated carbons (granular and powdered forms) is low. The low ash content makes it an attractive candidate for adsorption studies. The ash content of commercial activated carbon is around 2% (Veena Devi et al., 2012). If ash content is high it will interfere with pore structure development and hence adsorption will be less (Devi et al., 2012). The result in Table 2 shows that the specific surface area increased with increase in activation temperature. A similar observation has been reported (Veena Devi et al., 2012). In addition, the values of specific surface area of granular and powdered coconut shell activated carbon produced at $900\text{ }^\circ\text{C}$ of activation temperature is within the value of $500\text{ to }2000\text{ m}^2/\text{g}$ recommended for commercial activated carbon (). These values for coconut shell activated carbon are in agreement with other studies (Veena Devi et al., 2012). Thus, the coconut shell activated carbons produced at $900\text{ }^\circ\text{C}$ were used for further studies.

The powdered coconut shell activated carbon showed higher surface area than the granular coconut shell activated carbon (i.e. surface area increased with decreased particle size). The iodine numbers of coconut shell activated carbons prepared in this investigation lies between $480\text{-}700\text{ m}^2/\text{g}$. Generally, higher the iodine number, greater is the sorption capacity. From Table 2, it can be seen that the iodine number increased as the activation temperature increased and particle size decreased. This suggests that surface area has increased in terms of microscopic pores. The value of iodine number for GCSAC and PCSAC revealed that the adsorbents are significantly porous and this porosity imparts a higher surface area to the adsorbents which was confirmed by

the high surface area value obtained. The interaction of GCSAC and PCSAC with deionized water showed that pH of the water was lowered, which indicates that the prepared carbonaceous adsorbent comes under 'L' type carbon according to Steenberg Mattson classification (No.7). The powdered coconut shell activated carbon showed higher iodine number than the granular coconut shell activated carbon.

As shown in Fig. 1, it is seen that for each of the coconut shell particle size, the yield of carbon increases with increase in activation temperature. Similar observations have been reported (Legrouri et al., 2012). It is seen from Fig. 2 that the adsorption capacity of powdered coconut shell-derived activated carbon (< 1 mm particle size) was relatively higher than that of the granular coconut shell-derived activated carbon (> 1 mm particle size). This is in agreement with the observation that adsorption capacity increased with decrease in particle size diameter (Annadurai et al., 2000;) Percentage phenol removal is relatively higher with powdered coconut shell-derived activated carbon than with granular coconut shell-derived activated carbon and this may be due to increased surface area (i.e. smaller particles have higher surface area per unit mass) as well as micro pore volume (Agarry and Aremu, 2012b). Smaller particle size means more interior surface and micro pore volume and hence more will be the area of active sites for adsorption. Also for larger particles the diffusion resistance to mass transfer is higher and most of the internal surfaces of the particle may not be utilized for adsorption and consequently the amount of phenol adsorbed is small (Lakshmi et al., 1994; Annadurai et al., 2000, Dabhade et al., 2009).

It was observed that percentage of phenol removal increased with increase in adsorbent dose (Fig. 3(a) and 3(b)). This kind of a trend is mostly attributed to an increase in the adsorptive surface area and the availability of more active binding sites on the surface of the adsorbent (Nasuha et al., 2010; Das and Mondal, 2011). However, the equilibrium adsorption capacity showed an opposite trend. As the adsorbent dosage was increased from 0.5 to 10 g, the adsorption capacity reduced from 6.34 to 0.35 mg/ using granular coconut shell-derived activated carbon g (Fig. 3(a)) and from 6.44 to 0.38 mg/g for powdered coconut shell-derived activated carbon (Fig. 3(b)), respectively. This may be due to the decrease in total adsorption surface area available to phenol resulting from overlapping or aggregation of adsorption sites (Crini et al., 2007; Akar et al., 2009; Agarry et al., 2013b). Thus, with increase in the adsorbent mass, the amount of phenol adsorbed onto unit mass of adsorbent gets reduced, thereby causing a decrease in q value with increasing adsorbent mass concentration. Furthermore, maximum phenol removal (99%) lies between the use of 2.5 and 5 g of powdered coconut shell-derived activated carbon and further increase in adsorbent dose did not significantly change the adsorption yield. This is due to the non-availability of active sites on the adsorbent and establishment of equilibrium between the phenol on the adsorbent and in the wastewater (Agarry et al., 2013b).

The estimated constants of Langmuir isotherm from the linear plot of $(1/q_e \text{ vs. } 1/C_e)$ (Fig. 4(a) are given in Table 3. It can be explained apparently that when $a > 0$, sorption system is favorable (Chen et al., 2008). In this study, a is 0.3376 L/mg and the maximum monolayer adsorption capacity (Q_{\max}) is 7.58 mg/g obtained for granular coconut shell-derived activated while the corresponding a and Q_{\max} value of 12.5 L/mg and 4.31 mg/g was obtained for powdered coconut shell-derived activated carbon. Sathishkumar et al. (2009) obtained 17.94 mg/g as the maximum monolayer adsorption capacity of maize cob carbon for the adsorption of 2,4-dichlorophenol while 14.25 mg/g was obtained by Agarry et al. (2013b) as the maximum monolayer adsorption capacity of modified plantain peels for the adsorption of 2,6-dichlorophenol.

The evaluated constants of Freundlich isotherm from the linear plot of $\log q_e \text{ vs. } \log C_e$ (Fig. 4(b)) as given in Table 3 revealed that K_f and n values were found to be 2.01 mg/g(L/mg)^{1/n} and 1.05 for granular coconut shell-derived activated carbon while corresponding K_f and n value of 3.63 mg/g(L/mg)^{1/n} and 1.55 was obtained for powdered coconut shell-derived activated carbon, respectively. Namasivayam and Kavitha (2004) obtained K_f and n values of 1.2 and 0.7 for the adsorption of 2, 4, 6-trichlorophenol (TCP) onto coir pith carbon while Radhika and Palanivelu (2006) correspondingly obtained a K_f and n values of 2.05 and 1.5 for the adsorption of 2, 4, 6-trichlorophenol (TCP) onto coconut shell activated carbon. Generally, Langmuir and Freundlich isotherm models fitted well to the equilibrium adsorption experimental data with high correlation coefficient. However, for the granular and powdered coconut shell-derived activated carbon, the Freundlich isotherm model provided the best fit with a higher correlation coefficient ($R^2 = 0.9940$ and 0.9920) to describe the adsorption process. A similar observation has been reported for the adsorption of 2, 4-DCP onto activated bamboo charcoal (Ma et al., 2010) and the adsorption of 2, 4, 6- trichlorophenol (TCP) onto coir pith carbon (Namasivayam and Kavitha, 2004) and coconut shell carbon (Radhika and Palanivelu, 2006).

For Langergren pseudo first-order kinetic model, the parameter values of q_e and k_1 were calculated from the slope and intercept of the linear plots of $\ln(q_e - q_t)$ vs t (Fig. 5(a) and 5(b)). The respective values as given in Table 4 showed that the adsorption rate constant (k_1) is relatively higher for powdered coconut shell-derived activated carbon than the granular coconut shell-derived activated carbon. Also, the parameter values of k_2 and q_e for pseudo second-order kinetic model were calculated from the plots of t/q_t vs. t (Fig. 5(c) and 5(d) for granular and powdered coconut shell-derived activated carbon. The respective constant values as given in Table 4 revealed that the rate constant k_2 of 35 mg/l phenol adsorption is relatively higher for powdered coconut shell-derived activated carbon than that for granular coconut shell-derived activated carbon.

As shown in Fig. 5(e) and 5(f) for intra particle diffusion model, the linear plot of q_t vs. $t^{1/2}$ did not pass through the origin. This deviation from the origin is due to difference in the rate of mass transfer in the initial and final stages of the adsorption (Agarry et al., 2013b). This indicated the existence of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step. The calculated diffusion coefficient K_p values are listed in Table 4. The K_p value is higher for granular coconut shell-derived activated carbon than for powdered coconut shell-derived activated carbon. Generally, all the tested adsorption kinetic models fitted well to the adsorption kinetic data with high correlation coefficient for granular and powdered coconut shell-derived activated carbon; however, the pseudo second-order kinetic model gave the best fit with a higher correlation coefficient to describe the adsorption behaviour of phenol onto granular and powdered coconut shell-derived activated carbon. Similar observations have been reported for the adsorption of chlorophenols onto other agricultural by-product-derived carbon adsorbents (Sathishkumar et al., 2009; Ma et al., 2010; Sharaani and Hameed, 2010; Hamad et al., 2011; Wang et al., 2011).

Conclusion

In this study, phosphoric acid activated carbon was produced from coconut shell. It was tested and evaluated as a possible adsorbent for removal of phenol from paint wastewater using batch adsorption technique. The adsorption process is also dependent on some factors such as the contact time, adsorbent particle size (granular and powdered form) and adsorbent dosage. The percentage removal of phenol from paint wastewater increased with increase in contact time and adsorbent dose up to a certain level and relatively higher for adsorbent with small particle size (powdered form). Adsorption equilibrium data fitted very well to both Langmuir and Freundlich isotherm models, however, the Freundlich isotherm equation gave the best fitting, confirming the non-ideal heterogeneous adsorption capacity of phenol onto coconut shell-derived activated carbon with an adsorption capacity (K_f) of 2.01 mg/g and adsorption intensity (n) of 1.07 for granular coconut shell activated carbon and corresponding 3.63 mg/g and 1.55 for powdered coconut shell activated carbon at 30 °C. The adsorption kinetics followed pseudo second-order kinetic model with a very good correlation coefficient suggesting that the biosorption process is presumably chemisorption. Intra-particle diffusion was not the sole rate controlling factor.

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