



Journal of Environmental Science and Technology

ISSN 1994-7887

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>



Research Article

Adsorption Isotherm and Kinetic Studies of Pentachlorophenol Removal from Aqueous Solution onto Coconut Shell-based Granular Activated Carbon

¹Mohd Hafizuddin Muhamad, ^{1,2}Siti Rozaimah Sheikh Abdullah, ^{1,2}Hassimi Abu Hasan, ^{1,2}Reehan Adnee Abd. Rahim, ¹Siti Nur Hatika Abu Bakar, ¹Nur 'Izzati Ismail and ³Mohd Izuan Effendi Halmi

¹Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

²Chemical Engineering Programme, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

³Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Abstract

Background and Objective: Pentachlorophenol (PCP) is the most toxic organic pollutants of chlorophenols especially found in pulp and paper mill wastewater. Recently, contagion of PCP in water body has become typical issue due to its toxicity and strong resistance to degradation. The aim of this study was to assess the adsorption isotherms and kinetics of PCP from aqueous solution using granular activated carbon (GAC) from coconut shell. **Methodology:** The effect of equilibrium time, initial concentration and adsorbent dose were investigated in batch mode. Two models namely, Freundlich and Langmuir were used to analyze the equilibrium data via linear regression technique while X-ray Fluorescence spectroscopy (XRF) was used to analyze the adsorbent surface. **Results:** It was found that the adsorption equilibrium data were absolutely fit with a Freundlich isotherm hence, the adsorption of PCP onto coconut shell-based GAC is heterogeneous. The Freundlich adsorption capacity, K_f , was 23.31 mg g^{-1} at 37°C . In the kinetic studies conducted, it was also found that the adsorption process follows a pseudo-first-order model ($R^2 > 0.97$). Analysis of the XRF data exhibited that PCP was adsorbed onto the GAC. **Conclusion:** Coconut shell-based GAC is an attractive material for use as a low cost adsorbent to eliminate PCP from aqueous solutions.

Key words: Pentachlorophenol, coconut shell, granular activated carbon, Freundlich isotherm, pseudo-first order

Citation: Mohd Hafizuddin Muhamad, Siti Rozaimah Sheikh Abdullah, Hassimi Abu Hasan, Reehan Adnee Abd. Rahim, Siti Nur Hatika Abu Bakar, Nur 'Izzati Ismail and Mohd Izuan Effendi Halmi, 2018. Adsorption isotherm and kinetic studies of pentachlorophenol removal from aqueous solution onto coconut shell-based granular activated carbon. *J. Environ. Sci. Technol.*, 11: 68-78.

Corresponding Author: Siti Rozaimah Sheikh Abdullah, Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia Tel: +6-03-89216407 Fax: +6-03-89216148

Copyright: © 2018 Mohd Hafizuddin Muhamad *et al.* This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

For decades, lethal organic compounds that contaminate water body become one of the largest environmental topics. There is increasing public attraction concerning the amassing of such compounds in surface water and groundwater due to incomplete eradication of massive number of metabolites from wastewater. Toxic compounds such, as these, can be classified into numerous classes of contaminants. Chlorophenols (CPs), an aromatic compounds is an important contaminant of adsorbable organic halide (AOX) compounds, are repeatedly identified in the discharge of several manufacturing sectors, including the pulp and paper mill¹. The toxicity, weak biodegradability and carcinogenic and recalcitrant properties of CPs are an important environmental concern. Contamination even at low concentrations can be harmful to living organisms and preventing straightforward reuse of water². Further, such compounds can be carcinogenic when present at high levels in the water³.

Mukherjee *et al.*⁴ reported concentrations of phenol and related phenolics in industrial wastewater generally lied between 100 and 1,000 mg L⁻¹. In particular, CPs like pentachlorophenol (PCP), 2,4,5-Trichlorophenol (2,4,5-TCP) and 2,4-Dichlorophenol (2,4-DCP) are included in the US EPA (EPA, Office of Water) Water Quality standard database list of priority contaminants⁵. PCP, the most toxic CP is normally generated from industrial production practices in the pulp and paper, pesticide, paint, wood conserving chemical as well as pharmaceutical industries⁶. To illustrate, thousands of tons of PCP has been generated annually by the pulp and paper industry¹. Left untreated, PCP from this industry's effluents will accumulate in sediment and aquatic systems due to slow biodegradation rate⁷ thus, inducing reproductive and other health problems in organisms because it can enter the food chain⁸. Indeed, detailed information on the toxicity of PCP towards humans is well documented in the literature⁹. Therefore, removal of such pollutants is of major importance.

Several treatment choices were studied and demonstrated to efficiently treat PCP-containing wastewater, such as, activated carbon adsorption, biological treatment and state of the art of oxidation processes¹⁰. Nevertheless, an adsorption approach utilizing activated carbon appears to serve the most ideal treatment approach because of the great adsorption potential along with inexpensive operational expense, particularly for the effluent consists of an extent of contaminants.

To reduce operational expense, efforts to identify inexpensive raw materials have been carried out. Fortunately, agricultural waste including coconut shells^{11,12}, almond shells⁸,

pine bark¹³, palm shells¹⁴, coir piths¹⁵, empty fruit bunches¹⁶, olive-waste cakes¹⁷, rice hulls¹⁸ and pineapple waste biomass¹⁹ can be used to produce activated carbon.

Granular activated carbon (GAC) from coconut shell is a promising adsorbent for the elimination of toxic organic compounds. In many developing countries, the need for inexpensive raw material is often considered. Currently, raw materials that are biodegradable, abundant and easily available and are produced from waste resources²⁰ are more preferred. The most feasible raw material for producing GAC especially in Malaysia is coconut shells which are considered abundant because of large plantation area of coconut (*Cocos nucifera*) covering approximately 142,000 ha of the cultivated land¹². Further, coconut shells are accountable for ~18% (w/w) of the worldwide production of commercial activated carbon²¹. Regarding the transformation of solid coconut residue to activated carbon, the use of the coconut shell negates wasteful decay and its utilization as a fuel source, which can lead to negative environmental impact¹². Moreover, owing to its solidity and resistance to abrasion, coconut shells are ideal to be transformed into activated carbon¹².

Furthermore, particle size plays a major role in adsorption efficiency²². The particle size in full-scale GAC adsorbents is typically 12 × 40 or 8 × 30 U.S. Standard mesh. In this study, the 8 × 30 mesh (particle size range between 1.5-1.7 mm) GAC was used. A smaller particle size can be used to achieve high removal percentages, besides produce faster adsorption kinetics. However, the smaller particle size can cause contaminant breakthrough and increase head loss that results to more frequent backwashing and lower net water production. Based on adsorption study by Radhika and Palanivelu²³, the potential of coconut shell-based GAC was explored in the removal of parachlorophenol and 2,4,6-Trichlorophenol from aqueous solution. This study focused on the adsorption of PCP from aqueous solution using coconut shell-based GAC. Commonly, PCP concentration in industrial wastewater especially in pulp and paper mill effluent is less than 100 mg L⁻¹²⁴. In extreme conditions, influent PCP concentration could reach more than 100 mg L⁻¹²⁵. Thus, initial PCP concentration of 100-500 mg L⁻¹ was used in the study during the assessment of operational parameters.

The objective of paper was to investigate the adsorption effectiveness of coconut shell-based GAC for the elimination of PCP from aqueous solution. The effect of equilibrium time, initial concentration and adsorbent dose was assessed. The equilibrium isotherms as well as kinetic data of the adsorption process were then evaluated to identify the adsorption features together with its mechanism.

MATERIALS AND METHODS

Study area: This study was conducted in 2015 at Environmental Laboratory, Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia.

Adsorbent and adsorbate: Commercial coconut shell-based activated carbon was used as adsorbent in this study. The commercial 8×30 mesh (particle size range between 1.5-1.7 mm) GAC was purchased from Concepts Ecotech, Selangor, Malaysia. Distilled water was used to remove any leachable matter from the GAC before dried at 105°C for 24 h in oven and stored in desiccator's prior usage. The PCP supplied by Sigma-Aldrich (M) Sdn Bhd, Malaysia, was applied as the adsorbate in this research. PCP has the chemical formula C_6Cl_5OH and a molecular weight of 266.34 g mol⁻¹. The stock solution of PCP was prepared by completely dissolving 5 g of the respective adsorbate with 500 mL of methanol in an appropriate volumetric flask. More dilutions of the stock solution into deionized water should be made to obtain desired initial concentration.

Characteristics of activated carbon: X-ray Fluorescence spectroscopy (XRF, MiniPal 2, PANalytical, Netherlands) was used to investigate the elemental change especially the PCP content, in the GAC before and after the adsorption process.

Adsorption experiments in batch mode: Experimentation on adsorption by batch mode was performed by implementing a series of 250 mL Erlenmeyer flasks with 100 mL of PCP solutions. For every experiment conducted, the flasks were positioned in an incubator shaker (37±1°C, 130 rpm). The effects of the adsorbent dose (0.5-10 g L⁻¹), initial concentration (100-500 mg L⁻¹) and equilibrium time (0-24 h) were investigated by varying one variable and fixing other parameters. Small number of hydrochloric acid or sodium hydroxide droplets (each 0.01 M) was added to maintain pH of 7. Aqueous samples to be analyzed were taken from the solutions. Prior to the analysis, all samples were filtered to decrease interference from fine carbon. Double beam UV-Vis spectrophotometer (Libra S12, Biochrom, UK) was used, maximum wavelength of 305 nm to measure PCP concentrations in the supernatant solution before and after adsorption occurred.

Isotherm studies: To obtain the isotherms, the experiments were performed using 100 mL of the PCP solution at an

adsorbent dose of 5 g L⁻¹. Under varying initial PCP concentrations, ranging from 100-500 mg L⁻¹, the flasks were shaken (130 rpm, 37°C) up till equilibrium. The PCP uptake at equilibrium, q_e (mg g⁻¹), was calculated by adopting Eq. 1²⁶:

$$q_e = \frac{V(C_0 - C_e)}{X} \quad (1)$$

where, C_e and C_0 (mg L⁻¹) are the equilibrium and initial liquid-phase concentrations of PCP, respectively, V (L) is the solution volume and X (g) is the mass of dry adsorbent used.

Investigation on kinetic studies: The kinetic studies were performed using a fixed initial PCP concentration of 100 mg L⁻¹ with varying adsorbent doses (1-5 g L⁻¹). Each 100 mL sample of the PCP solution was shaken in an incubator shaker at 130 rpm at 37°C. Sampling was done at certain time intervals to determine the residual adsorbate concentration.

Adsorption isotherm models: Generally, adsorption isotherms describe the interactions that occur between the adsorbent and adsorbate species at equilibrium conditions. Furthermore, isotherms indicate the load of adsorbate adsorbed by a given quantity of adsorbent once the adsorption process attains equilibrium. Evaluation of the isotherm data by their fit to several isotherm models have to be performed to obtain the ideal model for design purposes application¹⁶. Numerous models have been written describing the experimental data of adsorption isotherms. Particularly, the Freundlich and Langmuir models are commonly applied to fit the adsorption isotherms and to assess the isotherm parameters^{12,16}. The Langmuir isotherm was formulated on the presumption that the adsorption process occur specifically on comparable sites in the adsorbent exterior with a consistent energy distribution. Meaning, once a site was filled by the adsorbate, adsorption process was inhibited indicate that adsorption occurs as a monolayer whereas, Freundlich isotherm, infer that adsorption occur on heterogeneous sites with a non-uniform energy distribution. Freundlich model express a reversible adsorption process and is not restricted to the monolayer structure¹². The linear equations of the Freundlich and Langmuir models are depicted as in Eq. 2 and 3, respectively.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_d} \quad (3)$$

where, q_e indicates adsorption capacity at equilibrium (mg g^{-1}), C_e is the adsorbate concentration at equilibrium (mg L^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}) and K_d represents a Langmuir constant. For the Langmuir model, a plot of C_e/q_e versus C_e provide a straight line of slope $1/q_{\text{max}}$ and intercept $1/q_{\text{max}}K_d$. For the Freundlich model, a plot of $\ln q_e$ versus $\ln C_e$ allows the determination of the constant K_f and the exponent $1/n$. The K_f ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$) is the Freundlich constant and $1/n$ is a dimensionless heterogeneity factor.

A normalized standard deviation q (%) was used to significantly examine in contrast the applicability of each model and is expressed in Eq. 4:

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{e,\text{exp}} - q_{e,\text{cal}}) / q_{e,\text{exp}}]^2}{n - 1}} \quad (4)$$

where, $q_{e,\text{exp}}$ and $q_{e,\text{cal}}$ are the experimental and calculated amounts of the PCP adsorbed at equilibrium onto the GAC, respectively and n is the number of data points. The q signifies the fit between the experimental and calculated data of the adsorption capacity, whereas the linear correlation coefficients (R^2) signify the fit between the experimental data and linearized forms of the isotherm equations²⁷.

Adsorption kinetic models: Adsorption kinetics is crucial in process design because these models determine the adsorption rate by the adsorbent. Moreover, models bid comprehensive information on the sorption mechanism of the solute onto an adsorbent. The kinetics are fitted with the pseudo-first-order and pseudo-second-order models, which are widely applied in kinetic studies. Eq. 5 and 6 expressed linear equations of pseudo-first and -second order kinetics^{28,29}.

$$\ln[q_e - q_t] = \ln q_e - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (6)$$

where, q_t is the amount of solute adsorbed per unit weight of adsorbent at time (mg g^{-1}), k_1 is the rate constant of pseudo-first-order sorption (h^{-1}) and k_2 is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1} \text{h}^{-1}$).

Equation 5 and 6 may also be written in the form proposed by Simonin³⁰, as presented in Eq. 7 and 8, respectively.

$$q(t) = q_e [1 - \exp(-k_1 t)] \quad (7)$$

$$q(t) = q_e \frac{k_2 t}{1 + k_2 t} \quad (8)$$

with

$$k_2^* = k_2 q_e$$

If q_e is determined from experiment, the fractional uptake (with respect to equilibrium),

$$F(t) = q(t) / q_e \quad (9)$$

may be computed. The Eq. 7 and 8 may be rewritten as presented in Eq. 10 and 11, respectively.

$$F(t) = 1 - \exp(-k_1 t) \quad (10)$$

$$F(t) = \frac{k_2^* t}{1 + k_2^* t} \quad (11)$$

The values of the R^2 and the average absolute relative deviation (AARD) for the two rate laws were computed, as proposed by Simonin³⁰ in order to compare the models.

RESULTS AND DISCUSSION

Characteristics studies on the activated carbon: The main inorganic elemental content of the GAC before and after the adsorption of PCP presents in Fig. 1. Based on Fig. 1, some inorganic elements have been confirmed by the XRF analysis, such as Cl, K, Fe and Cu. The main inorganic elements for the GAC before adsorption (Fig. 1a) were Cl (36.8%), K (53%), Fe (6.5%) and Cu (3.7%). For the GAC after adsorption (Fig. 1b), the main inorganic elements were Cl (95.2%), K (3.8%), Fe (0.63%) and Cu (0.36%). In Fig. 1b, the peak representing Cl is clearly visible for the GAC after adsorption with a high count per second (cps), which can be related to a high Cl concentration. This high concentration can be attributed to an increase in the amount of PCP following the adsorption process, suggesting that PCP was adsorbed onto the GAC.

Effect of equilibrium time: The adsorption capacity, q_e , versus adsorption time at discrete initial PCP concentrations demonstrates in Fig. 2. The necessary equilibrium time was determined at various initial concentrations for the removal

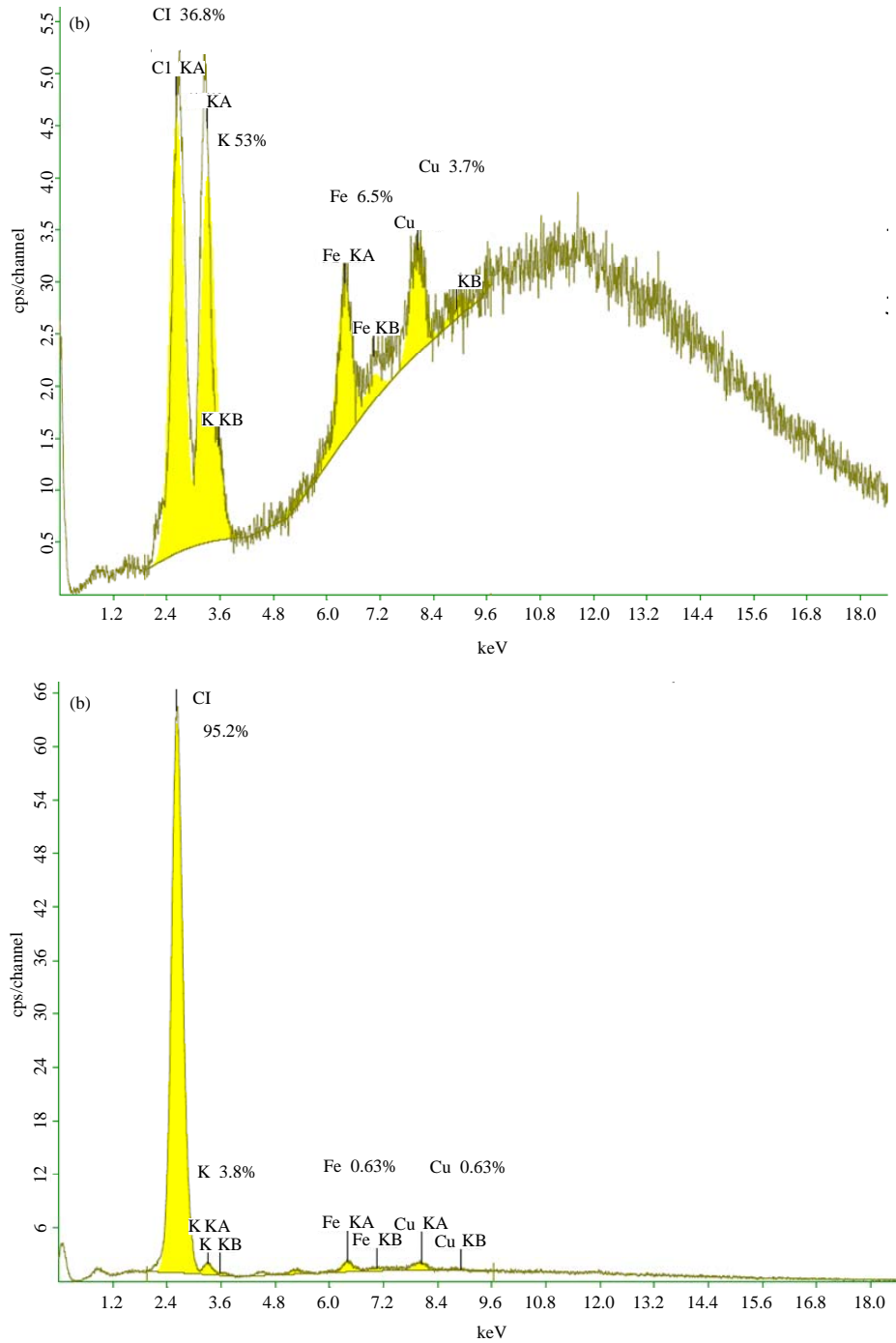


Fig. 1(a-b): XRF spectrum of GAC samples (a) before and (b) after PCP adsorption

of PCP on the GAC (Fig. 2). The adsorption of PCP onto the GAC involved two phases: A preliminary stage with rapid adsorption and a final stage with a relatively slow adsorption (Fig. 2). During early stages of the adsorption process, the first 1 h of adsorption, the adsorption rate was quite rapid, leads to rapid adsorbates accumulation on the outer surface of the

GAC. Massive number of unoccupied surface sites that were accessible for adsorption had caused high rate of PCP uptake ($36.82 \text{ mg g}^{-1} \text{ h}^{-1}$) was obtained in the first 1 h of adsorption at initial PCP concentration of 500 mg L^{-1} . It could be detected that adsorption rate act inversely proportional to the adsorption time until steady state achieved. This may be due

to the crisis in filling the empty surface sites produced by repulsive forces among the PCP molecules in the solid surface and in the bulk phase³¹.

The mass transfer driving force amidst the total liquid phase and solid phase over time becomes limited due to the microscopic size of PCP, allowing them to simply diffuse into

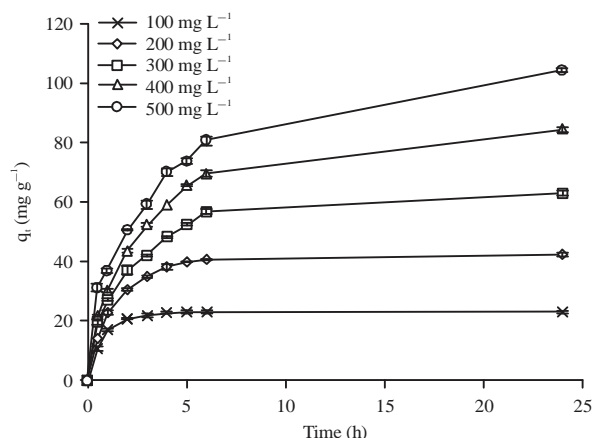


Fig. 2: Effect of equilibrium time on PCP adsorption (initial concentrations = 100-500 mg L⁻¹, adsorbent dose = 5 g L⁻¹, pH = 7 at 37°C)

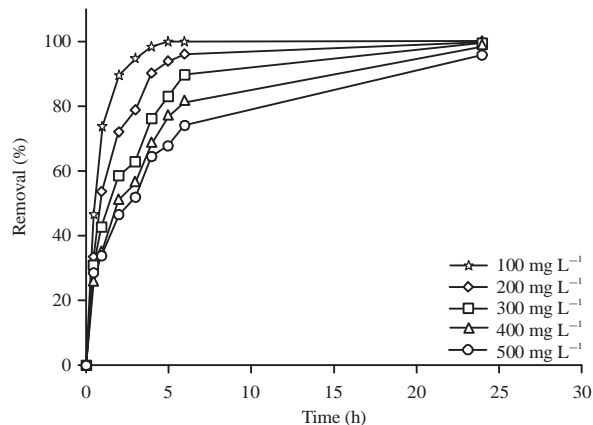


Fig. 3: Effect of the initial PCP concentration on adsorption (initial concentrations = 100-500 mg L⁻¹, adsorbent dose = 5 g L⁻¹, pH = 7 at 37°C)

the inner pores until saturation point achieved. Afterwards, the PCP molecules experience much higher resistance to diffuse deeper into the pores³². Upon reaching steady state, the adsorption rate decreased and plateau lines were observed after 6 h (Fig. 2). Non-significant PCP removal and slow after 6 h of adsorption time shown in Fig. 2. At initial PCP concentration of 500 mg L⁻¹, the PCP uptake rate (8.76 mg g⁻¹ h⁻¹) at 6 h of adsorption time was found to decrease compared with the first 1 h of adsorption time. This phenomenon required longer contact time. Therefore, 6 h was considered as the optimal equilibrium time for PCP adsorption at the initial concentrations of 100-500 mg L⁻¹. The equilibrium time of 6 h used in this study comparable to the equilibrium time reported in other studies with adsorbents variations displayed in Table 1. Zheng *et al.*²⁶ used 4 days as the equilibrium time for the adsorption of PCP on flake-type chitosan. In order to assure complete equilibrium, Estevinho *et al.*⁸ applied 24 h as the equilibrium time for the adsorption of PCP on almond shell.

The PCP uptake rate escalates as the initial concentration increased in Fig. 2. In the first 1 h of adsorption, the PCP uptake rates were 16.96, 27.11 and 36.82 mg g⁻¹ h⁻¹ for initial concentrations of 100, 300 and 500 mg L⁻¹, respectively. Obviously, the uptake rate increases linearly with the initial concentration.

Effect of initial concentration: The effect of PCP concentration variations on its removal by GAC is described in Fig. 3. As, the removal efficiency of PCP was tremendously rely on the initial concentration of PCP in the solution. As the initial PCP concentration increases, PCP removal using GAC decreases. This was believed because of availability of high adsorbate concentration that accelerates saturation binding capacity of the adsorbent that consequently lessen the entire uptake³³. In the first 1 h of adsorption, the removal of PCP decreased from 74-34% as the initial PCP concentration escalated from 100-500 mg L⁻¹. For a fixed amount of GAC (5 g L⁻¹) and optimal equilibrium time (6 h), a PCP concentration of 100 mg L⁻¹ was determined to be the optimal concentration to achieve the highest PCP removal.

Table 1: Compilation of experimental conditions and results from various PCP adsorption studies

Types of adsorbent	Equilibrium time	Initial concentration	Adsorbent dose (g L ⁻¹)	Freundlich isotherm		References
				K _f [mg g ⁻¹ (L mg ⁻¹) ^{1/n}]	1/n	
Coconut shell based GAC	6 h	100-500 mg L ⁻¹	5.0	23.31	0.25	Present study
Flake type chitosan	4 days		1.0	0.40-0.17	1.57-1.96	Zheng <i>et al.</i> ²⁶
Almond shell	24 h	100 µg L ⁻¹	0.1-100	0.075 ± 0.081	1.882 ± 0.289	Estevinho <i>et al.</i> ⁸
Pine bark	24 h	5 mg L ⁻¹	0.2-10	1.700 ± 0.20	1.060 ± 0.020	Bras <i>et al.</i> ¹³
Black carbon	24 h	0.1-20 mg L ⁻¹		12.290 ± 0.99	0.320 ± 0.040	Bayram <i>et al.</i> ³³

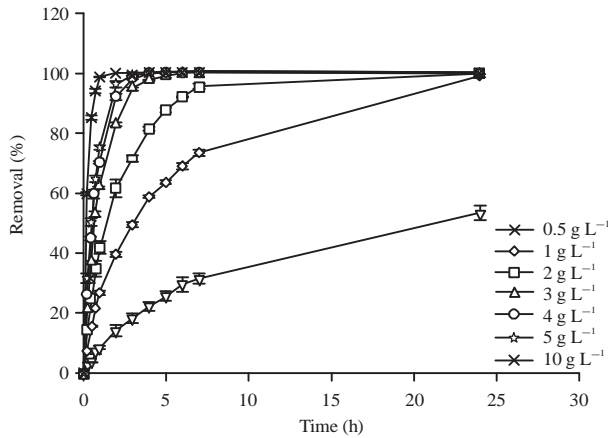


Fig. 4: Effect of the adsorbent dose on PCP adsorption (initial concentration = 100 mg L⁻¹, adsorbent dose = 0.5-10 g L⁻¹, pH = 7 at 37°C)

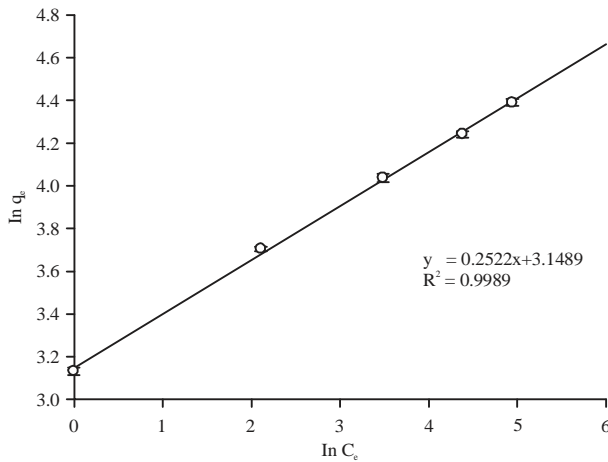


Fig. 5: Langmuir isotherm plots of PCP adsorption onto GAC (initial concentrations = 100–500 mg L⁻¹, adsorbent dose = 5 g L⁻¹, pH = 7 at 37°C)

Effect of adsorbent dose: The effect of adsorbent dose on PCP elimination, revealing that the elimination of PCP escalates proportionally with adsorbent dose, as shown in Fig. 4. As, the removal of PCP negotiate an adsorbent dose more than 3 g L⁻¹ remained essentially identical. Therefore, 3 g L⁻¹ of GAC was considered to be the optimal dose at an initial PCP concentration of 100 mg L⁻¹. Increase in adsorption with the addition of adsorbent because of a larger number of binding sites available for PCP. Therefore, an adsorbent dose of 3 g L⁻¹ provides adsorption sites that are adequate for 100% adsorption under the experimental conditions.

Adsorption isotherms: The linearized Freundlich and Langmuir isotherm plots involving the adsorption of PCP by

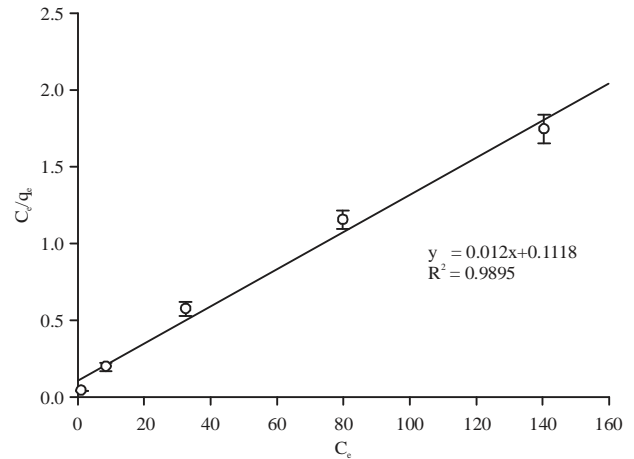


Fig. 6: Freundlich isotherm plots of PCP adsorption onto GAC (initial concentrations = 100–500 mg L⁻¹, adsorbent dose = 5 g L⁻¹, pH = 7 at 37°C)

GAC are represented in Fig. 5 and 6, respectively. The R² values were >0.98, with values of 0.9989 and 0.9895 for the Freundlich and Langmuir isotherms, respectively (Fig. 5-6). From the R² values, the best fit is obtained using the Freundlich isotherm rather than the Langmuir isotherm. As reported by Ho³⁴, the use of the linear regression coefficient for differentiating ideal fits of several isotherms is incompatible. In unison with Kinniburgh³⁵, the highest correlation coefficient was not actually signifies the ideal transformation but the one that produce error distribution most closely fits the “true” error distribution does.

The parameters from the two models examined (i.e., R² and Δq (%) where the Δq (%) value for the linearized Freundlich isotherm model was lower than the Δq (%) value for the Langmuir isotherm model summarized in Table 2. Thus, shows that the adsorption of the PCP on the coconut shell-based GAC follows the Freundlich isotherm and that the corresponding parameters, K_f, n and 1/n, which were obtained from the linear form of the Freundlich model, were 23.31, 3.9651 and 0.25, respectively. The higher K_f value for the coconut shell-based GAC used in this study indicated that relatively more PCP was adsorbed onto the adsorbent surface than other adsorbents (Table 1). Moreover, the 1/n values between 0.1 and 0.5 indicate very good adsorption characteristics under the conditions studied. In addition, for a higher value of 1/n, the affinity and heterogeneity of the adsorbent sites will be higher³⁶.

Kinetic studies: Non-linear plots of the pseudo-first-order and pseudo-second-order kinetic models for PCP adsorption onto GAC are presented in Fig. 7. In this study, data for which the

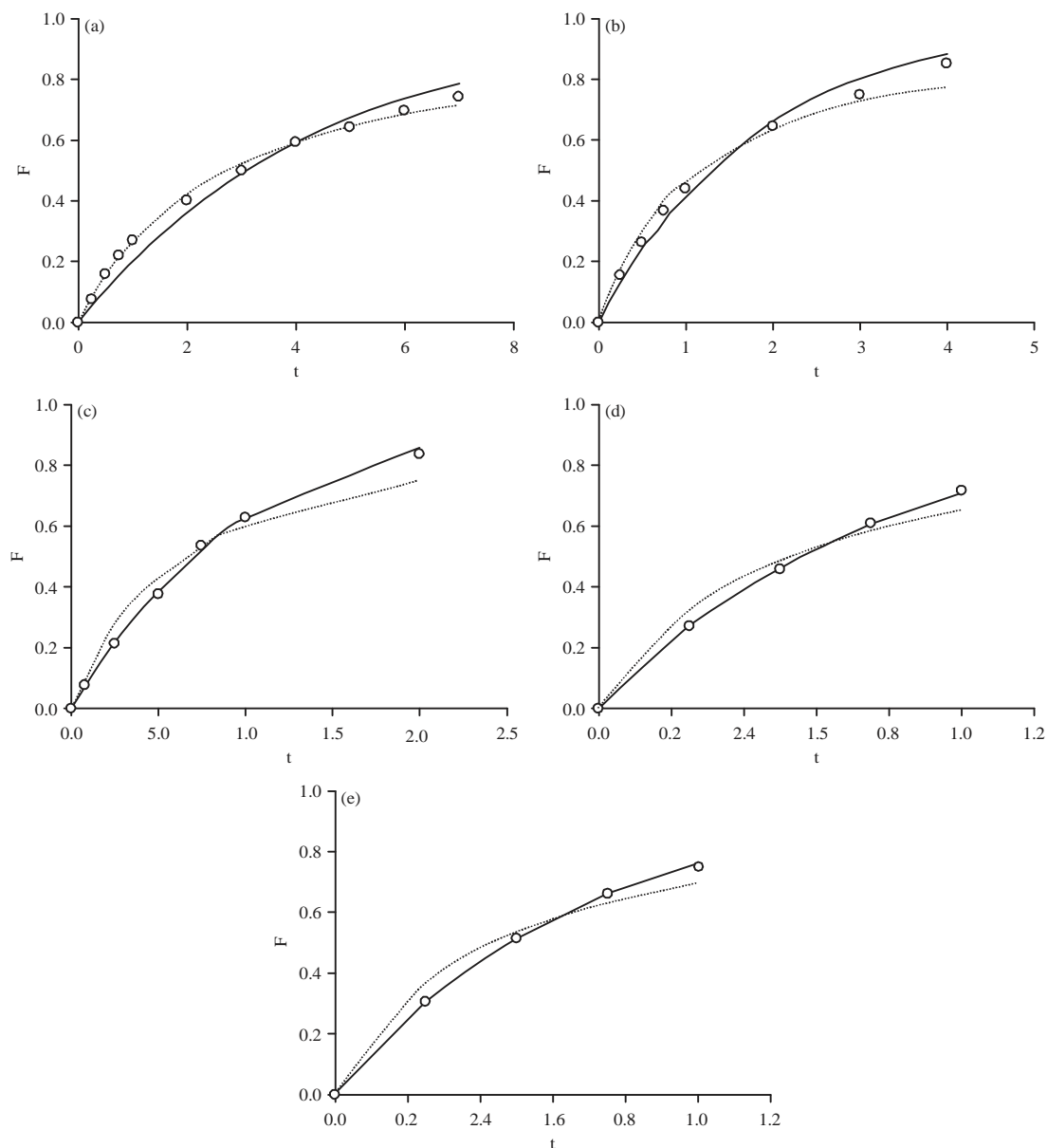


Fig. 7(a-e): Pseudo-first-order (K1) and pseudo-second-order (K2) kinetic model plots for PCP adsorption onto GAC with varying adsorbent doses at (a) 1 mg L⁻¹, (b) 2 mg L⁻¹, (c) 3 mg L⁻¹, (d) 4 mg L⁻¹ and (e) 5 mg L⁻¹. F: Fractional uptake, t: Time (h), (o): Experimental data, solid line = Fit with K1 (Eq. 1), dashed line = Fit with K2 (Eq. 2)

Table 2: Coefficients of Freundlich and Langmuir model

Adsorbent	Freundlich isotherm model					Langmuir isotherm model			
	K _f	n	1/n	R ²	Δq (%)	q _{max} (mg g ⁻¹)	k _d	R ²	Δq (%)
GAC	23.31	3.9651	0.25	0.9989	1.63	83.33	0.107	0.9895	33.46

fractional uptake, F was lower than 85% have been considered³⁰. The parameters of the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of PCP on GAC are summarized in Table 3. Based on Table 3, the R², earned from the two kinetic models were >0.98 for all

adsorbent doses. The relevance of the kinetic models is discerned by evaluating the R² and AARD values. It may be seen that the adsorption of PCP by coconut shell-based GAC can be best described by the pseudo-first order model using non-linear regression fit, which is supported by the

Table 3: Parameters of the pseudo-first and second order kinetic models

Adsorbent dose (g L ⁻¹)	q _{e,exp} (mg g ⁻¹)	N ^a	Pseudo-first-order kinetic model (K ₁)				Pseudo-second-order kinetic model (K ₂)					
			q _{e,cal} (mg g ⁻¹)	k ₁ (h ⁻¹)	R ²	AARD _F	q _{e,cal} (mg g ⁻¹)	k ₂ (g mg ⁻¹ h)	R ²	AARD _F	K1 ^b	K2 ^c
1	105.71	11	105.22	0.2239	0.971	2.1	94.78	0.003	0.998	3.1		✓
2	51.00	8	49.80	0.5352	0.989	3.8	43.73	0.017	0.984	7.4	✓	
3	34.81	6	34.56	0.984	0.998	2.1	30.77	0.044	0.969	10.3	✓	
4	25.30	5	24.70	1.245	0.999	0.2	21.52	0.075	0.978	8.8	✓	
5	19.93	5	19.66	1.436	0.999	1.0	17.42	0.116	0.981	8.1	✓	

^aNumber of data, ^bK1>K2, ^cK2>K1

higher R² value for this model than the lower R² value obtained for the pseudo-second-order model. The fit of pseudo-first-order model depicted in Fig. 7 by solid line. Similar kinetic models were also obtained for the removal of copper (II) by peanut hull carbon³⁷ and methylene blue by calcium alginate-bentonite-activated carbon composite beads³⁸. The data at 1 mg L⁻¹ are fitted with pseudo-second-order model with a higher R² value of 0.998 but AARD_F is a bit large (~3.1%). Since this adsorption study was only conducted with simple matrix solution (i.e. deionized water), the adsorption capacity with the complex matrix still obscure due to their molecular characteristics. Therefore, further studies on effects of the competitive pollutants in real wastewater (i.e. multiple organic pollutants) at various conditions (e.g., pH and temperature) will be considered for practical application. Another point to take into account in future studies is possible regeneration of the coconut shell-based GAC which is a critical aspect in the cost effectiveness.

CONCLUSION

The adsorption of PCP using a coconut shell-based GAC was investigated. The optimized experimental parameters for PCP adsorption include equilibrium time (6 h), initial PCP concentration (100 mg L⁻¹) and adsorbent dose (3 g L⁻¹). The results of the adsorption kinetic analysis showed that a pseudo-first-order model provided the best fit to the experimental data. Analysis of the XRF data showed that PCP was adsorbed onto the GAC. Based on the results earned, it shows that coconut shell-based GAC constitutes an effective adsorbent for removing PCP from aqueous solutions.

SIGNIFICANCE STATEMENT

This study discovered the potential of coconut shell-based GAC for the removal of PCP from aqueous solution with higher adsorption capacity that can be beneficial for

treatment of water and wastewater containing toxic organic compounds. This study will help the researchers to identify the adsorption features together with its mechanism by evaluating the equilibrium isotherms as well as kinetic data of the adsorption process. Thus, a new approach in treating water and wastewater containing toxic organic compounds has been obtained.

ACKNOWLEDGMENTS

The authors admirably acknowledge the “Arus Perdana” (AP-2015-013) along with “Dana Impak Perdana” (DIP-2016-030) from the Universiti Kebangsaan Malaysia for funding this research project.

REFERENCES

1. Singh, S., R. Chandra, D.K. Patel, M.M.K. Reddy and V. Rai, 2008. Investigation of the biotransformation of pentachlorophenol and pulp paper mill effluent decolorisation by the bacterial strains in a mixed culture. *Bioresour. Technol.*, 99: 5703-5709.
2. Mangrulkar, P.A., S.P. Kamble, J.Meshram and S.S. Rayalu, 2008. Adsorption of phenol and o-chlorophenol by mesoporous MCM-41. *J. Hazard. Mater.*, 160: 414-421.
3. Ozkaya, B., 2006. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. *J. Hazard. Mater.*, 129: 158-163.
4. Mukherjee, S., B. Basak, B. Bhunia, A. Dey and B. Mondal, 2013. Potential use of polyphenol oxidases (PPO) in the bioremediation of phenolic contaminants containing industrial wastewater. *Rev. Environ. Sci. Bio/Technol.*, 12: 61-73.
5. Sharma, H.A., J.T. Barber, H.E. Ensley and M.A. Polito, 1997. A comparison of the toxicity and metabolism of phenol and chlorinated phenols by *Lemna gibba*, with special reference to 2,4,5-Trichlorophenol. *Environ. Toxicol. Chem.*, 16: 346-350.

6. Jianlong, W., Q. Yi, N. Horan and E. Stentiford, 2000. Bioadsorption of pentachlorophenol (PCP) from aqueous solution by activated sludge biomass. *Biores. Technol.*, 75: 157-161.
7. Chen, Y.X., H.L. Chen, Y.T. Xu and M.W. Shen, 2004. Irreversible sorption of pentachlorophenol to sediments: Experimental observations. *Environ. Int.*, 30: 31-37.
8. Estevinho, B.N., N. Ratola, A. Alves and L. Santos, 2006. Pentachlorophenol removal from aqueous matrices by sorption with almond shell residues. *J. Hazard. Mater.*, 137: 1175-1181.
9. Czaplicka, M., 2004. Sources and transformations of chlorophenols in the natural environment. *Sci. Total Environ.*, 322: 21-39.
10. Tanjore, S. and T. Viraraghavan, 1994. Pentachlorophenol-water pollution impacts and removal technologies. *Int. J. Environ. Stud.*, 45: 155-164.
11. Gratuito, M.K.B., T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya and A. Dutta, 2008. Production of activated carbon from coconut shell: Optimization using response surface methodology. *Bioresour. Technol.*, 99: 4887-4895.
12. Mohd Din, A.T., B.H. Hameed and A.L. Ahmad, 2009. Batch adsorption of phenol onto physiochemical-activated coconut shell. *J. Hazard. Mater.*, 161: 1522-1529.
13. Bras, I., L. Lemos, A. Alves and M.F.R. Pereira, 2005. Sorption of pentachlorophenol on pine bark. *Chemosphere*, 60: 1095-1102.
14. Adinata, D., W.M.A. Wan Daud and M.K. Aroua, 2007. Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 . *Bioresour. Technol.*, 98: 145-149.
15. Namasivayam, C. and D. Sangeetha, 2005. Kinetic studies of adsorption of thiocyanate onto $ZnCl_2$ activated carbon from coir pith, an agricultural solid waste. *Chemosphere*, 60: 1616-1623.
16. Shaarani, F.W. and B.H. Hameed, 2010. Batch adsorption of 2,4-Dichlorophenol onto activated carbon derived from agricultural waste. *Desalination*, 255: 159-164.
17. Baccar, R., P. Blanquez, J. Bouzid, M. Feki, H. Attiya and M. Sarra, 2013. Modeling of adsorption isotherms and kinetics of a tannery dye onto an activated carbon prepared from an agricultural by-product. *Fuel Process. Technol.*, 106: 408-415.
18. De Luna, M.D.G., E.D. Flores, D.A.D. Genuino, C.M. Futralan and M.W. Wan, 2013. Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from waste rice hulls-optimization, isotherm and kinetic studies. *J. Taiwan Inst. Chem. Eng.*, 44: 646-653.
19. Mahamad, M.N., M.A.A. Zaini and Z.A. Zakaria, 2015. Preparation and characterization of activated carbon from pineapple waste biomass for dye removal. *Intl. Biodeterior. Biodegrad.*, 102: 274-280.
20. Sanghi, R. and P. Verma, 2013. Decolorisation of aqueous dye solutions by low cost adsorbents: A review. *Colorat. Technol.*, 129: 85-108.
21. Smith, N., N.M. Ha, V.K. Cuong, H.T.T. Dong, N.T. Son, B. Baulch and N.T.L. Thuy, 2009. Coconuts in the Mekong Delta: An assessment of competitiveness and industry potential. Prosperity Initiative Report, Prosperity Initiative. <http://eprints.leedsbeckett.ac.uk/1434/>
22. Summers, R.S., D.R.U. Knappe and V.L. Snoeyink, 2010. Adsorption of Organic Compounds. In: *Water Quality and Treatment: A Handbook on Drinking Water*, Edzwald, J.K. (Ed.), 6th Edn., American Waterworks Association, McGraw Hill, USA.
23. Radhika, M. and K. Palanivelu, 2006. Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent-kinetics and isotherm analysis. *J. Hazard. Mater.*, 138: 116-124.
24. Chandra, R. and R. Singh, 2012. Decolourisation and detoxification of rayon grade pulp paper mill effluent by mixed bacterial culture isolated from pulp paper mill effluent polluted site. *Biochem. Eng. J.*, 61: 49-58.
25. Paliwal, R., S. Uniyal and J.P.N. Rai, 2015. Evaluating the potential of immobilized bacterial consortium for black liquor biodegradation. *Environ. Sci. Pollut. Res.*, 22: 6842-6853.
26. Zheng, S., Z. Yang and Y.H. Park, 2004. Removal of chlorophenols from groundwater by chitosan sorption. *Water Res.*, 38: 2315-2322.
27. Hamdaoui, O. and E. Naffrechoux, 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *J. Hazard. Mater.*, 147: 381-394.
28. Langergren, S. 1898. Zurtheorie der sogenannten adsorption geloeesterstoffe. *Veternskapsakad Handlingar*, 24: 1-9.
29. Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. *Proces. Biochem.*, 34: 451-465.
30. Simonin, J.P., 2016. On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chem. Eng. J.*, 300: 254-263.
31. Hameed, B.H., I.A.W. Tan and A.L. Ahmad, 2008. Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon. *Chem. Eng. J.*, 144: 235-244.
32. Srivastava, V.C., I.D. Mall and I.M. Mishra, 2006. Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chem. Eng. J.*, 117: 79-91.
33. Bayram, E., N. Hoda and E. Ayranci, 2009. Adsorption/electrosorption of catechol and resorcinol onto high area activated carbon cloth. *J. Hazard. Mater.*, 168: 1459-1466.

34. Ho, Y.S., 2004. Selection of optimum sorption isotherm. *Carbon*, 42: 2115-2116.
35. Kinniburgh, D.G., 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.*, 20: 895-904.
36. Mane, V.S., I.D. Mall and V.C. Srivastava, 2007. Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *J. Environ. Manage.*, 84: 390-400.
37. Periasamy, K. and C. Namasivayam, 1996. Removal of copper (II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater. *Chemosphere*, 32: 769-789.
38. Benhouria, A., M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala and B.H. Hameed, 2015. Calcium alginate-bentonite-activated carbon composite beads as highly effective adsorbent for methylene blue. *Chem. Eng. J.*, 270: 621-630.