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Removal of Paranitrophenol from aqueous solution onto activated Carbons

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Abstract
In this study, the commercial powdered (PAC) and granular activated (GAC) carbons was tested as adsorbents for removing paranitrophenol (PNP) from aqueous solution. The batch adsorption experimental results indicated that the equilibrium time for PNP adsorption by commercial PAC and GAC was respectively 90 min and 120 min. The adsorption data was modeled by kinetic and equilibrium models. The pseudo- first (PFO) and second order (PSO) kinetic models were applied to fit the experimental data was assessed for describing the mechanism of adsorption. The data were found to be best fitted to the PSO model. The equilibrium study was performed using two models including Langmuir and Freundlich. The results revealed that the Freundlich isotherm fitted well the equilibrium data of PNP onto PAC and GAC. The adsorption for PAC was found to be feasible and spontaneous, with a removal capacity of PNP of more than 30 mg g^{-1}. With regard to the retention area, this removal capacity (30.98 μg_{PNP} $m^{-2}{}_{PAC}$) was 79 % better than that GAC (6.55 μg_{PNP} $m^{-2}{}_{GAC}$).

1. Introduction
Pollution of aquatic environments by organic chemicals occurs from natural products of aquatic microorganisms and artificial contaminants from industrial chemicals or human wastes [1-3]. The effects of organic pollutants reach several domains as rivers, lakes and ponds, reservoirs, groundwater and drinking water. Micropollutants, also called emerging contaminants, consist of an extensive group of synthetic and natural substances, including pharmaceuticals, personal care products, steroid hormones, and agrochemicals [3-5].

Among these pollutants, Phenols are released to the environment from the wastewater produced from many industries including paint, coal conversion, petroleum and petrochemical industries, polymeric resin, pesticides [6-8].

Paranitrophenol (PNP), by United States Environmental Protection Agency, is one of the toxic chemicals, non-degradable and bioaccumulative [9-11]. Its main sources vary such as the paint industry, pesticides, coal conversion, olive presses, in the oil refining and it can also be found in human and animal waste [12]. Some methods have been applied for the elimination of PNP such as microbiological [13], reverse osmosis [14], photocatalytic [15], electrochemical oxidation [16] and adsorption [17]. Because of the toxicity of PNP, their elimination from water is a vital question.

Efforts have been made to the p-nitrophenol (PNP) removal from aqueous solutions by adsorption onto active carbons (ACs) using Nine ACs were prepared from acid-precipitated eucalyptus kraft lignin [18]. El Ouardi et al. shown that the montmorillonite clay was very attractive as an efficient, low-cost, eco-friendly, and recyclable adsorbent for the remediation of hazardous phenolic compounds in industrial effluents [19]. In other study, the synthesized composite of aluminum metal–organic framework in combination with reduced graphene oxide exhibit good performances for p–nitrophenol (PNP) adsorption from aqueous solution [20].

Encouraging results obtained by the cheapest and unconventional groundnut shell used as low cost sorbent to remove paracetamol from aqueous solution [21], have incited us to search new routes to extract PNP. It is the aim of this study. The kinetic and equilibrium data for the adsorption studies were processed to understand the adsorption mechanism of PNP onto commercial activated carbons.

2. Material and Methods

2.1. Adsorbate preparation and analysis

All chemicals used in this study were of analytical reagent grade. Some properties and chemical structures of the PNP are given in Table 1.

The stock solution is prepared by adding 1 g of the PNP to 1L of ultrapure water. PNP solutions were prepared by diluting stock solution of PNP to the desired concentrations in ultrapure water. PNP was measured using a High Performance Liquid Chromatography (HPLC). The flow-rate used was kept at 0.5 mL min^{-1} and the mobile phase is composed methanol- ultrapure water (80:20) (v/v).

2.2. Activated carbons

Two commercial activated carbons were used in this study: a powdered activated carbon (PAC) and a granular activated carbon (GAC). The PAC and GAC were respectively FLUKA and PROLABO (physical characteristics shown in Table 2).

Table 1. Some physico-chemical properties of PNP

Formula	$C_6H_5NO_3$
Molecule weight (g mol^{-1})	139.1
Solubility in water at 25 °C (g L^{-1})	17
pKa at 25 °C	7.15
Log K_{ow}	1.91

Table 2. Physical and chemical characteristics of the PAC and GAC

Parameters	**PAC**	**GAC**
Specific surface (m^2 g^{-1})	1002	1045
Particle size (µm)	10–50	2000-3000

2.3. Batch experiments

In order to investigate the effect of contact time on PNP removal by adsorption, 0.015 g of PAC or 0.5 g of GAC was added to 25 mL of PNP at 5 mg L^{-1}; the whole was stirred at 70 rpm at room temperature. The kinetic study was done for the PAC and GAC in order to estimate the equilibrium time of adsorption and the pseudo-first order (PFO) and pseudo-second order (PSO). Adsorption isotherms were obtained by varying the initial PNP concentration from 5 to 100 mg L^{-1}. The concentrations of PNP in the solutions before and after adsorption were determined using a HPLC. At the end of each experiment, the stirred solution mixture was micofiltered and the residual concentration of adsorbate was determined. The adsorption uptake at equilibrium time, q_e, was expressed by equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

Where q_e is the amount of PNP adsorbed by adsorbent (mg g^{-1}), C_i is the initial liquid-phase concentrations of PNP (mg L^{-1}), C_e is the liquid-phase concentration of PNP (mg L^{-1}), V is the solution volume (L) and m is the mass of adsorbent used (g). All batch experiments were conducted in triplicate and the mean values are reported.

2.4. Adsorption kinetics

Kinetic profiles of PNP removal were generated for commercial PAC and GAC by assessing the equilibrium time in order to test the suitability of PFO and PSO kinetic models. The nonlinear kinetics PFO model may be expressed by equation (2):

$$q_t = q_e(1 - \exp^{-k_1 t}) \qquad (2)$$

Where q_t is the amount of PNP adsorbed per unit mass of adsorbent (mg g^{-1}) at time t, k_1 is the pseudo-first order rate constant (L min^{-1}), and t is the contact time (min). The nonlinear kinetics PSO model may be expressed as in equation (3):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (3)$$

Where k_2 (gm $gmin^{-1}$) is the rate constant for adsorption, q_e (mg g^{-1}) the amount of PNP adsorbed at equilibrium and q_t (mg g^{-1}) is the amount of PNP adsorbed at time t.

2.5. Adsorption isotherms

In this work, the two parameter isotherm equations, namely Langmuir [22] and Freundlich [23] were used for describing the experimental results. The nonlinear Langmuir model can be expressed by equation (4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (4)$$

Where q_e is the amount of PNP adsorbed per unit mass of sorbent (mg g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of PNP in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of sorbent (mg g^{-1}).

Where C_0 is the higher initial concentration of PNP, while and q_m is the Langmuir constant and the maximum adsorption capacity respectively. The nonlinear representation of the Freundlich model is as in equation (5):

$$q_e = K_F C_e^{1/n} \qquad (5)$$

Where K_F (mg g^{-1}) (L mg^{-1})^n and 1/n are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

To optimize the design of an adsorption system for the removal of PNP, it is important to establish the most appropriate correlation for the equilibrium data. Various isotherm equations have been used to describe the isotherm curve. The relative parameters of each equation are obtained using Sum of the Squares of the Errors (SSE) and the coefficient of determination R^2 between the calculated data and the experimental data by nonlinear regressive analysis using the solver Excel. The SSE and R^2 values are determined respectively by following equation (6) and (7):

$$\text{SSE} = \left(q_{\exp} - q_{\text{mod}}\right)^2 \qquad (6)$$

$$R^2 = 100\left(1 - \frac{\left\| q_{\exp} - q_{\text{mod}} \right\|^2}{\left\| q_{\exp} - q_{\text{avr}} \right\|^2}\right) \qquad (7)$$

Where q_{exp} (mg g^{-1}) is equilibrium capacity from the experimental data, q_{avr} (mg g^{-1}) is equilibrium average capacity from the experimental data and q_{mod} (mg g^{-1}) is equilibrium from model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

3. Results and discussion

3.1. Kinetic study

The sorbed PNP concentration at equilibrium q_e was plotted against time for the PAC and GAC (Figure 1 and 2). From the Figure 1 and 2, we can see that sorption was relatively faster onto PAC than onto GAC, the equilibrium is reached in about 90 min for PAC and 120 min for GAC. We can observe that the sorption capacity of the two sorbents can be classified as follows (for C_0 = 5 mg L^{-1}): PAC (6.8 mg g^{-1}) > GAC (0.248 mg g^{-1}). Sorption kinetics was studied at initial PNP concentration 5 mg L^{-1}. The sorption data kinetics was analyzed by using the PFO and PSO models (Table 3). The value of R^2 is compared and between kinetic models, PFO model were shown higher value than other kinetic.

Therefore it can be concluded that the experimental data were fitted with PSO kinetic model. The Figures 3 and 4 confirmed that the suitable PSO model for our experimental equilibrium curves, suggesting that the adsorption process is governed by chemisorption. This hypothesis has been described by several authors [24].

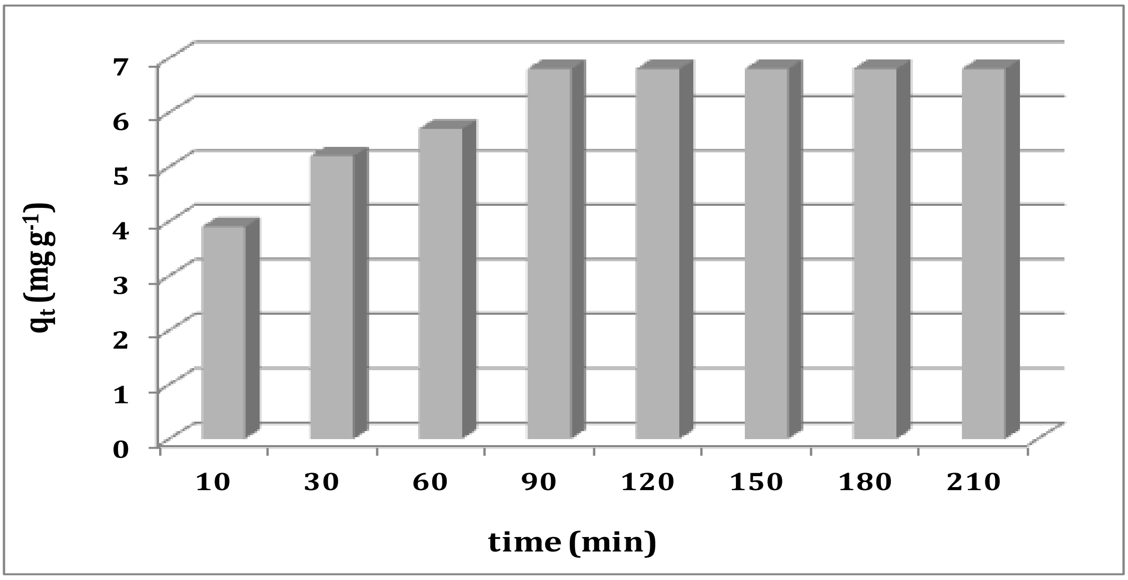

Figure 1. Variation of PNP uptake onto PAC against time

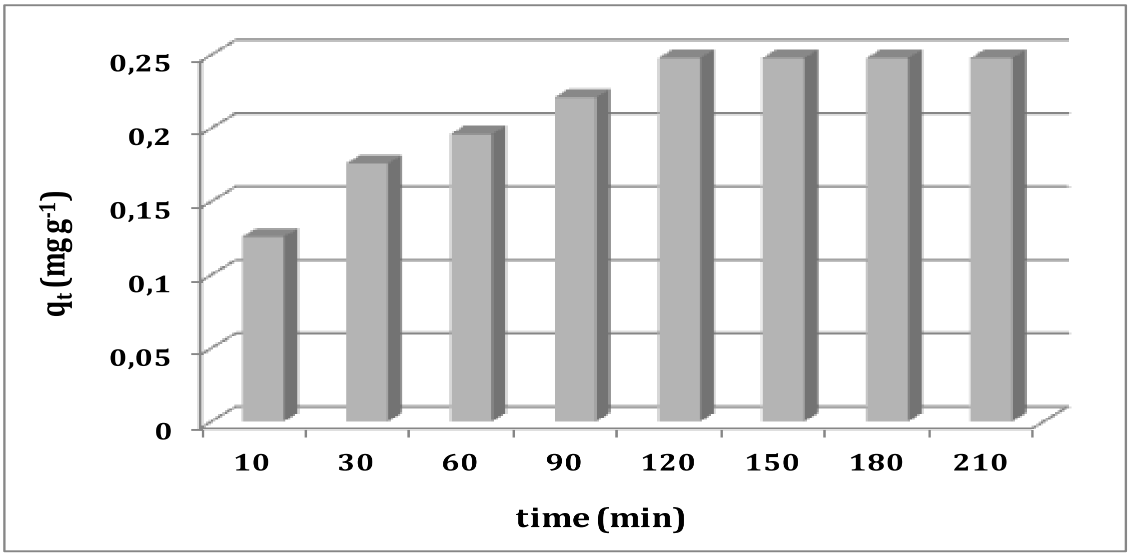

Figure 2. Variation of PNP uptake onto GAC against time

Table 3. Non Linear kinetic model parameters of the studied PNP by activated carbons

		PFO			PSO		
adsorbents	q_{exp}	q_e	K_1	R^2 (%)	q_e	K_2	R^2 (%)
PAC	6.8	6.59	0.070	81.5	7.16	0.015	94.2
GAC	0.248	0.237	0.053	81.4	0.262	0.289	94.2

3.2. Adsorption isotherms

Equilibrium data are commonly represented by Langmuir and Freundlich isotherm models as defined by equations (4) and (5). The isotherm parameters obtained using nonlinear forms, are given in Table 4 for PAC and GAC. The results revealed that the Freundlich isotherm showed the highest R^2 value and lower SSE value compared to Langmuir for the sorption of PNP onto both activated carbons.

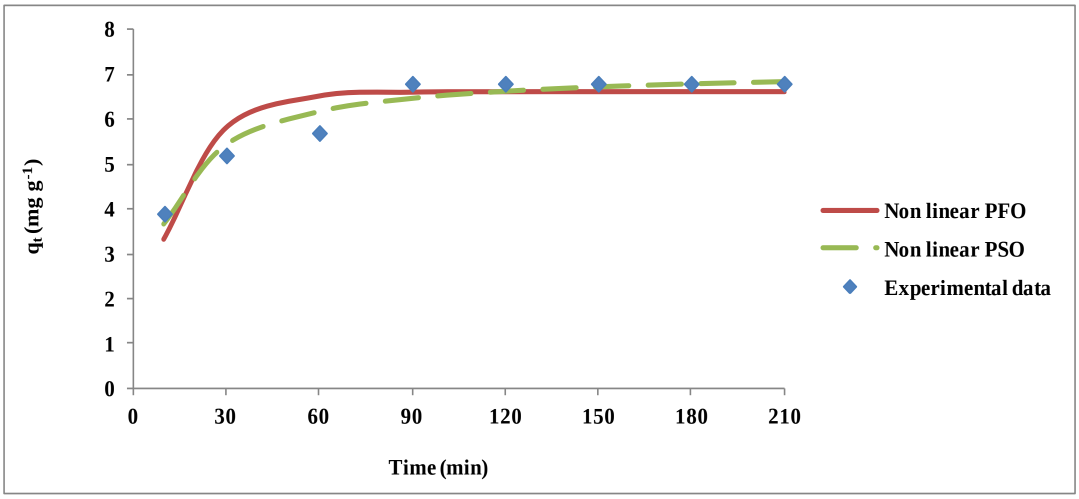

Figure 3. PFO and PSO nonlinear for PAC adsorbent

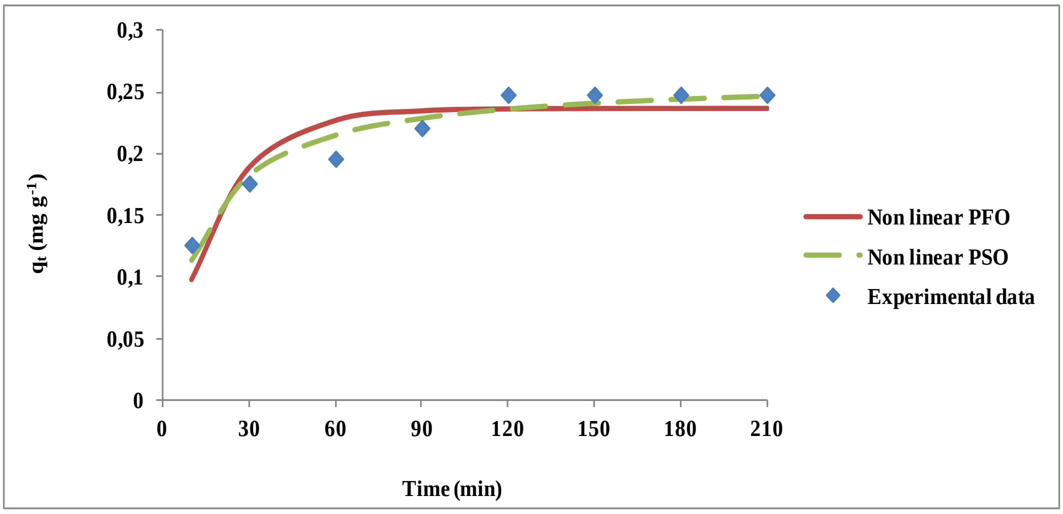

Figure 4. PFO and PSO nonlinear for GAC adsorbent

The Figures 5 and 6 confirmed that the suitable isotherm model for our experimental equilibrium curves was the Freundlich for both materials. Furthmore, it can be seen from Table 4 that all values of K_L and 1/n are in between zero and one. This confirms that the adsorption of PNP onto both sorbents is favorable. The adsorption capacity q_m of PAC and GAC is found to be respectively 31.04 and 6.84 mg g^{-1}, while the K_F values of PAC and GAC is found to be respectively 7.39 and 1.91.

Table 4. Nonlinear isotherm parameters adsorption of PNP by activated carbons

Models	Parameters	PAC	GAC
Langmuir	q_m	31.04	6.84
	K_L	0.12	0.38
	SSE	22.4	0.48
	R^2 (%)	99.93	99.96
Freundlich	1/n	0.31	0.53
	K_F	7.39	1.91
	SSE	15.9	0.25
	R^2 (%)	99.96	99.98

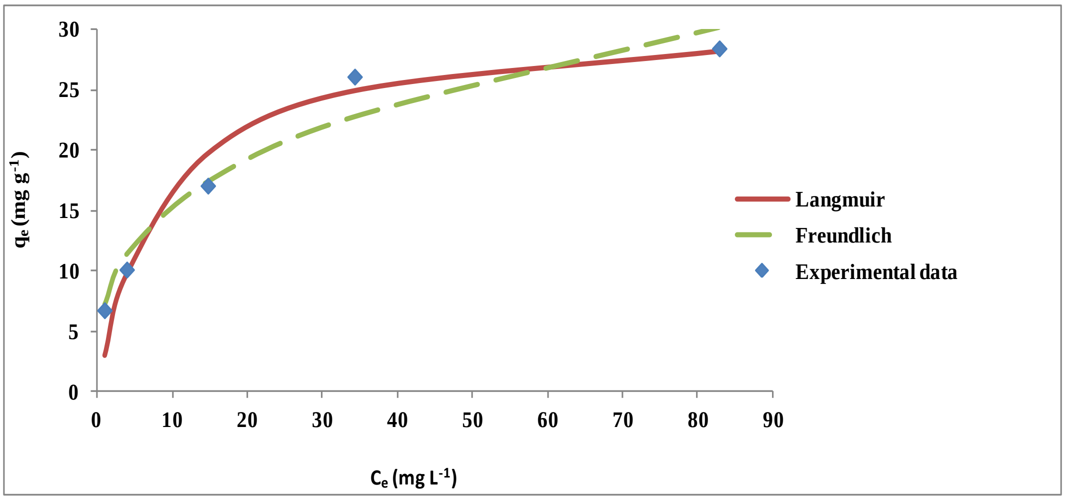

Figure 5. Langmuir and Freundlich nonlinear for PAC adsorbent

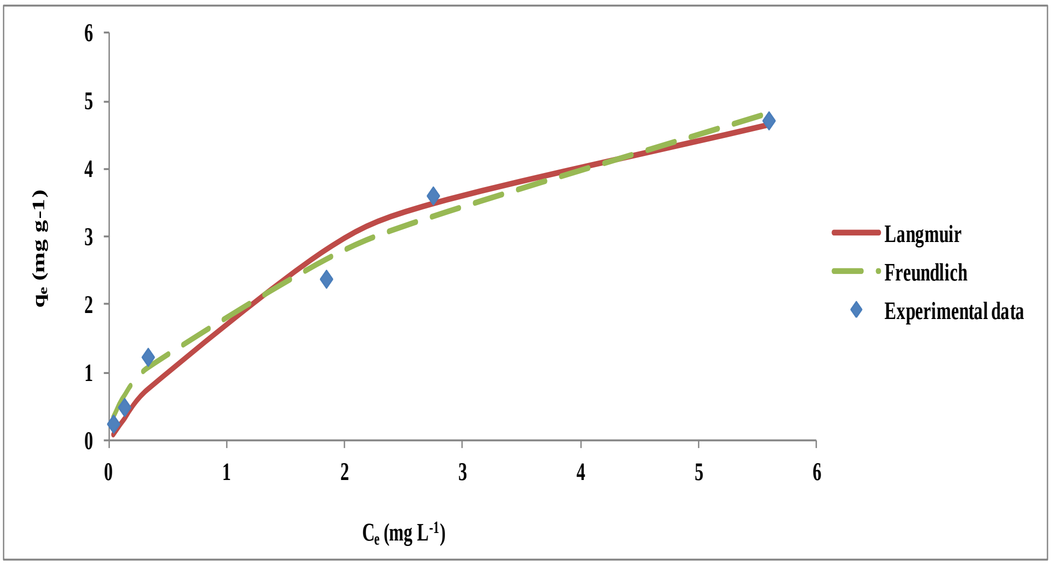

Figure 6. Langmuir and Freundlich non linear for GAC adsorbent

From these values, the adsorption capacity q_m of PAC for PNP is slightly 6 times higher than those of GAC, suggesting the higher effectiveness of PAC for the adsorption removal of PNP. We can notice that the better PNP retention was achieved onto the PAC even if this latter offers the same specific area than the GAC one (Table 2). Functional groups on the surface may account for the difference in PNP retention between the PAC and GAC.

The associated oxygen present on the carbon surface also influences the adsorption of PNP through the formation of a bond with the oxygen surface groups. Similar observations are reported in the literature [24;25]. On the other hand, the PAC with higher carbon content (99.95 %) than the GAC offers more binding sites, confirming the higher effectiveness of PAC for the adsorption removal of PNP. This hypothesis has been described by [26] reports that carbon fraction in the adsorbent determines the capacity of adsorption.

The adsorption capacity q_m of PNP onto PAC is very high compared to the adsorption capacity reached by [27] with commercial Bentonite (0.29 mg g^{-1}) and by [28] with a char ash (11.63 mg g^{-1}), although PNP has a high solubility in water.

In addition, when comparing the sorption capacity for the specific surface area of PAC and GAC, the amount of PNP adsorbed per square meter of PAC (30.98 μg_{PNP} $m^{-2}{}_{PAC}$) is higher than that of GAC (6.55 μg_{PNP} $m^{-2}{}_{GAC}$).

Without forgetting that the addition of small amounts of PAC has been shown to considerably reduce the concentrations of PNP. This finding is in agreement with reported by [29] an others organic molecules.

Conclusion

The present study has described the adsorption of PNP by PAC and GAC. The adsorption was found to follow the PSO order kinetic model, suggesting that diffusing and chemisorption are equally limiting rate step in the whole sorption process.

The equilibrium study was performed using two models including Langmuir and Freundlich. The results revealed that the Langmuir and Freundlich isotherms showed good correlation coefficients R^2 values respectively for the sorption of PNP onto PAC and GAC. The comparison of the sorption capacity for the specific surface area of PAC and GAC showed that the amount of PNP adsorbed per square meter of PAC (30.98 μg_{PNP} $m^{-2}{}_{PAC}$) is higher than that of GAC (6.55 μg_{PNP} $m^{-2}{}_{GAC}$).The results of the present study showed the efficiency of using PAC as an adsorbent for the removal of PNP from aqueous solution.

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