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## Highly Efficient Adsorption of P-Xylene from Aqueous Solutions by Hierarchical Nanoporous Biochar Derived from Crab Shell

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### ABSTRACT

The global consumption of p-xylene (PX) for the production of polymers has raised serious concerns about its impact on the environment. As various reports have shown the risks that PX could pose to human health, research into cost-effective remedial methods to remove PX from the environment has gained attraction. In this work, a hierarchical porous crab shell biochar (KCS) was synthesized, characterized, and evaluated for its efficiency to remove PX from aqueous solution. The characterizations of KCS, including the porous structure, surface functional group, phase structure, and surface morphology, were discussed by N<sub>2</sub> adsorption-desorption, FTIR, XRD, and SEM. Batch adsorption experiments showed that the maximum adsorption capacity of PX on KCS was 393 mg/g within 5 min, larger than most biological/biomass materials, mainly due to the higher specific surface area of 2046 m<sup>2</sup>/g, and abundant lipophilic functional groups. Subsequent adsorption kinetics study indicated a pseudo-second-order model which implied that the adsorption of PX was due to chemisorption. Thermodynamic parameters showed that the values of  $\Delta H^\circ$  and  $\Delta G^\circ$  were both negative, indicating that the PX adsorption process on KCS was spontaneous and exothermic. The performance of KCS in delivering a cost-effective, fast, and efficient solution for the removal of PX from aqueous solution would greatly benefit current environmental remediation efforts.

### KEYWORDS

Crab shell; porous biochar; p-xylene; adsorption; wastewater

## 1 Introduction

In the past few decades, the demand for xylene (PX) has increased exponentially owing to its widespread application as a chemical feedstock for the production of various polymers [1]. Only as a raw material of polyethylene terephthalate (PET) [2], its global demand has reached 45 million tons in 2016 [3] and was



expected to rise further. Due to its widespread usage, it potentially can leak into the soil, surface water, and groundwater, hence raising environmental concerns [4,5]. It may also pose a risk to human health, causing kidney, liver, and nervous system damage [6]. Therefore, the removal of these hazardous and harmful compounds from wastewater is of great significance to resolve the issues of environmental organic pollutants. Several methods have been reported for its removal, such as non-thermal plasma [7], air sparging [8], chemical oxidation [9,10], and adsorption [11,12]. Among these solutions, adsorption was one of the most attractive methods due to its low cost, high efficiency, and superior stability [13,14].

Biochar has been recently identified as a novel material with high adsorption capacity and demonstrated high efficiency for the removal of organic [15–17], inorganic [18–20], and biological contaminants [2,21] from wastewater. This was attributed to its good electrical conductivity, stable chemical properties, high specific surface areas, and controllable pore structures [22]. Biochar was usually produced from biomass, and crustacean waste was seen as a viable source since it is one of the most abundant biomass in nature. As an abundant and cheap food waste, crab shells can be obtained readily from Zhoushan local seafood market. Previously, crustacean waste has been utilised as a raw material for the production of chitin and chitosan [23] as well as electrode materials for supercapacitors [24]. Oxidation was the method to introduce the functional groups, change the surface area, surface charge, and hydrophobicity [25–27]. Arshadi et al reported that the presence of the free carboxyl groups of citric acid raises the density of electron donating groups, and it was the responsible for higher uptake of BTEX [28]. Similarly, Cai et al showed that crab shell treated with potassium hydroxide was found to exhibit mesoporous structures and contained hydroxyl and carboxyl functional groups, leading to its high adsorption capacity for diesel oil [29]. The purpose of this study was to examine the feasibility of using crab shell waste as a novel p-xylene adsorbent. In addition, crab shell-based biochar can not only make use of the superior natural structure of crab shells, but also effectively solve the environmental pollution caused by a large number of discarded crab shells. However, to our best of knowledge, the application of crab shell biochar for the adsorption of PX has not yet been reported.

In this work, crab shell biochar treated with potassium hydroxide was studied for its performance for the removal of PX from aqueous solution. The as-prepared biochar was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transformed infrared (FTIR) and its surface area was determined using the Brunauer–Emmett–Teller (BET) method. Batch adsorption experiments were also carried out to investigate the effects of adsorption time and pH on the efficiency of PX removal from aqueous solution. Adsorption kinetics study of PX was performed using pseudo-first order, pseudo-second order, and intraparticle diffusion models. Adsorption isotherm of PX was investigated using Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. Lastly, the amount of PX adsorbed at equilibrium was also measured at different adsorption temperatures, and the thermodynamic parameters of the adsorption process were investigated.

## 2 Materials and Methods

### 2.1 Materials

Crab shell was purchased from a local seafood market in Zhoushan, washed repeatedly with distilled water to eliminate surface impurities, and dried at 105°C for 12 h in the oven. HCl, KOH and PX were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The chemicals used in this study were analytical grade and were used at the time of reception without further purification unless specified otherwise.

### 2.2 Preparation of Activated Crab Shell Powder

Crab shell (30 g) was immersed in 2 mg/L HCl solution for 12 h to remove calcium carbonate. The crab shell was subsequently rinsed with distilled water to remove HCl and salts remaining on the surface and dried in the oven at 80°C overnight. The pretreated crab shell (CS) was then crushed into powder, and carbonized

in a tubular furnace under nitrogen flow (200 mL/min) with a temperature ramping rate of 10°C/min, and held at 700°C for 120 min.

Then, the pre-carbonized crab shell was ground into a powder and used in the subsequent activation experiments. The pre-carbonized CS was mixed with KOH (CS weight/KOH weight = 2.5:1) and activated in the tubular furnace under nitrogen flow (200 mL/min) with a temperature ramping rate of 10°C/min, and held at 800°C for 60 min. After cooling down to room temperature, the obtained activated biochar was washed with a large amount of distilled water until the filtrate was neutral, and further dried in an oven at 80°C overnight. It was then stored in an air-tight sample vessel. The as-prepared activated biochar was denoted as KOH activated crab shell (KCS). The activation mechanism was referred to in the following reactions Eqs. (1)–(4) [30]. Finally, we were obtained 3.15 g KCS and the yield of biochar was 10.5%.



### 2.3 Characterization of CS and KCS

N<sub>2</sub> adsorption isotherm was performed on the static capacity adsorption analyzer (NOVA 2200e, Quanta chrome, Florida, USA). Surface groups were characterized by Fourier-transform infrared (FTIR, IRAffinity-1S, Tokyo, Japan) in the range of 400–4000 cm<sup>-1</sup>. X-ray diffraction (XRD) patterns of samples were recorded on an Ultima IV X-ray Diffractometer (XRD, DX-2700, Liaoning, China) in the range of 2θ from 10° to 80°. Scanning electron microscopy was conducted to visualize the microstructure and morphology of the samples (SEM, Hitachi S-4800, Tokyo, Japan).

### 2.4 Batch Adsorption of PX

0.01 g KCS and CS were respectively added into 50 mL PX aqueous solution with the concentration range of 10, 20, 40, 60, 80, 100 mg/L for adsorption to analyze the impact of initial concentration. The solution pH was adjusted from 5.0 to 9.0, and the adsorption reaction time is from 5 to 120 min. Centrifuge the mixed solution at a speed of 4000 r/min for 5 min, then sample the transparent liquid on the top and measure its adsorption value (UV 2600, Shimadzu, Shanghai, China). Calculate the concentration of PX in the adsorbent based on the absorption value, and further calculate the amount of PX adsorbed by CS or KCS.

### 2.5 Study on Adsorption Kinetics and Thermodynamics

To investigate the kinetics of PX adsorption, 0.01 g of KCS was added into 50 mL of 80 mg/L PX solution at time intervals from 0 to 120 min. For adsorption isotherms data, 50 mL PX with different initial concentration (10, 20, 40, 60, 80, 100 mg/L) was treated with 0.01 g KCS. Initial and final concentrations of PX were analyzed using a UV–Vis spectrophotometer (UV 2600, Shimadzu, Shanghai). The thermodynamic behavior was investigated at 25, 30, 35, and 40°C by using 0.01 g KCS and 50 mL 80 mg/L PX solution (pH = 7).

### 2.6 Data Analysis

#### 2.6.1 Adsorption Calculation

The adsorption amount  $q_t$  (mg/g) and removal efficiency  $R$  (%) of PX were respectively calculated according to the formula below:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (5)$$

$$R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (6)$$

where  $q_t$  (mg/g) was the amount of PX taken up by the adsorbents,  $C_0$  (mg/L) and  $C_t$  (mg/L) represented the initial concentration and the concentration at some reaction time point,  $V$  was the volume of the solution (L), and  $m$  (g) is the weight of KCS and CS.

### 2.6.2 Adsorption Kinetics Study

Adsorption kinetics is a common method to study the adsorption efficiency of adsorbents. Pseudo-first-order Eq. (7), pseudo-second-order Eq. (8), and Weber-Morris intraparticle diffusion Eq. (9) models were used for the kinetics model fitting of PX adsorption data.

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

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

$$q_t = k_{id} t^{1/2} + C \quad (9)$$

where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the concentrations of contaminants on adsorbent at time “ $t$ ” and equilibrium, respectively.  $k_2$  (g/mg•min),  $k_1$  (min<sup>-1</sup>) and  $k_{id}$  (mg/g•min<sup>1/2</sup>) are second-order model constant, pseudo-first-order model constant, intraparticle diffusion model constant, respectively.  $t$  (min) is time and  $C$  (mg/g) is boundary layer thickness constant.

### 2.6.3 Adsorption Isotherms Study

In order to perceive the process of adsorption onto KCS, the experimental results are correlated with the help of isotherm models such as Langmuir Eq. (10), Freundlich Eq. (11), Dubinin-Radushkevich Eqs. (12) and (13).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (10)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (11)$$

$$\ln q_e = \ln q_m - B\epsilon^2 \quad (12)$$

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (13)$$

where  $C_e$  (mg/g) is the equilibrium concentrations of PX and  $q_e$  (mg/g) is the adsorption capacity of contaminants in water.  $K_L$  (L/mg) is the adsorption equilibrium constant of the Langmuir model;  $q_m$  (mg/g) is the maximum adsorption capacity;  $K_F$  (mg/g) and  $n$  are Freundlich constants related to the adsorption capacity and surface heterogeneity of the adsorbents, respectively.  $B$  is a constant related to the mean free energy of adsorption (mol<sup>2</sup>/J<sup>2</sup>);  $\epsilon$  is the Polanyi potential,  $R$  (J/(mol•K)) is the gas constant and  $T$  (K) is the absolute temperature.

### 2.6.4 Adsorption Thermodynamics Study

The thermodynamic parameters (Gibbs free energy  $\Delta G^0$ , enthalpy  $\Delta H^0$ , and entropy  $\Delta S^0$ ) for the adsorption process of PX were conducted at four different temperatures (25°C, 30°C, 35°C and 40°C). The adsorption process is represented by the following Eqs. (14)–(16).

$$\Delta G^0 = -RT \ln K_C \quad (14)$$

$$K_C = \frac{C_A}{C_S} \quad (15)$$

$$\ln(k_c) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (16)$$

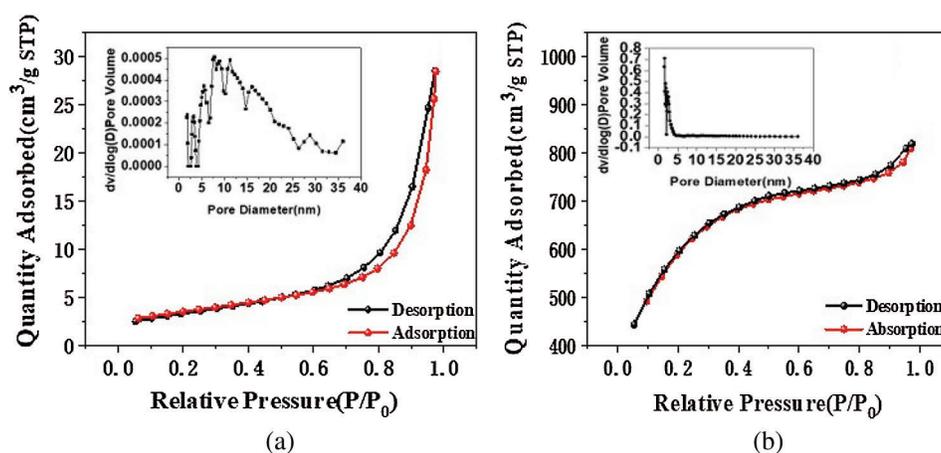
where  $\Delta G^0$  is Gibbs free energy of adsorption, R (J/mol•K) is the gas constant (8.314), T (K) is the absolute temperature and  $K_c$  (L/g) is the standard thermodynamic equilibrium constant defined by  $C_A/C_S$ ,  $C_A$  (mg/L) is the concentration of PX adsorbed at the equilibrium and  $C_S$  (mg/L) is the concentration of PX that remained at equilibrium.

## 3 Results and Discussion

### 3.1 Characterization of Crab Shell Biochar

#### 3.1.1 Porosity Analysis

Fig. 1 shows the  $N_2$  adsorption-desorption isotherms and pore size distributions for CS and KCS. The isotherm of CS showed convex to the  $p/p_0$  axis, which corresponded to a type III isotherm based on IUPAC classification [31]. Accordingly, the adsorbent adsorbate interaction was relatively weak and the adsorbed  $N_2$  molecules were clustered around localized sites on the surface of the suspected nonporous or microporous CS. On the other hand, the isotherm of KCS presented a hysteresis loop at  $P/P_0 > 0.4$ , and its profile suggested a type IV isotherm [32]. The adsorption capacity increased slowly due to capillary condensation of the suspected mesoporous KCS after multilayer adsorption. Subsequent pore size analysis of KCS using non-local density functional theory (NLDFT) method suggested porosity in the narrow range of 1–15 nm, predominantly mesoporous.



**Figure 1:**  $N_2$  adsorption-desorption isotherm pore size distributions of CS (a) and KCS (b)

As shown in Tab. 1, the specific surface area and pore volume of CS analyzed from the  $N_2$  adsorption isotherm data were 12 m<sup>2</sup>/g and 0.04 cm<sup>3</sup>/g. After activation with potassium hydroxide, the specific surface

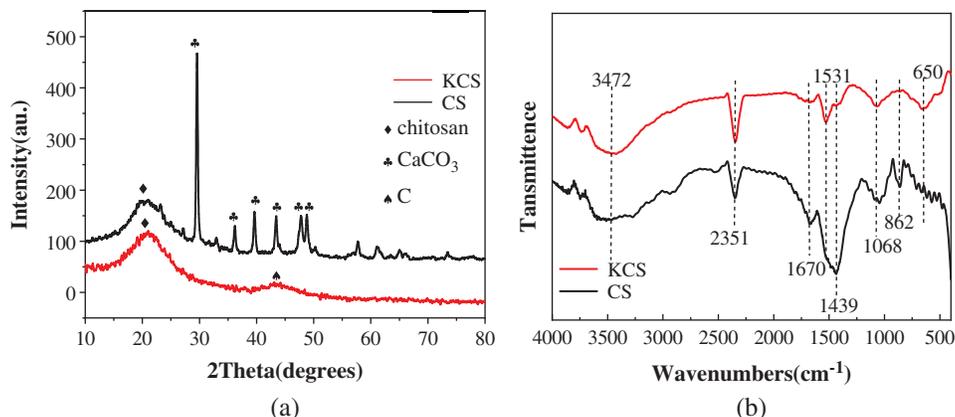
area and pore volume of KCS increased to 2046 m<sup>2</sup>/g and 1.15 cm<sup>3</sup>/g, which were increments of 165 times and 30 times, respectively. This could be due to the removal of the calcium carbonate skeleton of the crab shell upon treatment with hydrochloric acid and subsequently the formation of mesopores upon activation of potassium hydroxide at high temperature. Therefore, the activated crab shell biochar has a significantly high specific surface area as well as high and uniform porosity, which could provide abundant adsorption sites and strongly enhance the adsorption capacity for PX.

**Table 1:** Specific surface area, pore volume, and average pore size of CS and KCS

Absorbent	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
CS powder	12	0.04	3.83
KCS powder	2046	1.15	2.48

### 3.1.2 Phase Structure Analysis

XRD pattern showed that the crystal structure and phase analysis of CS and KCS (Fig. 2a). The wide diffraction peaks at 23.2°, 29.4°, 36.0°, 39.4°, 43.2°, 47.5°, and 48.5° could be indexed to the (012), (104), (110), (113), (202), (018) and (116) crystal planes of CaCO<sub>3</sub>. In addition, there was a diffraction peak at approximately 2θ = 20°, corresponding to (21-2) crystal planes of chitosan. Upon activation with potassium hydroxide, the CaCO<sub>3</sub> peaks disappeared, and only two diffraction peaks located at 20.3° and 43.1° were observed in KCS. These peaks were characteristic of chitosan (21-2) and crystalline graphite (100) planes [33]. The broad weak peak at 2θ = 43.1° further suggested the presence of amorphous carbon.



**Figure 2:** (a) XRD patterns and (b) FTIR spectra of CS and KCS

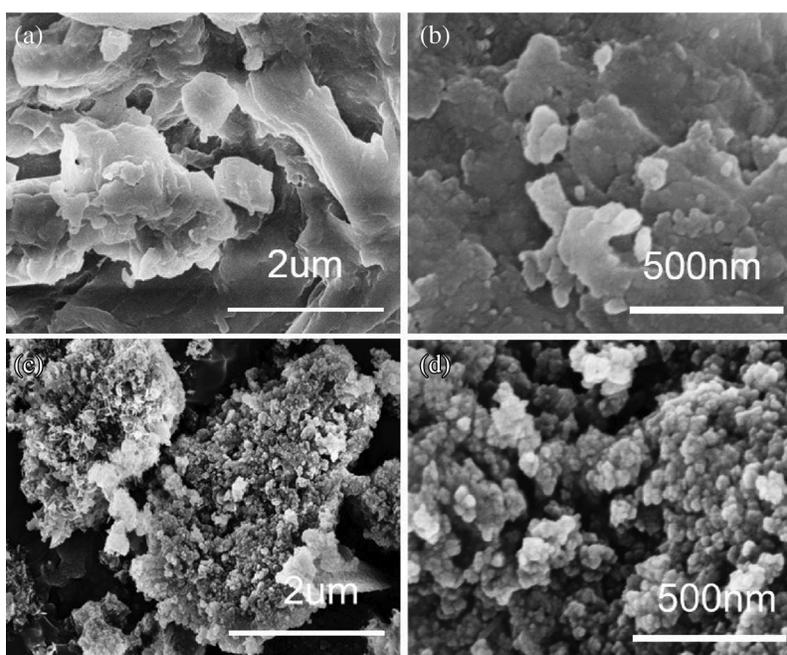
### 3.1.3 Surface Functional Group Analysis

FTIR analyses were subsequently carried out to investigate the chemical compositions of CS and KCS surfaces (Fig. 2b). The FTIR spectra of CS and KCS exhibited a broad band at 3250–3750 cm<sup>-1</sup> attributed carboxylic acid O–H stretch. The bands at 2830, 2508 cm<sup>-1</sup> corresponded to asymmetric and symmetric alkyl –CH stretch. A signal at 2351 cm<sup>-1</sup> was due to RH=C=N stretching mode. The absorption band at 1670 cm<sup>-1</sup> in CS spectrum arose from the axial C=O stretching of acetamido moieties (amide I), which exhibited red-shift to 1531 cm<sup>-1</sup> in KCS spectrum associated with the C=O stretching of amide II [34]. The adsorption band at 1068 cm<sup>-1</sup> was due to C–O stretching mode of the glycosidic ring [35]. In addition, the adsorption bands at 1439 and 862 cm<sup>-1</sup> were characteristic peaks of calcite [36], which disappeared in KCS spectrum due to the pyrolysis process. Instead, an adsorption peak at 650 cm<sup>-1</sup> was present in KCS

spectrum due to O–H bending. The presence of characteristic peaks of chitin in the FTIR spectra of CS and KCS was consistent with their XRD patterns. The types of functional groups present on the surface of biochar strongly dictate its adsorption performance. The methyl-modified surface has been reported to demonstrate excellent adsorption performance for PX [37]. With CS and KCS, the presence of oxygen-containing functional groups such as –OH and C=O alongside alkyl functional groups, which could serve as potential adsorption sites was expected to bestow improved performance for the adsorption for PX [38].

### 3.1.4 Morphology Analysis

The surface morphologies of CS and KCS were subsequently analyzed with SEM (Fig. 3). The microstructure of CS showed a typical loose layered surface with an uneven arrangement. Upon activation with potassium hydroxide, the surface of KCS exhibited a stratified porous structure with uniform mesopores. In addition, the etching effect of potassium hydroxide on surface structures also resulted in the presence of depressions, dents, and cracks, which increased the overall surface area of KCS [39]. The multi-hierarchical surface of KCS could potentially enhance the adsorption for PX.

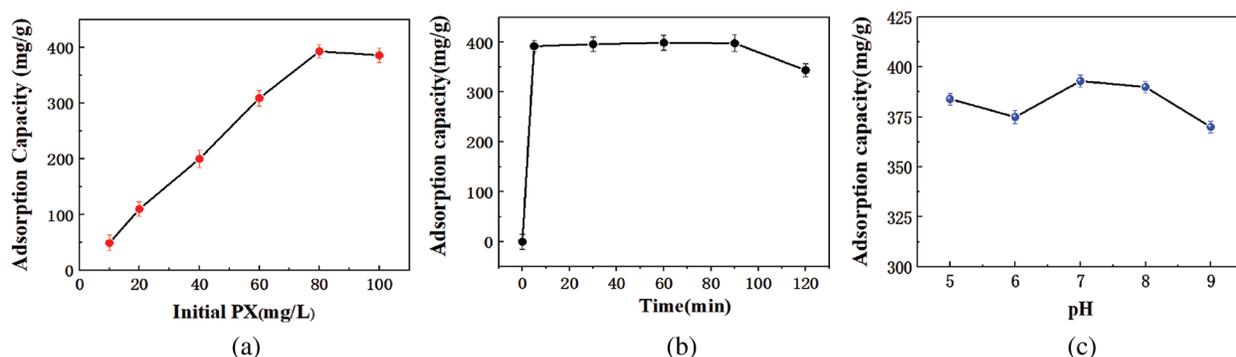


**Figure 3:** SEM images of CS (a, b) and KCS powders (c, d)

## 3.2 Study on Adsorption Performance of PX

### 3.2.1 Effect of Different Initial Concentrations of PX

Fig. 4a shows the adsorption capacity of KCS to different initial concentrations of PX. It was observed that as the concentration of PX in solution increased from 10 to 80 mg/L, the adsorption capacity of KCS increased from 44 to 393 mg/g. However, a further increment of PX concentration beyond 80 mg/L did not result in an increase of adsorption capacity of KCS, which suggested that KCS has reached its equilibrium adsorption capacity. Hence, subsequent experiments were conducted using PX at a concentration of 80 mg/L.



**Figure 4:** Effect of various factors on adsorption capacity of KCS for PX: (a) initial PX concentration, (b) adsorption time, (c) solution pH

### 3.2.2 Effect of Adsorption Time

Fig. 4b illustrates the effect of adsorption time on the adsorption capacity of KCS for PX. The adsorption efficiency increased with increasing adsorption time for KCS until equilibrium is attained, and the maximum adsorption capacity of 390 mg/g was attained within 5 min and with a removal rate of up to 97.5% PX. The maximum adsorption capacity retained for the subsequent 85 min before it decreased after 90 min of exposure. This could be attributed to the desorption of PX from KCS due to competitive adsorption by water molecules. The initial high adsorption efficiency of KCS for PX could be due to an abundance of active sites available on the surface of KCS, as seen from earlier FTIR analysis. As a result, the adsorption equilibrium was attained within such a short time [9,40]. In addition, the low solubility of PX in aqueous solution and the hydrophobicity of PX could also promote its adsorption to KCS surface via hydrophobic interactions.

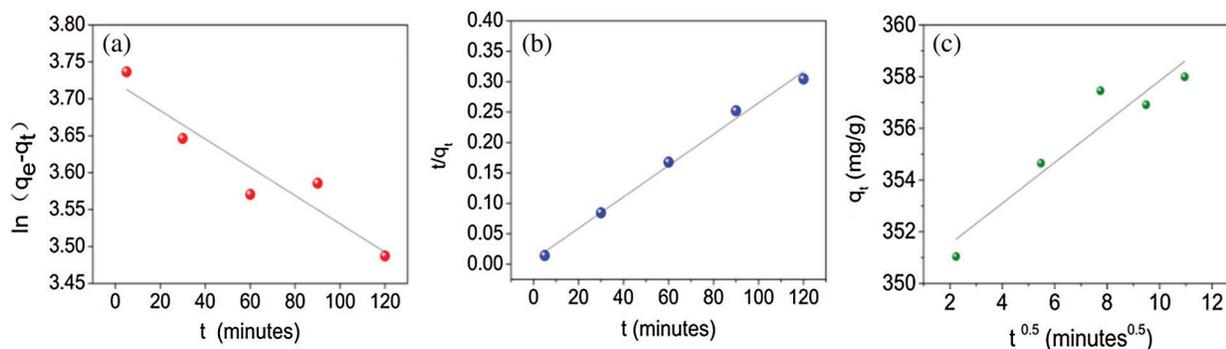
### 3.2.3 Effect of pH

As the surface of KCS contained various functional groups, the pH of the solution would inevitably affect the extent of active sites available for adsorption process. Fig. 4c illustrates the adsorption capacity of KCS for PX in aqueous solutions of pH 5 to 9. The adsorption capacity of KCS for PX was at the highest at 393 mg/g at pH 7. In acidic conditions, because of the high concentration of the competitive  $H^+$  in solutions, the protonation of functional groups in the adsorbents made the number of available functional groups decreased, and rendering less effective binding sites for PX [9]. In alkaline conditions, deprotonated functional groups could exert electrostatic repulsion, and thus reduced the adsorption efficiency [41]. In addition, the surface groups ( $-COOH$ ) was essential for the binding of hydrophobic contaminants and the pH of the solution will be protonated and deprotonated by organic compounds. As for the neutral condition, the interactions of negatively charged oxygen-bearing functional groups on KCS and positively charged  $\pi$  electrons of ring structures could cause strong electrostatic interactions through which the adsorption capacity was increased [42]. This result indicated that the electrostatic interaction was involved in the adsorption process.

### 3.2.4 Adsorption Kinetics Study

Fig. 5 indicates the fitting of experimental data with the respective kinetics models for PX. Tab. 2 provides the results of the kinetics model fittings for the adsorption of PX on KCS. It can be observed that the pseudo-second-order model showed the highest  $R^2$  value of 0.980, as compared to the pseudo-first-order with an  $R^2$  value of 0.862, and the Weber-Morris intraparticle diffusion model with an  $R^2$  value of 0.870. Hence, the pseudo-second-order model was the best model to describe the adsorption of PX on KCS. Based on the least-squares regression, the obtained adsorption amount at equilibrium was

387 mg/g, which was in good agreement with the experimental data of 393 mg/g. In accordance with the pseudo-second-order kinetics mechanism, the adsorption's mechanism is chemically rate-controlling, which incorporates the valence forces by sharing or exchanging electrons between adsorbent and adsorbate [9]. Besides, it was also noted that the least-squares regression analysis on the intraparticle diffusion model provided a line that did not pass through the origin, implying that intraparticle diffusion was not the sole rate controlling adsorption process. Therefore, the overall adsorption kinetics might also be dependent on diffusion across the boundary layer, in addition to intraparticle diffusion [4].



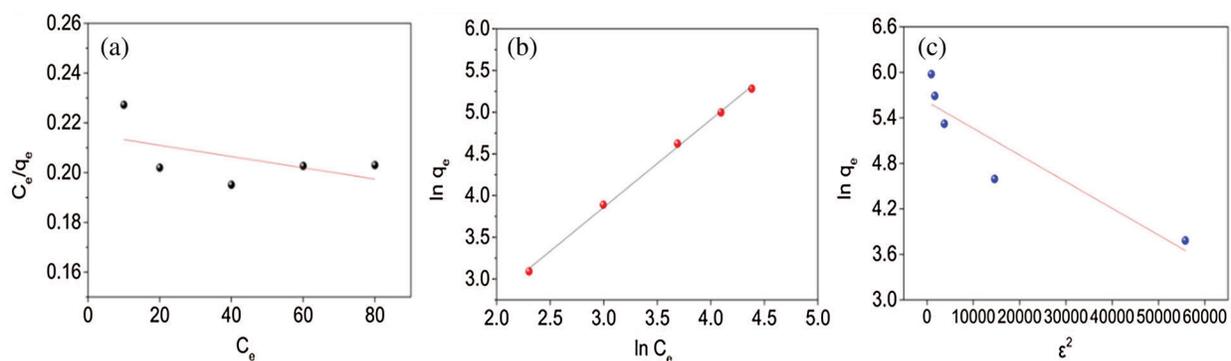
**Figure 5:** Adsorption kinetics model fitting using (a) pseudo-first-order, (b) pseudo-second-order, and (c) Weber-Morris intraparticle diffusion model for PX

**Table 2:** Kinetic model parameters for PX adsorption adsorbed by KCS

Model	Parameters	PX
Pseudo-first-order	$q_e$ (mg/g)	41
	$k_1$ ( $\text{min}^{-1}$ )	0.019
	$R^2$	0.862
Pseudo-second-order	$q_e$ (mg/g)	387
	$k_2$ ( $\text{g/mg}\cdot\text{min}$ ) $\times 10^{-4}$	8.86
	$R^2$	0.980
Intraparticle diffusion model	$C$ (mg/g)	350
	$K_{id}$ ( $\text{mg/g}\cdot\text{min}^{1/2}$ )	0.790
	$R^2$	0.870

### 3.2.5 Adsorption Isotherms Study

Fig. 6 indicates the fitting of data with isotherm models while adsorption parameters and regression data of the models are calculated and presented in Tab. 3. The regression coefficient ( $R^2$ ) of the Freundlich model has the highest value for the adsorption of PX on KCS, indicating that the Freundlich equation is more suited for describing the adsorption of PX on KCS and the adsorption process is multilayer adsorption. The value of  $n$  was close to 1, which indicated favorable adsorption of PX to KCS.



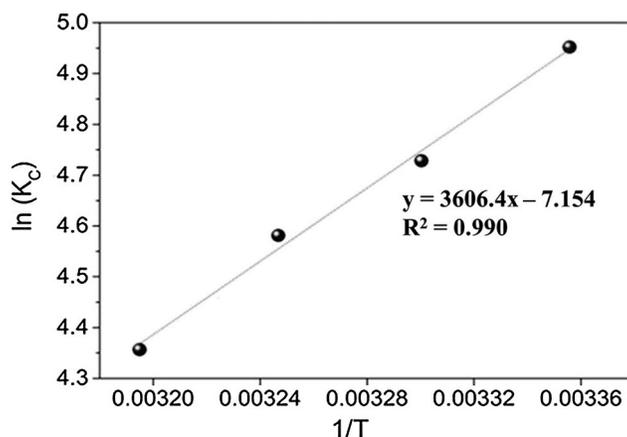
**Figure 6:** Adsorption isotherm model fittings using (a) Langmuir, (b) Freundlich, and (c) Dubinin-Radushkevich models for PX

**Table 3:** Isotherm models parameters for PX adsorption adsorbed by KCS

Model	Parameters	PX
Langmuir	$Q_{\max}$ (mg/g)	442
	$K_L$ (L/mg)	1.05
	$R^2$	0.037
Freundlich	$K_F$ (mg/g)	2.03
	$1/n$	1.051
	$R^2$	0.998
Dubinin-Radushkevich	$B$ (mol <sup>2</sup> J <sup>2</sup> )	$3.518 \times 10^{-5}$
	$Q_m$ (mg/g)	274.2
	$R^2$	0.472

### 3.2.6 Adsorption Thermodynamics Study

By plotting a graph of  $\ln Kc$  vs.  $1/T$  as illustrated in Fig. 7, the values  $\Delta H^\circ$  and  $\Delta S^\circ$  can be estimated from the slopes and intercepts. The thermodynamic parameters are shown in Tab. 4. The obtained  $\Delta H^\circ$  value was negative, which indicated the exothermic nature of PX adsorption onto KCS. Meanwhile, the  $\Delta S^\circ$  was negative, indicating that the entropy of the system decreased during the adsorption process. This result indicated that PX adsorption by the KCS was slightly temperature-dependent. As listed in Tab. 2, the values  $\Delta G^\circ$  turned out to be  $-12.26$ ,  $-11.97$ ,  $-11.67$  and  $-11.37$  kJ/mol at 298, 303, 308 and 313 K, respectively. Besides, the negative values of  $\Delta G^\circ$  indicated that the PX adsorption process on KCS was spontaneous and increasing the temperature would decrease the adsorption capability of KCS. Similar results have been presented by Yu et al. [43].



**Figure 7:** A plot of  $\ln K_c$  vs.  $1/T$  for adsorption of PX on KCS at various temperatures from 298 to 313 K

**Table 4:** Thermodynamic parameters of PX adsorption on KCS at different temperatures

T	$\Delta G^\circ/\text{kJ/mol}$	$\Delta H^\circ/\text{kJ/mol}$	$\Delta S^\circ/\text{J/mol}\cdot\text{K}$
298	-12.26	-29.99	-59.48
303	-11.97		
308	-11.67		
313	-11.37		

### 3.3 Comparison with Other Adsorbents

In order to evaluate the performance of KCS correctly, its performance was compared with the PX adsorption performance reported in other literatures. Tab. 5 shows a comparison of the maximum adsorption capacities of various adsorbents for PX. KCS attained the highest adsorption capacity at 393 mg/g when compared against other previously reported adsorbents. The high adsorption rate of PX on KCS upon initial contact could be attributed to the availability of more active sites and the high surface area of KCS for interaction with PX molecules. Biomass-based biochar has the advantages of high specific surface area, multi-layer porous nanostructure, availability and easy functionalization, which is an ideal material for the construction of high-efficiency adsorbents for adsorption of environmental pollutants [25,26,28]. The methyl and oxygen-containing functional groups on the surface of KCS have also contributed to its better adsorption properties for PX [37]. Through surface modification, the specific surface area and porosity can be increased, which is more conducive to the adsorption of PX [44–46]. Adsorption properties of ethylbenzene and xylene isomers by activated-MWCNTs have been found to depend significantly on mesopore volumes and hydroxyl groups [47]. Hydrophobic surface of ACFs (Six activated carbon fibers) was one of main factors influencing the adsorption, more hydrophobic micropore surface chemistry and high carbon content have the higher adsorption of BTEX [48]. In addition, the low solubility of PX in aqueous solution and hydrophobicity of PX were conducive for the binding of PX to the surface of KCS via hydrophobic interactions. Furthermore, crab shells as a by-product of seafood products could be easily obtained at a much lower cost than carbon nanotube or organosilica while eventually add value to global waste management efforts when exploited as starting material for biochar.

**Table 5:** Comparison of adsorption capacity of different adsorbents for PX removal

Adsorbent	PX $q_{\max}$ (mg/g)	BET surface area(m <sup>2</sup> /g)	Reference
Mesoporous silica nanoparticle	238	255	[11]
Modified periodic mesoporous organosilica	0.63	484	[44]
Smectite organoclay	0.75	61	[45]
Activated carbon	269	871	[46]
SWCNTs (HNO <sub>3</sub> )	85	284	[37]
MWCN (KOH)	96	534	[47]
Six activated carbon fibers	185	483	[48]
KCS	393	2046	This work

#### 4 Conclusions

In this work, activated biochar derived from crab shell was synthesized, characterized, and studied for its adsorption efficiency for PX removal from aqueous solution. The activated biochar KCS, demonstrated the highest adsorption capacity for PX at 393 mg/g, as compared to other adsorbents reported so far. The performance of KCS was attributed to its high specific surface area, hierarchical porous nanostructure, and an abundance of active sites, i.e., lipophilic functional groups, such as methyl and oxygen-containing functional groups, on its surface to aid effective adsorption of PX. Further adsorption kinetic study illustrated that the present adsorption process followed the pseudo-second-order model, while it was inferred from adsorption isotherm analysis that the Freundlich isotherm model fitted the data appropriately well. Consequently, the inexpensive activated crab shell biochar is expected to contribute significantly towards environmental remediation efforts.

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