

Removal of phosphate from aqueous solution by sewage sludge-based activated carbon loaded with pyrolusite

Sicong Yao, Meicheng Wang, Jilong Liu, Shuxiong Tang, Hengli Chen, Tiecheng Guo, Ge Yang and Yao Chen

ABSTRACT

Activated carbons were prepared from sewage sludge by chemical activation with pyrolusite (PAC) to develop an efficient adsorbent for phosphate removal from aqueous solution. One percent (wt.) pyrolusite addition was proved to have an important effect on pore formation of the produced carbon. PAC showed 17.06% larger Brunauer–Emmett–Teller (BET) surface area than the sewage sludge-based activated carbon without modification (SAC). The adsorption results showed that the phosphate removal by PAC was 13% higher than SAC's. The adsorption experiments also showed that PAC had very good performance with high phosphate removal rate (ca. 90%) in a wide pH range (pH = 4–8), and could be stable after 30 min reaction. Adsorption isotherm and kinetics studies demonstrated that phosphate adsorption onto the modified adsorbent was well fitted by the Langmuir isotherm and could be described by the pseudo-second-order kinetic model. The modified sewage sludge-based activated carbons were effective and alternative adsorbents for the removal of phosphorus from aqueous solution due to their considerable adsorptive capacities and the low-cost renewable sources.

Key words | activated carbon, adsorption, phosphorus, pyrolusite, sewage sludge

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INTRODUCTION

Phosphorus is crucial in water contamination (Xiong *et al.* 2017). Excess discharge of phosphorus into water often causes eutrophication, and results in deterioration of water quality. Phosphorus is released into aquatic environment by various human activities such as mining, industrial and agricultural utilization (Saha *et al.* 2016). Phosphorus pollution is ever increasing, and therefore there is an urgent demand to take highly effective, reliable, and economical methods for efficient phosphorus removal.

Phosphate removal is significant for the prevention of eutrophication in natural waters. Various treatment technologies are available for getting rid of phosphorus from wastewater, including chemical precipitation, biological

phosphorus removal, and adsorption (Guaya *et al.* 2015; Huang *et al.* 2015). However, in view of the trace level phosphorus concentration, chemical precipitation often suffers from high cost and low efficiency on residue sludge handling. Moreover, operational difficulties hinder the application of biological phosphate removing methods due to the low phosphorus concentration in water (Long *et al.* 2011). In contrast, the adsorption method was found to be superior to other techniques on phosphate removal from aqueous solution in terms of its flexibility and simplicity design, particularly with low phosphate concentration in wastewater (Han *et al.* 2015). Thus adsorption has attracted intensive interests on developing dephosphatation technology.

It was well known that adsorption capacity and efficiency were greatly dependent on the adsorbents' materials. Many types of adsorbents for phosphate removal have been investigated, which include aluminum and

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aluminum hydroxide, polymeric ligand exchanger, iron oxides, dolomite, red mud, zeolite, furnace slag, mesoporous silicates and so on (Pengthamkeerati *et al.* 2008; Yue *et al.* 2010; Xu *et al.* 2016). However, the direct addition of adsorbents in water treatment systems may cause large losses of adsorbents and reduce their reusability because of the adsorbents' tiny powder size, which are easily run out of the system and restrict the application of those adsorbents (Shi *et al.* 2011). To further improve recyclability and adsorption efficiency, it is necessary to develop some novel phosphate-specific adsorbents.

Activated carbons, with high surface area, microporous structure and great adsorptive capacity, are usually used as adsorbents for the removal of various pollutants from industrial wastewaters. However, the high cost of preparation and utilization of activated carbons is a major drawback of this technology. Currently, there is considerable research on the development of low cost adsorbents from the beneficial use of waste solid materials (Huang *et al.* 2017). Sewage sludge, the final production of wastewater treatment plants, is rich in carbonaceous organic matter, and contains a certain amount of inorganic components, including a variety of metal salts and oxides. After chemical activation and pyrolysis treatment, sewage sludge can be transformed into an excellent adsorptive material. The preparation of sewage sludge-based activated carbons has superiority in sludge volume reduction and high adsorbents production with low cost.

Modified materials have been reported to play important roles in the development of pore structures and surface chemistry on the activated carbons (Goswami & Phukan 2017). Meanwhile, little research is available on activated carbons modified by natural minerals and their adsorption properties on the removal of phosphorus. Pyrolusite is an ordinary and economical natural material widely distributed in Sichuan province, China. In this work, pyrolusite was chosen as the modifier to prepare municipal sewage sludge-based adsorbent. The improvements of their adsorptive abilities on phosphorus removal in aqueous solution were studied. Its characteristics was also evaluated, especially the pore structure and surface chemistry. Operation parameters were investigated for the effective removal of phosphorus from aqueous solution. The equilibrium and kinetic data during the adsorption were analyzed to understand the phosphorus removal process.

It is expected that this work could be useful for an effective sewage sludge management and innovative utilization of sludge residues as low-cost precursors for the adsorbent production, also this work could provide feasibility for phosphorus removal from aqueous environments.

MATERIALS AND METHODS

Preparation of adsorbents

Municipal sewage sludge used as the raw material in this work was taken from a local wastewater treatment plant in Chengdu, China, where wastewater underwent a traditional active sludge process. The proximate analyses of the sludge showed that the moisture content of the raw material was 83.21%, the volatile content, ash content and fixed carbon in dewatered sludge was 66.24, 31.82 and 1.94%, respectively. The ultimate analyses of the dewatered sludge were briefly summarized as 32.61% carbon, 5.10% hydrogen, 5.12% nitrogen and 57.17% oxygen, while the oxygen content was calculated by difference. The ultimate analysis of the raw sludge was taken by Vario MICRO select Elemental Analyzer, Elementar, Germany, in accordance with the standard of JY/T 017-1996 elemental analyzer method. It determines not only the weight percent of carbon content, but also hydrogen and nitrogen contained in organic, inorganic and polymeric materials.

In order to improve the properties of activated carbons, pyrolusite was ground into fine powder and fully blended with the pretreated raw sludge in a certain weight ratio. The pyrolusite used in this study mainly consists of (wt. %): MnO₂ 41.3%, SiO₂ 30.2%, Fe₂O₃ 13.8%, CaO 3.6%, Al₂O₃ 3.4%.

Sewage sludge was first dried in an electric heating oven at 105°C for 48 h. Dried sludge was then ground into powder by a muller and passed through a 160-mesh sieve as pretreatment. The activating agents ZnCl₂ (6 mol/L) and H₂SO₄ (35 wt%) were mixed at a volume ratio of 4:1. The mixture of sludge and pyrolusite power was then impregnated into the activating agent at a ratio of 1:4 (g/mL) and kept for 24 h under room temperature. The impregnated samples were then put into a ceramic crucible and heated in a tubular furnace (KXG-2-13A, Shanghai, China) with a constant heating rate of 10°C/min to 550°C in nitrogen atmosphere (99.99%, 200 mL/min).

After 60 min pyrolysis at 550°C with purified nitrogen flow, the carbonization samples were cooled down to room temperature in the furnace. The samples were taken out and washed several times sequentially with 3M HCl and hot distilled water (70–80°C) to remove any residual chemicals. The carbon products were then dried in an electric heating oven at 105°C for 24 h, cooled in the desiccator, crushed and sieved through a 200-mesh filter to obtain the final sewage sludge-based adsorbents.

Activated carbons produced from sewage sludge with pyrolusite addition were designated as PAC, while the unmodified sewage sludge-based activated carbon was named as SAC for comparison.

Characterization of activated carbons

The Brunauer–Emmett–Teller (BET) surface area and pore structure of the produced carbons (outgassed under vacuum at 200°C before analysis) were obtained by N₂ adsorption isotherm at 77 K using a surface area analyzer (SSA-4200, China). From the isotherm data, BET surface area, micro- and mesopore volume and mean pore radius were calculated.

Scanning electron microscopy (SEM) images were recorded to visualize sample's morphology. Pore structure and structural changes after chemical activation could also be observed. In the present work, the surface morphology of the produced carbons (SAC, PAC) were obtained using a JSM-5900LV scanning electron microscope (SEM, Japan).

A Fourier transform infrared spectrometer (FTIR 6700 NEXUS Nicolet, USA) was used to analyze the main functional groups that may be involved in phosphate adsorption on SAC and PAC. The spectra were recorded from 4,000 to 400 cm⁻¹ using a KBr window.

The concentration of total phosphorus (TP) in the solution was analyzed by a UV1800 spectrometer. Iodine and methylene (MB) adsorptive capacity were tested according to the standard methods for the determination of iodine and methylene adsorption value of the produced carbons.

Batch adsorption experiments

Stock phosphorus solution was prepared by dissolving KH₂PO₄ in deionized water. All the chemicals used were analytical grade.

The experiments were conducted in a series of 150 mL Erlenmeyer flasks with magnetic stirring (150 rpm) and maintained at 25°C by a thermostatic bath to reach equilibrium. The solution pH was adjusted by HNO₃ or NaOH (1 mol/L). The samples were filtered out and the TP concentration of the supernatant was analyzed through a UV-spectrometer.

Batch experiments were carried out by adding a certain amount of the produced carbon into 50 mL synthetic solution with an initial TP concentration of 5 mg/L, to verify the adsorption efficiency at different reaction times.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by Equation (1):

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

where C_0 and C_e (mg/L) are the liquid-phase concentrations of metal ion at initial and equilibrium, respectively. V (L) is the volume of the solution, and m (g) is the mass of the dry adsorbent used.

The accuracy of analytical techniques has been checked by relative standard deviation (RSD), and the maximum standard deviation observed was <5%. All the adsorption experiments were conducted twice, and the results were the mean value of the tests.

RESULTS AND DISCUSSION

Characterization of adsorbents

Specific surface area and SEM of adsorbents

In this study, pyrolusite was chosen to improve the activated carbons' adsorptive capacity. According to our previous experiments, the most obvious TP adsorption occurred with 1% (wt.) pyrolusite loading on the produced activated carbon. Pyrolusite contains a variety of metal compounds which are favorable for pore formation during the process of carbonization and activation, thus enhancing the adsorption performance.

The iodine and methylene blue (MB) adsorption capacity were investigated for the produced adsorbent. The methylene blue adsorption experiments were carried out with 2 g/L adsorbents dosage under the initial MB

concentration of 300 mg/L. After 4 h adsorption at room temperature, the MB adsorption values of SAC and PAC were tested as 132.6 and 144.3 mg/g, respectively.

The surface morphology of SAC and PAC were observed using SEM and is shown in Figure 1. It can be seen from the micrographs that a considerable number of pores, cavities and crevices are present in both adsorbents' surface. Those spaces result from the reagent's evaporation during carbonization, which were previously occupied by the activating agents. As presented in Figure 1(b), the uneven and rough surface on PAC showed dramatically luxuriant pores comparing with SAC, which is probably due to the pyrolusite modification. It should be much more effective on forming the pore structure.

The specific surface area and pore structure of the produced activated carbons were measured and are listed in Table 1. A significant increment of the surface physical properties was observed for PAC. The BET surface area, total pore volume, mesopore and micropore volume of PAC were 17.06, 51.57, 57.04 and 43.34%, respectively, higher than those of SAC's. The obvious increase of specific surface area on the PAC was ascribed to the relatively high production of micro- and mesopores compared to SAC. It is expected that

the modified carbon could obtain adequate surface areas by mineral loading. Pyrolusite modification could increase adsorbents' porosity by enhancing oxygen functional groups interaction, dehydration and dehydrogenation reactions on the activated carbon. Also, the large pore volume could help mass transfer to easily ingress and egress between adsorbents and the external environment in the solution.

FTIR

Infrared spectroscopy was used to record the chemical changes occurring on the surface of the adsorbent. The FTIR spectra of the dried raw sewage sludge and PAC are presented in Figure 2. After the thermal treatment, the IR spectrum of PAC was obviously simplified compared with the raw sewage sludge's.

As shown in Figure 2, the bands observed at 2,923 and 2,852 cm^{-1} represented symmetric and asymmetric C-H stretching vibrations of aliphatic CH, CH₂, and CH₃ groups from the raw materials (Park & Jung 2002). It could be seen that after pyrolysis, the spectrum of raw material and PAC were obviously changed. There is a trough at

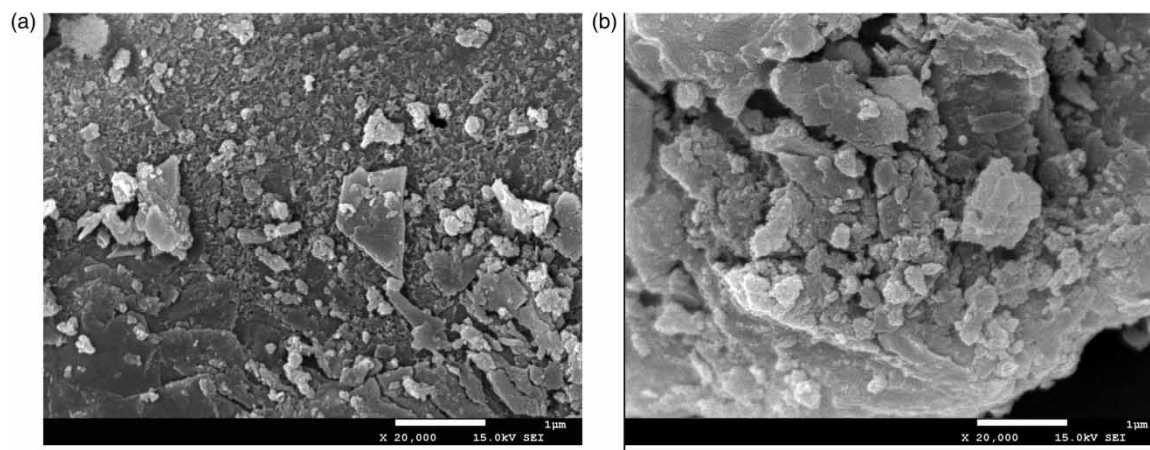


Figure 1 | SEM micrographs of (a) SAC and (b) PAC.

Table 1 | Characteristics of the produced activated carbons

Absorbents	S _{BET} (m ² /g)	Total pore volumes (cm ³ /g)	Mesopore volumes (cm ³ /g)	Micropore volumes (cm ³ /g)	Average diameter (nm)
SAC	218.37	0.2519	0.1506	0.1013	2.30
PAC	255.63	0.3818	0.2365	0.1452	2.99

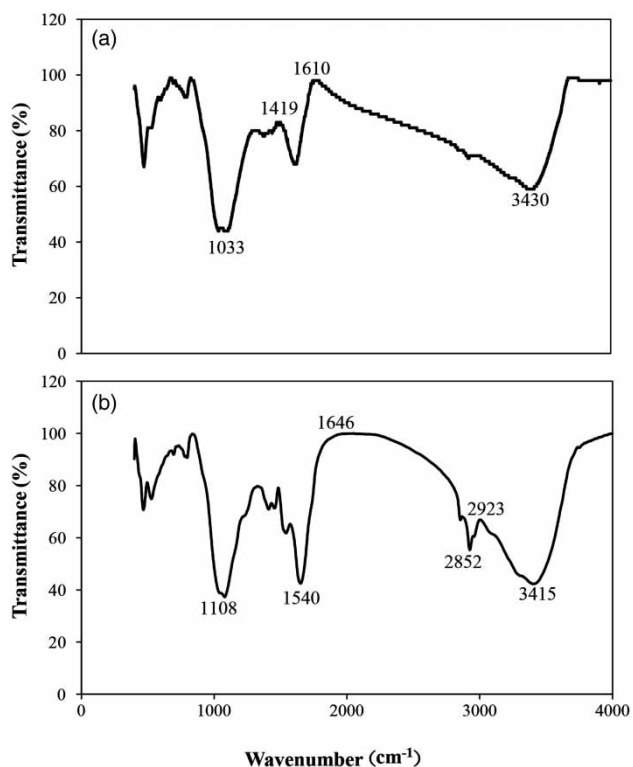


Figure 2 | FTIR spectra of (a) PAC and (b) raw sludge.

2,852 cm^{-1} for raw sludge and it becomes flattened after pyrolysis for PAC. This proved that alkane groups were involved during the carbonization and disappeared after pyrolysis (Demiral & Gunduzoglu 2010). Furthermore, the slight wavelength shifts from 1,540 to 1,419, 3,430 to 3,415 and 1,646 to 1,610 cm^{-1} can also be observed from Figure 2. These bands were ascribed to the organic parts of the raw sludge, which were shifted for the produced carbons during activation and carbonization (Xie *et al.* 2013).

The observation of these oxygenic functional groups' shifting wavelengths can be inferred that the modification has indeed occurred with a certain influence on the raw materials and indicates that modified carbons could improve the removal efficiency toward phosphorus.

Adsorption

Effect of dosage and contact time

Figure 3 shows the impact of contact time on phosphorus adsorption by PAC at the initial solution pH. To determine

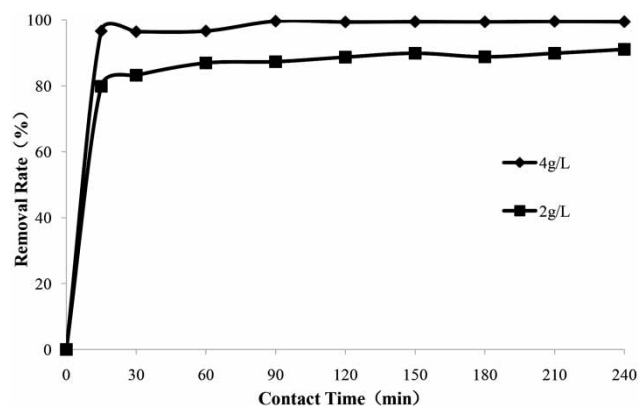


Figure 3 | The effect of PAC dosage on phosphorus adsorption.

the adsorption capacity of an adsorbent, the adsorbent dose is a major factor. The effect of adsorbent dosage on TP removal was studied at two different doses (2 and 4 g/L) at an initial TP concentration of 5 mg/L.

Figure 3 indicates that as the dose increases TP removal rate was also increased from 83% to nearly 100%. Greater availability of active sites and increment of adsorbent's surface area with an increase in adsorbent amount was reported (Deng & Shi 2015). Also, it was noticed that TP removal did not show any obvious increase after 30 min at 4 g/L adsorbent's dosage. This may be due to the fact that all phosphate ions were completely absorbed by PAC at 4 g/L dosage and the removal rate was close to 100%, the adsorbents cannot reach the adsorption saturation under this dosage condition and it was not sufficiently economical. In comparison, it was more efficient when adsorbent dosage was 2 g/L with more than 91% removal rate after 240 min. It can be determined that the optimum dosage for PAC was 2 g/L (Xiong *et al.* 2008).

As seen from Figure 3, the TP removal rate increased with the increasing contact time. The adsorption increased rapidly in the first 30 min, probably due to the readily accessible sites on the carbon surface. When the surface adsorption sites became exhausted, the uptake rate was slowed down and controlled by the transport rate from the outside to the inside of the adsorbent, finally reaching equilibrium at 4 h.

Yang *et al.* (2013) used a tablet porous material (TPM) developed as adsorbent for phosphate removal and the results showed that the experimental maximum adsorption removal rate was 21.9% when the initial phosphate

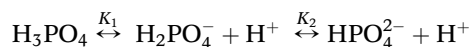
concentration was 80 mg/L (TPM dosage: 4 g/L). Karimaian *et al.* (2013) used natural and engineered waste pumice for phosphate removal and while the initial phosphate concentration was 5 mg/L and the pumice dosage was 6 g/L, the removal rate reached 63.6% after 140 min. Xiong *et al.* (2011) used powdered freshwater mussel shells for phosphate removal and after 720 min with 20 g/L dosage and an initial phosphate concentration of 20 mg/L, the removal rate was 96.01%.

Comparing the current work with reported data above showed that maximum TP removal was achieved using PAC, while other adsorbents take more time and higher adsorbent dosages to obtain an efficient TP removal rate.

Effect of pH

Generally, pH values display a significant impact on phosphate adsorption (Alkan *et al.* 2004). The initial pH of the adsorbate solution influences the adsorption process by changing the adsorbent's functional group (Gunay *et al.* 2007). The adsorption of phosphate under different pH was determined in the pH range of 2.0–8.0 for TP = 5 mg/L with a PAC dose of 2 g/L. The change of pH values in the adsorption process as a function of removal efficiency by PAC is shown in Figure 4. Figure 4 shows that the removal efficiency of phosphate increased sharply at the initial stage when the pH value was 2–3. The observed trend is related to phosphate proton dissociation equilibrium. The species of phosphate is different under different pHs, as shown by

the following reactions:



where $pK_1 = 2.13$ and $pK_2 = 7.20$. At pH 2.13, the predominant species of phosphate is H_3PO_4 which is weakly attached to the sites of the adsorbent. When pH is in the range of 2.13–7.20, PAC did perform well with the main phosphate species of monovalent H_2PO_4^- . The form of metal active sites is most likely through the protonation process: $\text{M}-\text{OH} + \text{H}^+ \leftrightarrow \text{M}-\text{OH}_2^+$, where $\text{M}-\text{OH}_2^+$ represents positive charged surface group. $-\text{OH}_2^+$ is easier to be displaced at low pH from the metal binding sites than hydroxyl groups, which can facilitate the ligand exchange process (Qian *et al.* 2017). So the electrostatic interactions and ion exchange should be the main mechanisms in this pH range. It also indicated that phosphate sorption onto PAC was primarily the result of an ion-exchange between phosphate and hydroxide groups on the adsorbent surface. An inner sphere complex is formed when phosphate is directly chemically bonded to the active sites which are deposited on the adsorbent surface.

Figure 4 depicts that TP removal was favored in weakly acidic to neutral conditions (pH = 6.0–7.0), and removal efficiency was observed to be 83% and 86% under 6.0 and 7.0 pH conditions for phosphate ion adsorption respectively. Thus the initial solution pH (around 6.4) was within the optimum pH range and no pH adjustment during the PAC adsorption process was necessary. It was also proved that PAC has good pH adaptability toward phosphorus removal.

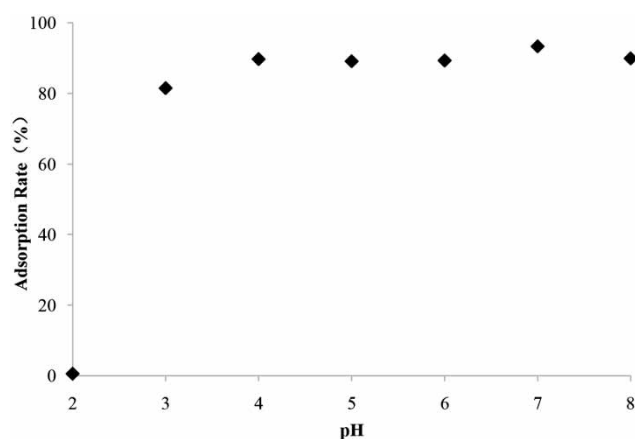


Figure 4 | The effect of pH on phosphorus adsorption by PAC.

Adsorption kinetic

Adsorption kinetic modeling is very useful for better understanding phosphate adsorption mechanisms onto modified activated carbon, such as the importance of the chemical reactions and the intra-particle diffusion processes. Kinetic studies are generally used to determine the uptake rate of the adsorbates, and to control the residual time of the whole adsorption process. In the present study, three kinetic models, viz. the pseudo-first-order, pseudo-second-order and intra-particle diffusion, were

selected for the description of the adsorption experimental results.

The pseudo-first-order kinetic model is the most widely used rate equation for the sorption of a solute from a liquid solution and is generally expressed as Equation (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where q_e and q_t (mg/g) are the amounts of total phosphate adsorbed at equilibrium and time t (h), respectively, and k_1 (1/h) is the rate constant of pseudo-first-order adsorption. The values of k_1 and q_e can be obtained from the linear plot of $\log(q_e - q_t)$ vs. t plots.

The pseudo-second-order kinetic model based on equilibrium adsorption can be represented as Equation (3):

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

where k_2 (g/mg·h) is the rate constant of the second-order adsorption. The values of q_e and k_2 are calculated from the linear plot of t/q_t vs. t .

The intra-particle diffusion model is generally expressed as Equation (4):

$$q_t = k_p t^{0.5} \quad (4)$$

where k_p (mg/(g·min^{1/2})) is the adsorption rate constant for the intra-particle model (Gunay et al. 2007; Subbaiah & Kim 2016).

The calculated parameters for all the kinetic models are listed in Table 2. In general, the adsorption process can be described as a series of steps: mass transfer from fluid phase to the particle surface across the boundary layer, diffusion within the porous particle, and adsorption itself onto the

surface. According to Table 2, the correlation coefficients were relatively low lying between 0.76 and 0.96 for the pseudo-first-order model and intra-particle model. These results state a bad fit between the model and the experimental data. As a consequence, phosphates adsorptions by SAC and PAC are not ideal pseudo-first-order or intra-particle diffusion reactions. The highest correlation coefficients for phosphate adsorption by SAC and PAC were obtained through the pseudo-second-order kinetic model. The R^2 values were greater than 0.99 for TP adsorption, while PAC ($R^2 = 0.9995$) had a higher R^2 value compared with SAC ($R^2 = 0.9955$). In addition, the difference between the experimental and theoretical adsorbed masses at equilibrium is very small (less than 1%). The applicability of the pseudo-second order kinetic model demonstrated the adsorption process well. It revealed that the limiting stage of the process was the adsorptive mechanism rather than the mass transfer from the solution to the adsorbent's surface. It also reflected that the adsorption behavior may involve the valence forces through sharing electrons between the phosphate and adsorbents.

Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules are distributed between the liquid phase and the solid phase at given pH values and temperatures, which was obtained by varying the initial concentrations of P (1–50 mg/L) at room temperature. The capacity of an adsorbent can be described by its equilibrium sorption isotherm, which is characterized by certain constants that express the surface properties and affinity of the adsorbent. To analyze the validity of the adsorption data, Langmuir and Freundlich adsorption isotherm models were discussed.

The Langmuir isotherm equation, which is the most commonly used for monolayer adsorption with a finite

Table 2 | Kinetic parameters for the adsorption of phosphorus onto SAC and PAC

Adsorbents	Pseudo-first-order				Pseudo-second-order			Intra-particle diffusion	
	q_e (exp)	q_e (cal)	k_1	R^2	q_e (cal)	k_2	R^2	k_p	R^2
SAC	1.6262	1.6254	0.0247	0.7954	1.6798	0.0495	0.9955	0.0559	0.9626
PAC	2.2347	2.2641	0.0147	0.7675	2.2614	0.1513	0.9995	0.0217	0.9647

q_e (exp) was obtained from experiments and q_e (cal) is calculated from models.

number of identical sites on the surface, is represented as Equation (5):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where C_e (mg/L) is the equilibrium concentration of phosphate, q_e (mg/g) is the amount of TP adsorbed onto the adsorbent at specified equilibrium, q_m (mg/g) is the theoretical maximum adsorption capacity of TP onto the adsorbent, and K_L (L/mg) is the Langmuir adsorption equilibrium constant related to the affinity of the binding sites.

The Freundlich isotherm equation, the most important multilayer adsorption isotherm for heterogeneous surfaces, is described by Equation (6):

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

where K_F ((mg/g)(L/mg)^{1/n}) and n are the Freundlich adsorption isotherm constants which are indicators of adsorption capacity, and adsorption intensity, respectively (Oguz 2005).

Equilibrium adsorption isotherms could provide useful data for understanding the mechanism of a given adsorption process. In the present study, adsorption isotherm experiments were conducted at room temperature with initial phosphorus concentrations of 1–50 mg/L, and the contact time of the experiments lasted 240 min. The calculated isotherm constants are presented in Table 3. In terms of the correlation coefficient R^2 , the experimental data could be well fitted to the Langmuir isotherm rather than the Freundlich isotherm model. Thus, it showed that the adsorption process occurred on the carbons' surface and was monolayer adsorption. The Langmuir model assumes that adsorbent is structurally homogenous and the adsorption process ends up in monolayer coverage with uniform

adsorption energies. The maximum TP adsorption capacity on PAC calculated by the Langmuir model was 10.78 mg/g.

Evaluation of the produced activated carbon

A comparative test was carried out to evaluate the performance among sewage sludge carbon (SAC), pyrolusite modified sludge carbon (PAC), commercial carbon prepared by coconut shell (AC), lithium-silicon powder (LS-Powder) and walnut shell-based carbon (WS-AC) for TP removal. It can be seen in Figure 5 that PAC had the highest removal rate compared with other adsorbents under the same experimental conditions (initial pH 5.0, contact time of 4 h, 25°C, and initial TP concentration of 5 mg/L). While the dosing of PAC (2 g/L) was only half the amount of other adsorbents (4 g/L) and much less than AC (6 mg/L), it also showed outstanding performances on TP removal. With 91.1% of TP removal rate by PAC, it is 4% higher than SAC, and 81.9, 84.8 and 87.14% higher than LS-powder, WS-AC and AC, respectively. According to previous research, lithium-silicon powder, a common nature mineral, had a significant influence on the activated carbon modification. Lithium-silicon powder had good performance on some specific pollutants treatment. Similarly, walnut shell-based carbon had a massive removal effect and is widely used in wastewater treatment. The commercial activated carbon prepared by coconut shells had massive specific surface area and mesopore volume based on the BET surface area examination, which had a considerable effect toward the adsorption of dye molecules and flue gas. However, as seen in Figure 5, LS-AC, WS-AC and AC were not suitable for phosphorus adsorption. It can be concluded that sewage sludge-based activated carbons modified with pyrolusite had a significant effect on phosphorus removal compared with other adsorbents.

Table 3 | Langmuir and Freundlich isotherm models for phosphorus adsorption onto SAC and PAC

Adsorbents	Q_e (mg/g)	Langmuir isotherm			Freundlich isotherm		
		Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g(L/mg) ^{1/n})	1/n (mmol/g)	R^2
SAC	2.6665	2.7755	1.1025	0.9540	2.1223	0.4289	0.8633
PAC	10.0734	10.7759	0.2791	0.9401	2.1223	0.4751	0.9283

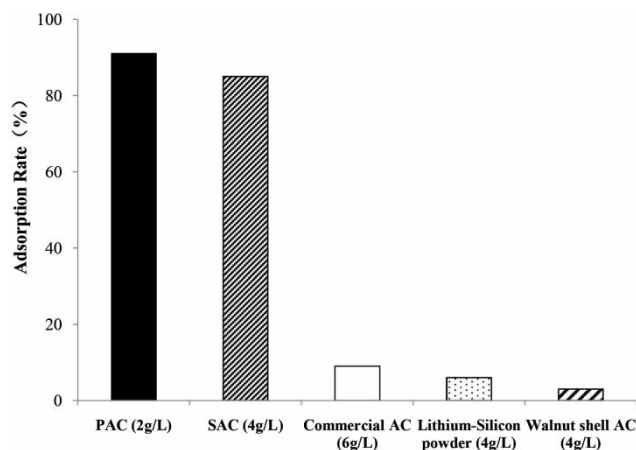


Figure 5 | Phosphorus adsorptive performance by various adsorbents under optimum reaction conditions.

According to our previous study, PAC also had preminent adsorption performance on the removal of heavy metal ions (e.g. Cu(II), Pb(II) and Cd(II) etc.) (Xie *et al.* 2013) and the treatment of dye wastewaters (Chen *et al.* 2012). This proved that PAC has relatively outstanding adaptability on various pollutants. The exploitation and utilization toward PAC has enormous economic benefit and potential for practical application.

CONCLUSIONS

Activated carbons produced from municipal sewage sludge with 1% (wt%) pyrolusite addition were proved to be efficient on the removal of phosphorus from aqueous solutions. Pyrolusite displayed an important role in the preparation of high-quality carbonaceous adsorbents. The FTIR result showed that after pyrolysis the hydroxyl and carboxyl groups on modified activated carbon's surface were shifted compared with the original sewage sludge and was thus beneficial for TP removal.

The produced adsorbents with pyrolusite loading (PAC) showed higher BET surface area and more micropores and mesopores than SAC, while PAC had much better adsorptive performance than SAC. The surface chemistry of the PAC was changed, and resulted in an enhanced TP removal rate with an economical and optimum dosage of 2 g/L. The pH adsorption experiments showed that PAC had a stable performance with a high phosphate removal rate in a wild

pH range, and TP adsorption under the original solution pH (around 6.4) was efficient. The pseudo-second-order kinetics provided a good correlation of the adsorption data, and the experimental adsorption data was well fitted by the Langmuir isotherm model. The comparison of PAC with other absorbents manifested that PAC had observable advantages towards TP removal. Modified carbons with pyrolusite addition had a massive improvement on the phosphorus adsorption from aqueous solution.

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REFERENCES

- Alkan, M., Demirbas, O., Çelikçapa, S. & Doğan, M. 2004 Sorption of acid red 57 from aqueous solution onto sepiolite. *J. Hazard. Mater.* **116** (1–2), 135–145.
- Chen, Y., Jiang, W., Jiang, L. & Ji, X. 2012 Treatment of dyeing wastewater by activated carbons derived from municipal sewage sludge. *Environ. Prog. Sustain. Energy* **31** (4), 585–590.
- Demiral, H. & Gunduzoglu, G. 2010 Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresour. Technol.* **101** (6), 1675–1680.
- Deng, L. & Shi, Z. 2015 Synthesis and characterization of a novel Mg–Al hydrotalcite-loaded kaolin clay and its adsorption properties for phosphate in aqueous solution. *J. Alloys Compd.* **637**, 188–196.
- Goswami, M. & Phukan, P. 2017 Enhanced adsorption of cationic dyes using sulfonic acid modified activated carbon. *J. Environ. Chem. Eng.* **5** (4), 3508–3517.
- Guaya, D., Valderrama, C., Farrana, A., Armijos, C. & Cortina, J. 2015 Simultaneous phosphate and ammonium removal from aqueous solution by a hydrated aluminum oxide modified natural zeolite. *Chem. Eng. J.* **271**, 204–213.
- Gunay, A., Arslankaya, E. & Tosun, İ. 2007 Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. *J. Hazard. Mater.* **146** (1–2), 362–371.
- Han, C., Wang, Z., Yang, H. & Xue, X. 2015 Removal kinetics of phosphorus from synthetic wastewater using basic oxygen furnace slag. *J. Environ. Sci.* **30**, 21–29.
- Huang, H., Liu, J. & Ding, L. 2015 Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant

- of activated sludge by chemical precipitation. *J. Clean. Prod.* **102**, 437–446.
- Huang, W., Zhang, Y. & Li, D. 2017 Adsorptive removal of phosphate from water using mesoporous materials: a review. *J. Environ. Manage.* **193**, 470–482.
- Karimaian, K. A., Amrane, A., Kazemian, H., Panahi, R. & Zarrabi, M. 2013 Retention of phosphorous ions on natural and engineered waste pumice: characterization, equilibrium, competing ions, regeneration, kinetic, equilibrium and thermodynamic study. *Appl. Surf. Sci.* **284**, 419–431.
- Long, F., Gong, J., Zeng, G., Chen, L., Wang, X., Deng, J., Niu, Q., Zhang, H. & Zhang, X. 2011 Removal of phosphate from aqueous solution by magnetic Fe-Zr binary oxide. *Chem. Eng. J.* **171** (2), 448–455.
- Oguz, E. 2005 Adsorption characteristics and the kinetics of the Cr(VI) on the Thuja orientalis. *Colloids Surf. A Physicochem. Eng. Asp.* **252** (2–3), 121–128.
- Park, S. J. & Jung, W. Y. 2002 Effect of KOH activation on the formation of oxygen structure in activated carbons synthesized from polymeric precursor. *J. Colloid Interface Sci.* **250** (1), 93–98.
- Pengthamkeerati, P., Satapanajaru, T. & Chularuengsoarn, P. 2008 Chemical modification of coal fly ash for the removal of phosphate from aqueous solution. *Fuel* **87** (12), 2469–2476.
- Qian, J., Shen, M., Wang, P., Wang, C., Li, K., Liu, J., Lu, B. & Tian, X. 2017 Perfluorooctane sulfonate adsorption on powder activated carbon: effect of phosphate (P) competition, pH, and temperature. *Chemosphere* **182**, 215–222.
- Saha, I., Kanrar, S., Gupta, K., Show, B., Nandi, D., Biswas, K., Manna, B., Chatterjee, D. & Ghosh, U. 2016 Tuned synthesis and characterizational insight into beta-cyclodextrin amended hydrous iron-zirconium hybrid oxide: a promising scavenger of fluoride in aqueous solution. *RSC Adv.* **6** (96), 93842–93854.
- Shi, Z., Liu, F. & Yao, S. 2011 Adsorptive removal of phosphate from aqueous solutions using activated carbon loaded with Fe(III) oxide. *New Carbon Mater.* **26** (4), 299–306.
- Subbaiah, M. V. & Kim, D. 2016 Adsorption of methyl orange from aqueous solution by aminated pumpkin seed powder: kinetics, isotherms, and thermodynamic studies. *Ecotoxicol. Environ. Saf.* **128**, 109–117.
- Xie, R., Jiang, W., Wang, L., Peng, J. & Chen, Y. 2013 Effect of pyrolusite loading on sewage sludge-based activated carbon in Cu(II), Pb(II), and Cd(II) adsorption. *Environ. Prog. Sustain. Energy* **32** (4), 1066–1073.
- Xiong, J., He, Z., Mahmooda, Q., Liu, D., Yang, X. & Islam, E. 2008 Phosphate removal from solution using steel slag through magnetic separation. *J. Hazard. Mater.* **152** (1), 211–215.
- Xiong, J., Qin, Y., Islam, E., Yue, M. & Wang, W. 2011 Phosphate removal from solution using powdered freshwater mussel shells. *Desalination* **276** (1–3), 317–321.
- Xiong, W., Tong, J., Yang, Z., Zeng, G., Zhou, Y., Wang, D., Song, P., Xu, R., Zhang, C. & Cheng, M. 2017 Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon nanofiber: performance and mechanism. *J. Colloid Interface Sci.* **493**, 17–23.
- Xu, K., Tao, H. & Deng, T. 2016 Removal of phosphate from coating wastewater using magnetic Fe-Cu bimetal oxide modified fly ash. *J. Water Reuse Desal.* **6** (3), 430–436.
- Yang, S., Zhao, Y., Chen, R., Feng, C., Zhang, Z., Lei, Z. & Yang, Y. 2013 A novel tablet porous material developed as adsorbent for phosphate removal and recycling. *J. Colloid Interface Sci.* **396**, 197–204.
- Yue, Q., Zhao, Y., Li, Q., Li, W., Gao, B., Han, S., Qi, Y. & Yu, H. 2010 Research on the characteristics of red mud granular adsorbents (RMGA) for phosphate removal. *J. Hazard. Mater.* **176** (1–3), 741–748.

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