

# Investigation of phosphate removal from aqueous solution by both coal gangues

Wei Ding, Shuqin Bai, Haorong Mu and Gaowa Naren

## ABSTRACT

Equilibrium studies were carried out for the adsorption of phosphate onto newly discharged coal gangue and spontaneous combustion coal gangue, which are industrial solid residues. The experimental data were fitted to the two-parameter equations of Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich and the three-parameter equations of the Redlich-Peterson, Sips and Toth isotherms by non-linear method. All three-parameter isotherm equations have a higher correlation coefficient than the two-parameter isotherm equations. For new discharged coal gangue, the maximum phosphate adsorption capacity is over 2.504 mg/g (as P), and the best two-parameter isotherm is Freundlich, which indicated multilayer adsorption takes place on the surface. For spontaneous combustion coal gangue, the maximum phosphate adsorption capacity is 7.079 mg/g (as P), two times larger than new discharged coal gangue, and the best two-parameter isotherm is Langmuir, suggesting that the adsorption process occurs on a homogenous surface by monolayer adsorption. The three-parameter isotherm model of Redlich-Peterson shows the best fitting in both cases, but parameter  $g$  is 0.6138 in new discharged coal gangue (the parameter  $g$  is nearly 1, which means that the equilibrium isotherm behaves as the Langmuir, not as the Freundlich isotherm),  $g$  approaches to unity in spontaneous combustion coal gangue, suggesting that the two kinds of coal gangues have different adsorption properties.

**Key words** | adsorption, equilibrium studies, industrial solid residues, isotherms

**Wei Ding**  
**Shuqin Bai** (corresponding author)  
**Haorong Mu**  
School of Ecology and Environment,  
Inner Mongolia University,  
No. 235 West University Road, Saihan,  
Hohhot 010021,  
China  
E-mail: baishuqin2000@163.com

**Gaowa Naren**  
Biochemical Engineering Institute,  
Hohhot Vocational College,  
Daxuecheng Saihan-qu,  
Hohhot 010021,  
China

## INTRODUCTION

One of the main causes of eutrophication is the large quantities of phosphate present in wastewater, which negatively affects both fresh water and marine water bodies (Filippelli 2008). Phosphate removal from wastewater before its discharge into receiving waterways is significant for the protection of the natural water streams because phosphate is a limiting nutrient for eutrophication (Oladoja *et al.* 2013; Bhardwaj *et al.* 2014). The removal of phosphate from water/wastewater has been widely investigated from the point of view on the prevention of the eutrophication of water bodies, phosphorus sustainability, and water resource scarcity (Wendling *et al.* 2013; Nur *et al.* 2014; Liu & Zhang 2015).

Several techniques for the removal and recovery of phosphates from aqueous systems have been extensively investigated such as chemical precipitation, biological processes, membrane filtration, and adsorption (Zhang *et al.* 2014; Chen *et al.* 2015; Huang *et al.* 2015; Lalley *et al.* 2015).

Compared to the other techniques, the adsorption method is a versatile treatment widely used in industries for water/wastewater treatment process due to its low operating cost, effective phosphate removal, lower sludge production, operational simplicity, and adsorbents reuse potential. Industrial wastes or by-products have been utilized as adsorbents for phosphate removal because it is cost effective. These are products such as fly-ash-based materials, biosorbents from organic residues, blast furnace slag, iron-rich residues, and so on (Wendling *et al.* 2013).

Coal gangue is a complex industrial solid residue created during coal mining activities (approximately 10–15% of raw coal production) and known for its high ash yield, low heating value, and low carbon content (Zhou *et al.* 2014). Currently, it is one of the largest industrial residues in terms of land-occupying area, annual emissions, and cumulative burden to China. The coal gangue wastes can cause serious environmental impacts such as atmospheric

pollution by spontaneous combustion. Therefore, the disposal of coal gangue becomes an increasingly important problem, both from an environmental as well as an economic standpoint. At present, the beneficial utilization of coal gangue includes power generation, construction material, and filling material for reclamation (Chugh & Patwardhan 2004; Li et al. 2011). The major mineralogical phase composition of coal gangue is quartz, montmorillonite, kaolinite, and illite, all of which have a certain adsorption potential for phosphate (Edzwald et al. 1976; He et al. 1994).

The objective of this work was to study the feasibility of using coal gangues as an adsorbent for phosphate removal from an aqueous solution and compare the adsorption characteristics of new discharged coal gangue and spontaneous combustion coal gangue. The experimental data obtained in this study were analyzed by the non-linear two-parameter equations of Freundlich, Langmuir, Temkin, Dubinin-Radushkevich and the non-linear three-parameter equations of the Redlich-Peterson, Sips and Toth isotherm models. Furthermore, the best adsorption model was determined, and the possible adsorption mechanisms were also speculated.

## MATERIALS AND ANALYSIS METHODS

### Materials and characterization

The two kinds of coal gangues (new discharged and spontaneous combustion coal gangue) used in this study were obtained from a coal mining district located in Baotou, Inner Mongolia, China. New discharged coal gangue refers to the black coal gangue discharged within a year, and spontaneous combustion coal gangue refers to the red coal gangue that is formed after stacking and spontaneous combustion under certain conditions. The air dried materials were crushed into powder and sieved by different mesh sieves to homogenize them for the subsequent analysis. They were stored in a desiccator for further use.

The chemical composition of the coal gangue was analyzed by wet chemical and inductively coupled plasma atomic emission spectrophotometer (ICP-AES) techniques. The specific surface area (Brunauer-Emmett-Teller (BET)

method) and average pore diameter (Barrett-Joyner-Halenda (BJH) method) of the coal gangues were determined at 77 K by N<sub>2</sub> adsorption/desorption isotherms using a Quantachrome Autosorb-IQ2-MP sorption analyzer. Besides the major compositions, the data of specific surface area and average pore diameter are shown in Table 1. The XRD analysis was performed to examine the crystalline nature of the sample using a X-ray diffractometer (X'Pert Pro, Panalytical Corporation, The Netherlands) with Cu-K $\alpha$  (30 kV, 15 mA) radiation. X-ray diffraction analysis showed that the main phases of the two coal gangues were quartz and kaolinite.

The phosphate species stock solution containing 500 mg/L (as P) was prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> powder with ultra-pure water (Mill-Q SP system, Millipore). Phosphate working solutions in different concentrations were prepared by diluting the phosphate stock solution with ultra-pure water.

### Batch adsorption studies

In order to evaluate the phosphate adsorption capacity of the two kinds of coal gangues, batch experiments were carried out by shaking 5 g coal gangue in 250 mL solutions with different initial phosphorus concentrations (ranging from 10 to 500 mg/L). The pH of the solutions were adjusted and maintained at 6.5  $\pm$  0.5. All experiments were carried out in an Erlenmeyer flask and shaken at 25 °C, 200 rpm using a thermostat oscillator (HZQ-X300C). The suspension was shaken up to 168 h, which is sufficient contact time. The suspension was filtered through a 0.45  $\mu$ m membrane filter and phosphate was analyzed. The amount of phosphorus adsorbed at equilibrium,  $q$  (mg/g), was calculated using the following equation:

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

where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of phosphorus in the solution,  $V$  is the volume of the solution (L) and  $m$  is the mass of coal gangues (g).

### Adsorption isotherms

The adsorption process can be understood through isotherms resulting from the adsorbate concentration in the

**Table 1** | Composition and properties of coal gangues

Composition and properties of coal gangue (W%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	Pore size (nm)	BET (m <sup>2</sup> /g)
New discharged	37.50	23.96	1.94	0.45	0.57	0.48	3.821	7.10
Spontaneous combustion	58.49	22.74	6.41	2.81	2.58	1.68	3.818	4.95

solution and the amount of adsorbate adsorbed on a unit mass of the adsorbent at a constant temperature. Batch equilibrium adsorption experiments were used for assessment of the adsorbents, which are the new discharged coal gangue and spontaneous combustion coal gangue, through plots of adsorption isotherms. Previously, Freundlich and Langmuir adsorption isotherms have mainly been used to assess adsorbents, both isotherm equations can be transformed to a linear form and their two adjustable parameters can be estimated easily. However, this method of transforming data sets may lead to distortions in the original error distribution. Thus, nonlinear methods have been developed, including two-parameter equations, three-parameter equations and equations with more parameters. In this work, to estimate the feasibility, adsorption characteristics, and mechanism of phosphate adsorption on the two kinds of coal gangues, the isotherm data on phosphate adsorption were fitted to four two-parameter equations (Freundlich, Langmuir, Temkin and Dubinin-Radushkevich) and three three-parameter equations (Redlich-Peterson, Sips and Toth) with nonlinear regression. Seven isotherms, as described below in Equations (2)–(8) (Langmuir 1918; Sips 1948; Dubinin 1960; Aharoni & Sparks 1991; Hasany & Chaudhary 1996), were used for fitting the result obtained by the adsorption experiment data.

Langmuir equation:

$$q = \frac{K_L Q_L C_e}{(1 + K_L C_e)} \quad (2)$$

Freundlich equation:

$$q = K_F C_e^{1/n_F} \quad (3)$$

Temkin equation:

$$q = A_T + B_T \ln C_e \quad (4)$$

Dubinin-Radushkevich equation:

$$q = Q_D \exp \left\{ -A_D \left[ \ln \left( \frac{1+1}{C_e} \right) \right]^2 \right\} \quad (5)$$

Redlich-Peterson equation:

$$q = \frac{A_{RP} C_e}{(1 + B_{RP} C_e^g)} \quad (6)$$

Sips equation:

$$q = \frac{[q_s (K_s C_e)^{1/n_s}]}{[1 + (K_s C_e)^{1/n_s}]} \quad (7)$$

Toth equation:

$$q = \frac{q_t K_t C_e}{[1 + (K_t C_e)^t]^{1/t}} \quad (8)$$

where  $q$  is the amount adsorbed at equilibrium (mg/g), and  $C_e$  is the equilibrium concentration of phosphate in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data, the meaning is shown in Table 2. In this study, all of the isotherms were fitted by nonlinear regression using the least squares coefficient method. The curve fitting and statistical analyses were performed with Origin 8.5.

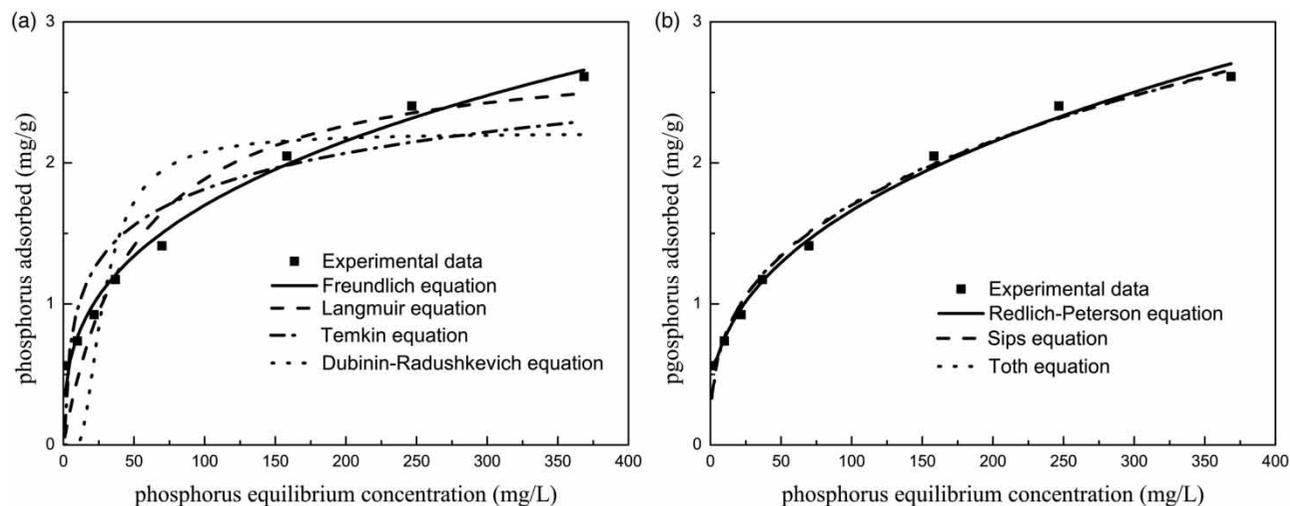
## RESULTS AND DISCUSSION

### Adsorption isotherms for new discharged coal gangue

The results of two-parameter isotherms by nonlinear regression for the phosphate adsorption of new discharged coal gangue are shown in Figure 1(a), and four correlation coefficients are shown in Table 3. As seen in Figure 1(a), adsorption increases with an increasing concentration of phosphate at low phosphate concentrations, and tends to a near constant value at high phosphate concentrations. In the high phosphate concentrations region, the maximum phosphate adsorption capacity is over 2.504 mg/g (as P) in all four isotherm models, suggesting that the coal gangue has the potential to be used as an adsorbent for phosphate removal. The Freundlich and Langmuir isotherms have higher correlation coefficients than the Temkin and Dubinin-Radushkevich isotherms according to the least squares coefficient values in Table 3. The Freundlich isotherm has a high coefficient of determination when compared to the Langmuir isotherm, which indicates better agreement between the experimental data and the adsorption isotherm. This phenomenon suggests that multilayer adsorption takes place on the surface of new discharged coal gangue, which is in agreement with the reported findings utilizing other adsorbents, such as sediments (Azzouz et al. 2012). The magnitude of the Freundlich adsorption capacity  $n_F$  is 2.913,

**Table 2** | Isotherms and the parameters involved in the different equilibrium sorption isotherms

Isotherm	Parameters	Meaning
Freundlich	$K_F$	Freundlich isotherm constant.
	$n_F$	2–10 indicating good adsorption capacity, 1–2 moderate adsorption capacity, <1 poor adsorption capacity.
Langmuir	$K_L$ (L/mg)	is related to the enthalpy of adsorption through the Van't Hoff equation.
	$Q_L$ (mg/g)	the maximum monolayer adsorption capacity.
Temkin	$A_T$	Temkin isotherm constant
	$B_T$	Temkin isotherm energy constant
Dubinin-Radushkevich	$Q_D$ (mg/g)	adsorption amount of adsorbate
	$A_D$	is related to the mean free energy of sorption
Redlich-Peterson	$A_{RP}$	Redlich-Peterson constant
	$B_{RP}$	Redlich-Peterson constant
	$g$	$g = 1$ , becomes the Langmuir equation, $g = 0$ , it becomes Henry's law.
Sips	$K_S$	equilibrium constant
	$q_S$ (mg/g)	adsorption amount of adsorbate
	$1/n_S$	$1/n_S = 1$ , indicates the process occurs on a homogenous surface.
Toth	$K_t$	equilibrium constant
	$q_t$ (mg/g)	adsorption amount of adsorbate
	$t$	$t = 1$ , indicates the process occurs on a homogenous surface.

**Figure 1** | Two-parameter (a) and three-parameter (b) isotherms of phosphate adsorption using new discharged coal gangue at 25 °C and pH 6.5 ± 0.5.**Table 3** | Isotherm parameters and coefficient for phosphate adsorption onto new discharged coal gangue obtained by nonlinear method (two-parameter isotherms)

Freundlich	Langmuir	Temkin	Dubinin-Radushkevich
$K_F = 0.349$	$K_L = 0.020$	$A_T = 0.117$	$Q_D = 2.211$
$n_F = 2.913$	$Q_L = 2.832$	$B_T = 0.368$	$A_D = 636.952$
$R^2 = 0.983$	$R^2 = 0.949$	$R^2 = 0.842$	$R^2 = 0.816$

indicates good adsorption characteristics of new discharged coal gangue to phosphate according to the report by Brdar *et al.* (Brdar *et al.* 2012).

The three types of three-parameter isotherm models were also applied to evaluate the adsorption characteristics of new discharged coal gangue to phosphate as shown in Figure 1(b). The calculated isotherm parameters and corresponding coefficient  $R^2$  are shown in Table 4. All

**Table 4** | Isotherm parameters and coefficient for phosphate adsorption onto new discharged coal gangue obtained by nonlinear method (three-parameter isotherms)

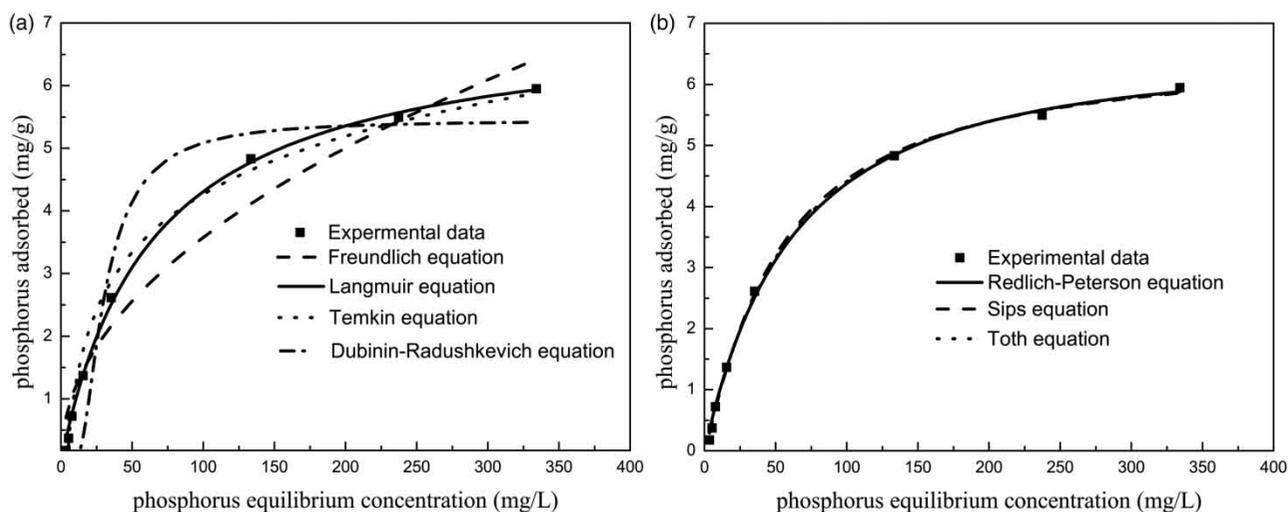
Redlich-Peterson	Sips	Toth
$A_{RP} = -0.5339$	$K_S = 5.1131 \times 10^{-19}$	$K_t = 4.7570 \times 10^8$
$B_{RP} = -1.9617$	$q_S = 6.6522 \times 10^6$	$q_t = 2.9228 \times 10^7$
$g = 0.6138$	$n_S = 2.9129$	$t = 0.0292$
$R^2 = 0.994$	$R^2 = 0.983$	$R^2 = 0.982$

three-parameter isotherm equations have higher coefficients than the two-parameter isotherm equations according to Table 4, suggesting that three-parameter isotherm models are more suitable to analyse the experimental data. The best correlation coefficient of the three-parameter isotherm models is the Redlich-Peterson isotherm, which includes features of the Langmuir and Freundlich isotherms. The exponent,  $g$ , ranges from 0 to 1. When  $g = 1$ , the Redlich-Peterson isotherm becomes the Langmuir isotherm (Redlich & Peterson 1959). The value of  $g$  is 0.6138 in Table 4, which is far less than unity, thus the adsorption process does not apply to the Langmuir isotherms. This result is consistent with the results in the two-parameter isotherms. Moreover, the value of  $t$  in the Toth isotherm and the value of  $1/n_S$  in the Sips isotherm also do not equal unity, which indicates the adsorption of phosphate on new discharged coal gangue occurs on an inhomogeneous surface. This results is consistent with the fact that coal gangue as a natural product has an inhomogeneous surface.

## Adsorption isotherms for spontaneous combustion coal gangue

Figure 2 shows the equilibrium adsorption of phosphate using spontaneous combustion coal gangue as an adsorbent. The isotherm curves rise sharply in the initial stages. Eventually they reached a plateau, which means the adsorbent is saturated with adsorbate at this level. The values of the two-parameter isotherms constants with correlation coefficient  $R^2$  are listed in Table 5. The value of the Langmuir correlation coefficient is 0.999, which is higher than the other three isotherm values. This result indicates the adsorption process occurs on a homogenous surface by monolayer adsorption when using spontaneous combustion coal gangue, which is in an agreement with modified kaolin clay by loading Mg-Al hydrotalcite (Deng & Shi 2015). The combustion process at high temperature may change the surface of coal gangue to be homogenous. The monolayer saturation capacity,  $Q_L$ , is 7.076 mg/g, which is higher than other natural materials such as kaolinite, montmorillonite, and illite but lower than peat (Edzwald et al. 1976; Xiong & Mahmood 2010). Especially, it is higher than the new discharged coal gangue described above.

From Table 6, the values of the three-parameter isotherms' correlation coefficient  $R^2$  are higher than the two-parameter isotherms, except for the Langmuir isotherm model. The correlation coefficients of  $R^2$  in Redlich-Peterson, Sips and Toth are 0.999, 0.999 and 0.998 respectively, suggesting the applicability of three-parameter isotherm models to represent the equilibrium adsorption of phosphate by spontaneous combustion coal gangue. The value of the



**Figure 2** | Two-parameter (a) and three-parameter (b) isotherms of phosphate adsorption using spontaneous coal gangue at 25 °C and pH 6.5 ± 0.5.

**Table 5** | Isotherm parameters and coefficient for phosphate adsorption onto spontaneous combustion coal gangue obtained by nonlinear method (two-parameter isotherms)

Freundlich	Langmuir	Temkin	Dubinin-Radushkevich
$K_F = 0.384$	$K_L = 0.015$	$A_T = -1.900$	$Q_D = 5.449$
$n_F = 2.064$	$Q_L = 7.076$	$B_T = 1.339$	$A_D = 697.355$
$R^2 = 0.965$	$R^2 = 0.999$	$R^2 = 0.988$	$R^2 = 0.963$

**Table 6** | Isotherm parameters and coefficient for phosphate adsorption onto spontaneous combustion coal gangue obtained by nonlinear method (three-parameter isotherms)

Redlich-Peterson	Sips	Toth
$A_{RP} = 0.0136$	$K_S = 0.0191$	$K_t = 0.0150$
$B_{RP} = 0.0105$	$q_S = 6.5739$	$q_t = 6.5545$
$g = 1.0555$	$n_S = 0.8840$	$t = 1.2070$
$R^2 = 0.999$	$R^2 = 0.999$	$R^2 = 0.998$

constant  $g$  in the Redlich-Peterson isotherm and the value of the constant  $1/n_S$  in the Sips isotherm approaches unity, which indicates that the isotherm is approaching the Langmuir isotherm but not the Freundlich isotherm. The value of the constant  $t$  in the Toth isotherm is approximately equal to unity too, suggesting that the uptake of phosphate by spontaneous combustion coal gangue occurs on a homogeneous surface. This result is also consistent with the two-parameter isotherm analysis.

Comparing the adsorption characteristics of two kinds of coal gangues, we concluded that spontaneous combustion coal gangue is more suitable for removing phosphate, according to the maximum adsorption amount being larger than for new discharged coal gangue, although both coal gangues showed good adsorption capacity. If new discharged coal gangue is treated at high temperature, the adsorption capacity is improved. However, using new discharged coal gangue as an adsorbent is economic from the perspective of the land occupation and environment protection. It is worth considering how to deal with the coal gangue after adsorption of phosphate. One possibility is making a mineral fertilizer using coal gangues after adsorption of phosphate.

### The possible adsorption mechanisms

The surface properties of the adsorbent (including surface potential, functional groups) and the chemical properties of the adsorbate have decisive roles in the adsorption rate and adsorption capacity. In aqueous solution, a large

number of hydroxyl groups exist on the surface of the adsorbent, and ionization and hydroxylation occur at different pH conditions. The first ionization constant and second ionization constant of phosphoric acid were  $pK_{a1} = 2.12$  and  $pK_{a2} = 7.20$  respectively, indicating that the main phosphate species exist as  $H_2PO_4^-$  in the experiment condition (pH at  $6.5 \pm 0.5$ ). The possible mechanisms of phosphate adsorption by coal gangues include: (1) van der Waals forces; (2) electrostatic function between the phosphate species and the coal gangues' surface groups; (3) ion exchange between the phosphate species and the surface groups on the coal gangue as Si-OH or Al-OH; (4) chemical bonding between the phosphate species and the surfaces groups on the coal gangue as M-OH and -COOH, etc. Both coal gangues belong to clay minerals according to material composition and properties, suggesting the Zeta potential of both coal gangues were negative (Vane & Zang 1997; Kaya & Yukseken 2005). Therefore, they were less likely to adsorb by electrostatic function. The adsorption rate of both coal gangues was fast, indicating that physical adsorption occurred in the initial adsorption process. However, the pH values of the solutions changed from 6.5 to 7.5 for new discharged coal gangue, and from 6.5 to 8.5 for spontaneous combustion coal gangue, indicating that ion exchange occurred between the phosphate species and  $OH^-$  groups on the surface of the coal gangues in aqueous solutions.

New discharged coal gangue is composed of inorganic compounds and organic compounds, which may play different roles in the adsorption process. In the solid-liquid interface of coal gangue, inorganic compounds exist as M-OH type, while organic compounds exist as -COOH or -NH type to provide the adsorption sites. Phosphate species not only interact with -OH groups, but may also interact with -COOH or -NH groups (coordination or hydrogen bond) to fix on the adsorbent. However, based on the adsorption isotherm analysis, the adsorption amount for spontaneous combustion coal gangue was larger than new discharged coal gangue, suggesting that few chemical bonds formed between the phosphate species and organic functional groups. For spontaneous combustion coal gangue, the organic compounds were decomposed in the high temperature combustion process, and only inorganic compounds provide the adsorption site. Comparing the maximum adsorption amount of spontaneous combustion coal gangue with the new discharged coal gangue, the inorganic adsorption sites may be more important for phosphate adsorption. Edzwald et al. (1976) also reported that the contents of free metal is far greater importance (particularly, Fe and Ca) than the alumina-silica molecular ratio for phosphate retention on

**Table 7** | The content of Si, Al, Fe oxides and phosphorus adsorption capacity for different materials (wt%)

Materials	P adsorbed <sup>a</sup>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Reference
Red mud	9.19	19.14	6.93	12.76	46.02	Li et al. (2006)
Red mud700 <sup>b</sup>	19.05	22.45	8.06	13.05	45.23	
Fly ash	2.49	56.38	25.36	7.35	2.72	
Fly ash700 <sup>b</sup>	8.20	57.20	28.47	6.09	2.14	

<sup>a</sup>Initial phosphate concentration is 155 mg P/L and without adjusting the pH, (mg/g).

<sup>b</sup>Calcined at 700 °C for 2 h.

minerals. The data in Table 7 is from the previous study by Li et al. (Li et al. 2006). Based on Table 7, we can conclude that the phosphate adsorption capacity increased as the sum of the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO content increased. The adsorption capacity of spontaneous combustion coal gangue was two times larger than new discharged coal gangue, perhaps due to the increase in the relative content of metal oxides. In detail, the sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO contents in new discharged coal gangue and spontaneous combustion coal gangue was 63.85% and 90.45% respectively, proportional to the adsorption amount of phosphate. This result is consistent with previous studies with raw red mud and fly ash after being calcined at 700 °C for 2 h, which resulted in phosphorus adsorption rapidly increasing (Li et al. 2006). In addition, new discharged coal gangue is a natural product, which has a heterogeneous surface, and the metal oxides exposed on the surface were relatively less, while the metal oxide exposed on the surface of spontaneous combustion coal gangue was larger due to high temperature combustion. Therefore, the adsorption capacity of spontaneous combustion coal gangue was larger than new discharged coal gangue. In other words, the multilayer adsorption occurring in the case of new discharged coal gangue and the monolayer adsorption occurring in the case of spontaneous combustion coal gangue, is due to the different surface properties of new discharged coal gangue (inhomogeneous) and spontaneous combustion coal gangue (homogeneous). Finally, the adsorption mechanisms were complex, but the ion exchange process may play a main role in the adsorption process. The adsorption capacity and mechanisms were different due to different performance of two kinds of coal gangues.

## CONCLUSIONS

The industrial solid residues of coal gangues were used as an adsorbent for removal of phosphate. In order to compare

the adsorption characteristics of new discharged coal gangue and spontaneous combustion coal gangue, two and three parameter isotherm equations were used to analyze the adsorption experiment data. The results of the adsorption isotherms indicated that both coal gangues shows good adsorption performance. The maximum phosphate adsorption capacity of new discharged coal gangue is over 2.504 mg/g (as P), while the maximum phosphate adsorption capacity of spontaneous combustion coal gangue is over 7.076 mg/g (as P), which indicated that the spontaneous combustion coal gangue is more suitable for use as an adsorbent. The three-parameter isotherm model shows better fitting with the experiment data than two-parameter isotherm model in both cases; especially, the Redlich-Peterson model shows the best fitting in both cases. However, the adsorption of new discharged coal gangue was regarded as a multilayer inhomogeneous adsorption process, while the adsorption of spontaneous combustion coal gangue was regarded as a monolayer homogeneous adsorption process. These different characteristics are due to the different nature of the surfaces of both adsorbents. The ion exchange process play the main role in the adsorption of phosphate by the two kinds of coal gangue.

## ACKNOWLEDGEMENTS

The present work is supported by Inner Mongolia Natural Science Foundation (2014MS0202).

## REFERENCES

- Aharoni, C. & Sparks, D. L. 1991 Kinetics of soil chemical reactions – a theoretical treatment. In: *Rates of Soil Chemical Processes*, D. L. Sparks & D. L. Suarez (eds), Soil Science Society of America, Madison, WI, pp. 1–18.
- Azzouz, S., Meribout, R. & Boukhalfa, C. 2012 Characterization of phosphate adsorption on sediments. *Procedia Engineering* 33 (3), 285–292.

- Bhardwaj, D., Sharma, P., Sharma, M. & Tomar, R. 2014 Removal and slow release studies of phosphate on surfactant loaded hydrothermally synthesized silicate nanoparticles. *Journal of the Taiwan Institute of Chemical Engineers* **45** (5), 2649–2658.
- Brdar, M., Šćiban, M., Takači, A. & Došenović, T. 2012 Comparison of two and three parameters adsorption isotherm for Cr(VI) onto Kraft lignin. *Chemical Engineering Journal* **183** (8), 108–111.
- Chen, Y., Li, B., Ye, L. & Peng, Y. 2015 The combined effects of COD/N ratio and nitrate recycling ratio on nitrogen and phosphorus removal in anaerobic/anoxic/aerobic (A<sup>2</sup>/O)-biological aerated filter (BAF) systems. *Biochemical Engineering Journal* **93** (10), 235–242.
- Chugh, Y. P. & Patwardhan, A. 2004 Mine-mouth power and process steam generation using fine coal waste fuel. *Resources Conservation & Recycling* **40** (3), 225–245.
- 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. *Journal of Alloys & Compounds* **637**, 188–196.
- Dubinín, M. M. 1960 The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. *Chemical Reviews* **60** (60), 235–241.
- Edzwald, J. K., Toensing, D. C. & Leung, C. Y. 1976 Phosphate adsorption reactions with clay minerals. *Environmental Science & Technology* **10** (5), 485–490.
- Filippelli, G. M. 2008 The global phosphorus cycle: past, present, and future. *Elements* **4** (2), 89–95.
- Hasany, S. M. & Chaudhary, M. H. 1996 Sorption potential of Haro river sand for the removal of antimony from acidic aqueous solution. *Applied Radiation and Isotopes* **47** (4), 467–471.
- He, Z. L., Yang, X., Yuan, K. N. & Zhu, Z. X. 1994 Desorption and plant-availability of phosphate sorbed by some important minerals. *Plant and Soil* **162** (1), 89–97.
- Huang, H., Liu, J. & Ding, L. 2015 Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation. *Journal of Cleaner Production* **102**, 437–446.
- Kaya, A. & Yukselen, Y. 2005 Zeta potential of clay minerals and quartz contaminated by heavy metals. *Canadian Geotechnical Journal* **42** (5), 1280–1289.
- Lalley, J., Han, C., Li, X., Dionysiou, D. D. & Nadagouda, M. N. 2015 Phosphate adsorption using modified iron oxide-based sorbents in lake water: kinetics, equilibrium, and column tests. *Chemical Engineering Journal* **284**, 1386–1396.
- Langmuir, I. 1918 The adsorption of gases on plane surface of glass, mica and platinum. *Journal of the American Chemical Society* **143** (9), 1361–1403.
- Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J. & Jia, Z. 2006 Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *Journal of Hazardous Materials* **137** (1), 374–383.
- Li, W., Chen, L., Zhou, T., Tang, Q. & Zhang, T. 2011 Impact of coal gangue on the level of main trace elements in the shallow groundwater of a mine reclamation area. *International Journal of Mining Science and Technology* **21** (5), 715–719.
- Liu, X. & Zhang, L. 2015 Removal of phosphate anions using the modified chitosan beads: adsorption kinetic, isotherm and mechanism studies. *Powder Technology* **277**, 112–119.
- Nur, T., Johir, M. A. H., Loganathan, P., Nguyen, T., Vigneswaran, S. & Kandasamy, J. 2014 Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. *Journal of Industrial & Engineering Chemistry* **20** (4), 1301–1307.
- Oladoja, N., Ololade, I., Adesina, A., Adelagun, R. & Sani, Y. 2013 Appraisal of gastropod shell as calcium ion source for phosphate removal and recovery in calcium phosphate minerals crystallization procedure. *Chemical Engineering Research and Design* **91** (5), 810–818.
- Redlich, O. & Peterson, D. L. 1959 A useful adsorption isotherm. *Journal of Physical Chemistry* **63** (6), 1024–1024.
- Sips, R. 1948 On the structure of a catalyst surface. *Journal of Chemical Physics* **16** (8), 1024–1026.
- Vane, L. M. & Zang, G. M. 1997 Effect of aqueous phase properties on clay particle zeta potential and electro-osmotic permeability: implications for electro-kinetic soil remediation processes. *Journal of Hazardous Materials* **55** (1), 1–22.
- Wendling, L. A., Blomberg, P., Sarlin, T., Priha, O. & Arnold, M. 2013 Phosphorus sorption and recovery using mineral-based materials: sorption mechanisms and potential phytoavailability. *Applied Geochemistry* **37** (10), 157–169.
- Xiong, J. B. & Mahmood, Q. 2010 Adsorptive removal of phosphate from aqueous media by peat. *Desalination* **259** (1), 59–64.
- Zhang, Z., Wang, Y., Leslie, G. L. & Waite, T. D. 2014 Effect of ferric and ferrous iron addition on phosphorus removal and fouling in submerged membrane bioreactors. *Water Research* **69C** (69C), 210–222.
- Zhou, C., Liu, G., Wu, S. & Lam, P. K. S. 2014 The environmental characteristics of usage of coal gangue in bricking-making: a case study at Huainan, China. *Chemosphere* **95** (1), 274–280.

First received 25 January 2017; accepted in revised form 13 April 2017. Available online 25 April 2017