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Preparation, characterization of wheat residue based anion exchangers and its utilization for the phosphate removal from aqueous solution

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ABSTRACT

Wheat residue based anion exchanger (WR-AE) was prepared by ETM (epichlorohydrin–triethylamine method), which is the reaction of wheat residue (WR) with epichlorohydrin and triethylamine in the presence of ethylenediamine and N,N-dimethylformamide. Characterization of WR-AE was measured, including BET surface area, SEM, zeta potential, nitrogen content and FTIR analysis. Batch experiments and statistical analysis were conducted to study its ion-exchange property for phosphate from aqueous solutions. Filter bed experiment was conducted for the regeneration test. The characteristic results validated the increased amine groups in WR-AE and its maximum sorption capacity (Q_{max}, mmol g^{-1}) of phosphate was 1.80 ± 0.06 mmol g^{-1}. More over, the WR-AE regenerated in both NaCl and HCl solutions can be repeatedly used in several sorption–desorption cycles without any significant loss of the sorption capacities.

1. Introduction

Eutrophication is a serious environmental problem in China and is caused by the nitrogen, phosphorus and other excessive nutrients for algae use. In surface freshwater systems, phosphorus is usually the limiting factor of algae growth, and the increase of phosphorus in surface freshwater systems will lead to excessive algae growth. So phosphorus removal is of great significance for the algae bloom control (Song, Hou, Wang, & Wang, 2006).

Phosphorus control in wastewater treatment plants is a central issue in the field of sewage treatment of China. Several methods have been used to remove phosphorus from water, including reverse osmosis (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009; Jeppesen, Shu, Keir, & Jegatheesan, 2009), electro-dialysis (Mohamed, 2002) and ion exchange (Fernandez-Olmo, Fernandez, & Irabien, 2007). Of all these, anion exchange is well recognized as one of the simplest and safest methods used for the removal of phosphorus from wastewater. Further development of ion exchange has been investigated, i.e., the research of ion exchangers prepared from agricultural residues (AR) (Han et al., 2010; Orlando, Baes, & Nishijima, 2002; Wang, Gao, Yue, & Yue, 2007a).

AR is regarded as abundant and available natural resources, while most of them are discarded or burned without proper utilization. The idea of converting AR into ion exchangers is based on the abundant cellulose and hemicelluloses existing in AR. Cellulose and hemicellulose structures have a large number of easily accessible hydroxyl groups which can be induced to react with other chemicals by condensation, polymerization or graft reactions for the preparation of some functional polymers (Varma, Kennedy, & Galgali, 2004).

There has been growing interest in ion exchangers prepared from AR (Nigam, Armour, Banat, & Singh, 2000) over the last decade for its simplicity, low cost and effectivity. Some agricultural residues including rice hull, sugarcane bagasse, persimmon tealeaf, coconut huskand and lauan sawdust have been converted into anion exchangers by Orlando (Orlando, Baes, & Nishijima, 2002; Orlando, Baes, Nishijima, & Okada, 2004; Orlando, Okuda, & Nishijima, 2003), and utilization of these anion exchangers has shown excellent removal for various anions.

The main objective of this paper is to study the phosphate sorption capacity of wheat residue based anion exchanger (WR-AE) prepared by ETM (epichlorohydrin–triethylamine method). In our previous work, WR-AE (and other agricultural residues based anion exchanger) has exhibited excellent sorption capacities for NO_3^- (Gao, Xu, Wang, Yue, & Xu, 2009; Wang et al., 2007a), anionic dye ions (Xu, Gao, Yue, & Zhong, in press) and other anions (AsO_3^{2-}, ClO_4^-, etc.). In this work, batch sorption experiments were performed to evaluate the effect of WR-AE dosage, pH and temperature on the phosphate removal. Various characteristic measurements have been conducted to determine the physicochemical properties of WR-AE. The equilibrium of sorption process was estimated, and the maximum sorption capacity (Q_{max}) of phosphate was determined from the equilibrium data measured

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by isotherm experiments. Fixed bed filter test and regeneration test were designed to determine the regeneration capacity of WR-AE.

2. Materials and methods

2.1. Materials

WR was obtained from Liao Cheng, Shandong, China. The raw WR was washed with water, dried at 60 °C for 12 h and sieved into particles with diameters from 100 to 250 μm.

2.2. Preparation of WR-AE

Six grams of WR was used to react with 20 mL of epichlorohydrin and 25 mL of N,N-dimethylformamide in a 250 mL three-neck round bottom flask at 85 °C for 60 min. An aliquot of 4 mL of ethylenediamine was added and the solution was stirred for 45 min at 85 °C, followed by adding 20 mL of 99% triethylamine (w/w) and the mixture was stirred for 120 min at 85 °C. The product was washed with 500 mL of distilled water to remove the residual chemicals, dried at 60 °C for 12 h and sieved to obtain particles smaller than 250 μm in diameter and then used in all the sorption experiments (Orlando et al., 2004; Orlando et al., 2003).

The preparation of WR-AE is the chain reactions between cellulose/hemicellulose chain and side chains of different grafting chemical reagents shown in Fig. 1(a). It is known that cellulose and hemicellulose are comprised of various glycosyl groups. The reaction between typical glycosyl in the cellulose/hemicellulose chain and the grafting chemical reagents is shown in Fig. 1(b). N,N-dimethylformamide is used as an organic medium which enhances the susceptibility of the epoxide ring. Except for its weak-based catalysis in organic solvent, ethylenediamine can also be used as a crosslinking agent for some synthesis reactions between epichlorohydrin and amine (Gurgel & Gil, 2009; Molinari, Argurio, & Poerio, 2004; Ragimov, Seiidov, & Nagiyev, 1983).

2.3. Characterization of WR-AE

Surface area measurements were performed with an automatic BET surface area analyzer (Model F-Sorb 2400, Beijing Jinaipu Technical Apparatus Co., Ltd., China). The detection limit of this instrument, using N^2, is 0.01 $m^2\,g^{-1}$.

Scanning electron micrographs (SEM) of the samples were obtained by JEOL JSM-6480LV scanning electron microscope. The sample was coated with platinum before the SEM micrograph was obtained.

Zeta potential measurements were carried out using a micro-electrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) to determine the zeta potential of WR-AE and WR. The WR-AE and WR particles in the sediment phase were diluted with the upper clear liquid to make the particles visible under the microscope before measurement. The initial pH of the mixed solutions was designed at range of 1.9–12.0.

The functional groups presenting in WR-AE and WR were investigated by using the FTIR technique (Perkin–Elmer "Spectrum BX" spectrometer). The spectrum was scanned from 400 to 4000 cm^{-1}.

Total nitrogen content of WR-AE was determined by elemental analyzer (Elementar Vario EL III, Germany).

2.4. Batch sorption tests

In all of the experiments, WR-AE dosage, initial pH, initial concentration and temperature were selected as experimental parameters.

To study the effect of WR-AE dosage on the phosphate removal, different quantities (0.025–0.8 g) of WR-AE were placed in several 100 mL Erlenmeyer flasks with 50 mL of 50 mg (P) L^{-1} $H_2PO_4^-$

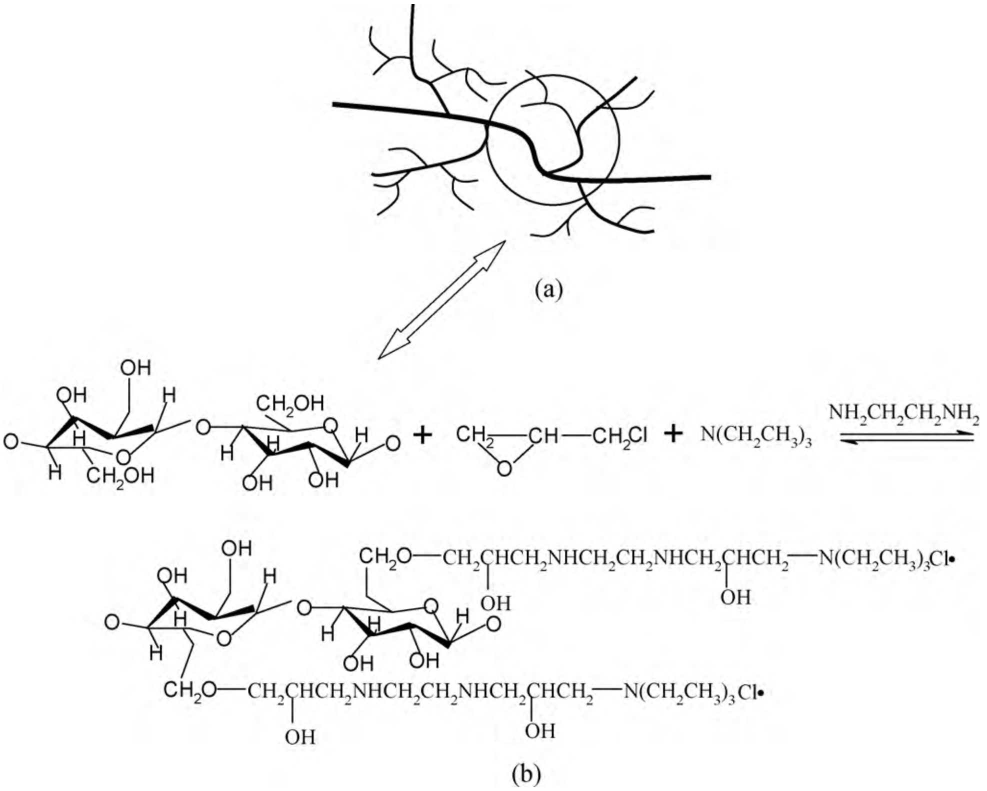

Fig. 1. Synthesis of WR-AE.

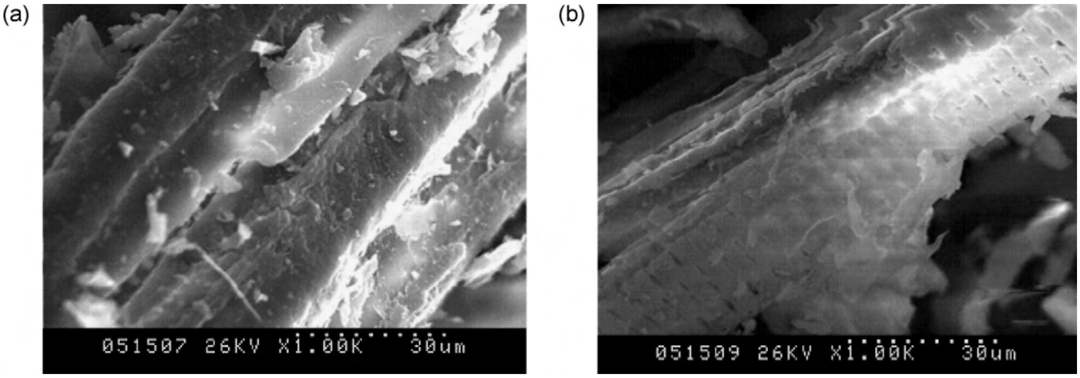

Fig. 2. SEM of WR and WR-AE. (a) WR and (b) WR-AE.

solutions. Erlenmeyer flasks were shaken at 120 rpm for 60 min in a thermostat. The concentrations of phosphates were determined spectrophotometrically by Ammonium-molybdate colorimetric method, using a UV–vis spectrophotometer (model UV754GD, Shanghai) at an absorbance wavelength of 700 nm.

In the pH effect experiment, the initial solution pH (2.0–12.0) was first adjusted and then 0.1 g of WR-AE was added to several 100 mL Erlenmeyer flasks with 50 mL of 50 mg (P) L^{-1} $H_2PO_4^-$ solutions. Then, equilibrium pH and the residual phosphate concentrations in solutions were determined.

Batch sorption experiments were carried out at three different temperatures (20, 30, and 40 °C) to determine the impact of temperature on the sorption process. An aliquot of 0.1 g of WR-AE was immersed in several 100 mL Erlenmeyer flasks with 50 mL of $H_2PO_4^-$ solutions in different concentrations (25–500 mg (P) L^{-1}).

2.5. Column regeneration experiment

Fixed bed filter test: An organic-glass column with 200 mm length and 12 mm diameter filled with 1 g of WR-AE was fed with 200 mg (P) L^{-1} of phosphate solution at flow rate controlled at about 5 mL min^{-1}. The effluent solutions were collected, and every 10 mL was selected as a sample to determine the concentrations of phosphate in the effluent solutions.

Regeneration test: Regeneration of the anion exchanger as well as recovery of adsorbate material was achieved by eluting a suitable solvent through the exhausted column. In the present studies, a dilute NaCl or HCl solution (0.1 mol L^{-1}) was eluted through the column. Aliquots of 10 mL of NaCl solution were passed through each column and totals of 200 mL of the eluent were used in WR-AE column. After washed with 500 mL of distilled water, the regenerated WR-AE was used again in the subsequent experiments for phosphate removal. The sorption and desorption cycles were repeated for several times and the concentrations of phosphate in the solution during sorption and desorption were continuously monitored with an UV–vis spectrometer.

The column adsorption capacity (q_{ed}) was calculated by the equation expressed as:

$$q_{ed} = \frac{c_o V_o - \sum c_n v_n}{m} \quad (1)$$

where q_{ed} is the amount of phosphate sorption per gram WR-AE at saturation (mg g^{-1}), c_o is the original concentration of phosphate (mg L^{-1}), V_o is the total volume of the influent solutions (L), c_n is the concentration of sample n (mg L^{-1}), and v_n is the volume of sample n (L), m is the amount of WR-AE (g).

2.6. Statistical analysis

All the data were processed by origin 7.5, and the analysis of variance (one-way ANOVA) was conducted using the statistical programs of SPSS V13.0 (SPSS Inc., Chicago, IL). Results were presented as means ± standard deviation. Significant levels were set at $\alpha = 0.05$.

3. Result and discussion

3.1. Characterization of WR-AE

3.1.1. BET surface area

BET surface areas of WR-AE and WR are 4.4 and 5.3 $m^2\,g^{-1}$, respectively. A decrease in the BET surface area of WR-AE is observed in comparison with that of WR, which is consistent with the work of Namasivayam for the preparation of biosorbent (BET surface area 1.9 $m^2\,g^{-1}$) from coconut coir (2.3 $m^2\,g^{-1}$, Namasivayam & Sureshkumar, 2008). BET surface area of WR-AE is very low in comparison with those of pore-structure adsorbents (BET surface area range of 500–2500 $m^2\,g^{-1}$), indicating the absence of pore adsorption in the potential sorption mechanism.

3.1.2. SEM

The results of the SEM measurements for the structure of WR-AE and WR are shown in Fig. 2. It is obvious that the surface of WR-AE is smoother in comparison with that of WR, which indicates that the order of cellulose has been improved after the removal of lignin, ash and extractives during the process of synthesis. This result also validates the decrease trend of BET surface area of WR-AE after the modification.

3.1.3. Nitrogen content (%)

Attachment of triethylamine into WR is evaluated by nitrogen analysis in the final product. A slight increase is observed in the carbon contents (41.11 ± 0.02–44.45 ± 0.03%) and hydrogen contents (6.10 ± 0.01–8.67 ± 0.02%) of WR-AE, respectively. However, nitrogen content (N%) of WR-AE increases significantly from 0.35 ± 0.00% to 11.64 ± 0.01%, indicating that the reactions proceed efficiently and a large number of amine groups from triethylamine have been introduced into the WR (Orlando, Baes, Nishijima, & Okada, 2002; Orlando et al., 2004; Orlando et al., 2003).

3.1.4. FTIR analysis of WR-AE

The FTIR spectral change between WR and WR-AE is shown in Fig. 3. For the WR, a large vibration of the band at 3415 cm^{-1}

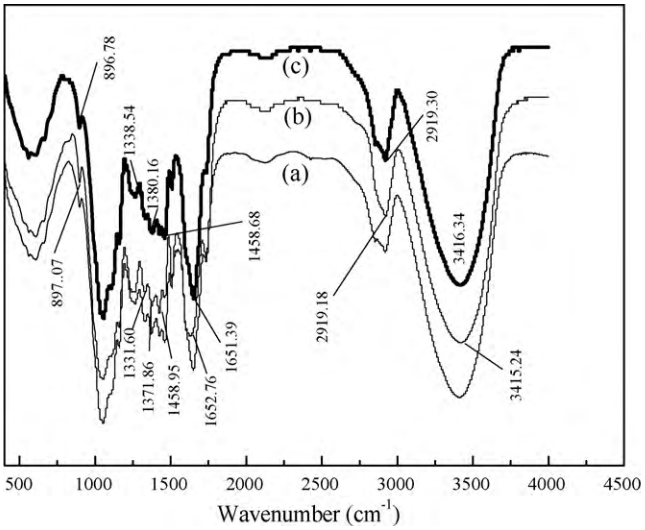

Fig. 3. FTIR analysis of WR and WR-AE. (a) WR; (b) WR-AE; (c) WR-AE saturated with phosphate.

indicates the existence of hydroxyl groups in the WR. The peak at 2919 cm^{-1} is associated with the special vibration of C–H aliphatic in WR. Aromatic cyclic groups are observed by the intensity of the band at 1651 cm^{-1}. The IR analysis of WR-AE shows a change in structure between WR-AE and WR. As shown in Fig. 3, chloric alky is observed in the WR-AE by the intense vibration of peak at 607 cm^{-1}. A large vibration in the peak at 1331 and 1371 cm^{-1} suggests the grafted amine groups in the structure of the WR-AE.

Comparison of the FTIR spectra between WR-AE and WR-AE saturated with phosphate, a significant shift is observed from 1331 to 1338 cm^{-1} and from 1371 to 1380 cm^{-1} in comparison with other peaks. The change in the 1331 and 1371 cm^{-1} band may be associated to the coordination of the phosphate anions with the amine groups in an R–N$^+$ $(CH_2CH_3)_3 \cdots H_2PO_4^-$ complex. Similar result was observed in Yoon's work for perchlorate adsorption onto anion exchange resin (Yoon et al., 2009).

Based on the discussion on amine content and FTIR above, it is clear that the WR-AE has been grafted with a mass of functional groups which would be beneficial to the sorption of phosphate from solution, and the mechanism of the phosphate removal by WR-AE should be anion exchange.

3.2. Sorption properties of phosphate

3.2.1. Effect of pH on the sorption capacity and zeta potential of WR-AE

The effect of pH on sorption of phosphate was studied by varying initial pH under constant process parameters. The equilibrium solution pH after WR-AE added has been monitored, and the initial pH and equilibrium pH are shown in Fig. 4(a). An examination of the solution pH values indicates that the equilibrium solution pH values after the sorption experiments decrease significantly in comparison with the initial solution pH values when the initial pH is in the range of 7.0–12.0. This can be attributed to the species of phosphate ions in the aqueous solution (i.e., H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}), which form a buffer solution in the aqueous solution. When phosphate ions are sorbed onto the WR-AE, the H$^+$ is released from the solution, which results in a decrease of pH in the solution.

Fig. 4(a) shows the phosphate removal with initial pH change. A sharp increase occurs in a narrow range of pH from 2.0 to 4.0. The high sorption is obtained at pH higher than 5.0, and the phosphate removal efficiency is almost constant in neutral and alkaline conditions (pH range of 5.0–10.0). With the original pH increasing from 10.0 to 12.0, a gradual decrease in phosphate removal is observed from 93% to 80%.

It seems likely that sorption process of phosphate onto WR-AE proceeds due to the interaction between the phosphate ions and the functional groups in WR-AE (R–N$^+$ $(CH_2CH_3)_3Cl^-$) formulated as follows:

$$\begin{aligned} &R\prime\text{–}N^+(CH_2CH_3)_3Cl^- + H_2PO_4^- \\ &R\prime\text{–}N(CH_2CH_3)_3{}^+ \cdots H_2PO_4^- + Cl^- \end{aligned} \qquad (2)$$

The protonation of WR-AE surface is caused by the high concentration of H$^+$ when the pH is lower than 3.0, which makes the species of phosphate in aqueous solution exists in the form of H_3PO_4 and $H_2PO_4^-$ (Wang & Cheng, 2007). As the pH increases from 4.0 to 10.0, the concentrations of $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} increase gradually with the significant decrease of protonation. The electrostatic attraction forces between exchanger and ion will be strengthened when the valence of ion increases. Therefore, at pH < 3.0, the increasing concentration of phosphoric acid will interfere with the sorption of phosphate onto the exchange sites in WR-AE. With the increase of pH from 4.0 to 10.0, the increase of concentrations of $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} will enhance electrostatic attraction forces between exchange sites and phosphate. When the pH increases beyond 10.0, the OH$^-$ will increase significantly, and the amine groups for phosphate sorption will decrease

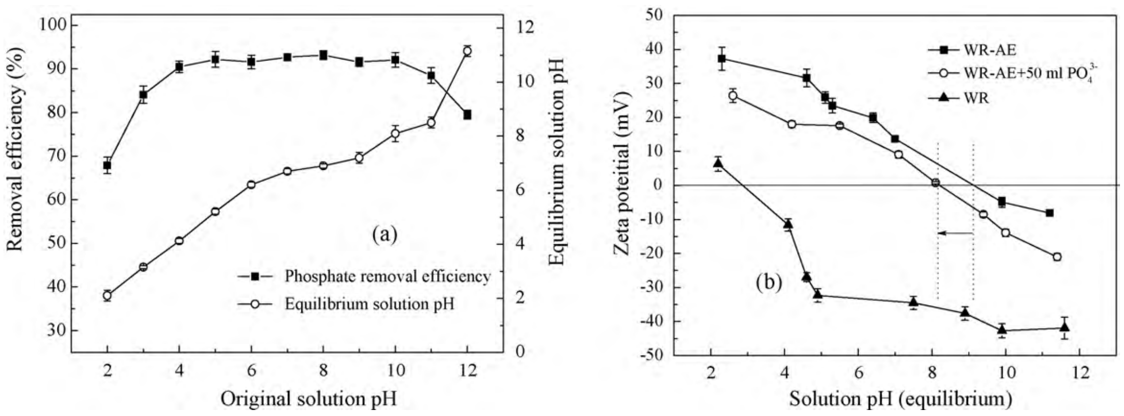

Fig. 4. Effect of pH on the sorption capacity and zeta potential of WR-AE (a), sorption capacity of WR-AE as a function of pH; (b), zeta potential of WR-AE as a function of pH (initial H_2PO_4: 50 mg L^{-1}; WR-AE dosage: 2 g L^{-1}; temperature: 20 °C; shaker speed: 120 rpm). The error bar represents the standard deviation of duplicate results ($0.01 < p < 0.05$).

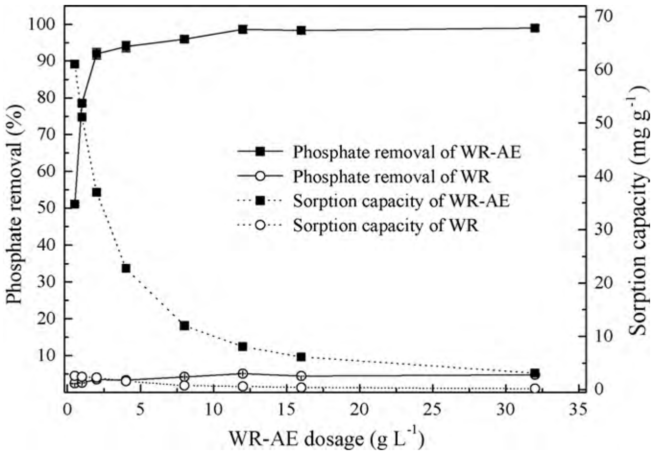

Fig. 5. Effect of sorbent dosage on sorption of phosphate by WR-AE and WR (initial $H_2PO_4^-$: 100 mg L^{-1}; temperature: 20 °C; shaker speed: 120 rpm). The error bar represents the standard deviation of duplicate results ($p < 0.01$).

on the outer surface of the sorbent due to the presence of excess OH^- ions competing with phosphate ions for sorption sites and a result of the sorption decreases.

The zeta potentials of WR and WR-AE as a function of pH are shown in Fig. 4(b). It is apparent that the zeta potentials of WR-AE are much higher than those of WR, indicating the existence of increased positive-charge functional groups in the framework of WR-AE. As the equilibrium pH increases from 1.9 to 12.0, the zeta potentials of WR decrease approximately from +8.6 to −42 mV in compared with those of WR-AE (without phosphate) from +38.6 to −8.9 mV. This result could be attributed to the pH-dependent functional groups existing in resins, such as hydroxyl, carboxyl and phenolic groups. These groups will exhibit a greater negative charge as the pH is increased, which results in the decrease in the positive charge.

It is observed in Fig. 4(b) that the point of zero charge pH (pH_{PZC}) of WR-AE is shifted significantly in the presence of phosphate, which indicates that the adsorption of phosphate onto WR-AE may change the surface charge of WE-AE. Similar research has been reported in the work of Yoon for the adsorption and desorption of perchlorate by activated carbon and anion exchange resin (Yoon et al., 2009).

3.2.2. *Effect of WR-AE dosage*

WR-AE dosage is an important parameter because it determines the capacity of an anion exchanger for a given initial concentration of the phosphate under operating conditions. The effect of WR-AE dosage on the sorption of phosphate is shown in Fig. 5. The removal efficiency of phosphate increases significantly from 52% to 92% with WR-AE dosage increasing from 1 to 2 g L^{-1}, and the sorption is almost constant at dosages higher than 2 g L^{-1}. With increasing WR-AE dosage, more sorption sites are available for sorption and nearly all the phosphate is sorbed when the WR-AE is increased to 2 g L^{-1}. So, it is reasonable that the phosphate removal should not increase much when the dosage of WR-AE is higher than 2 g L^{-1}. As indicated in Fig. 5, sorption capacity of the WR-AE decreases with increase in dosage. When the phosphate removal reaches near 100%, additional WR-AE added would not be used. The sorption capacity would become lower because the capacity is normalized by added WR-AE.

Fig. 5 also shows the phosphate removal capacity of raw WR. The low phosphate removal (3.2%) of raw WR indicates that raw WR has little effect on sorption of phosphate, and a chemical modification is required to introduce some functional groups into the structure of WR for phosphate removal (Swanand, Amanda, Eric, & William, 2007).

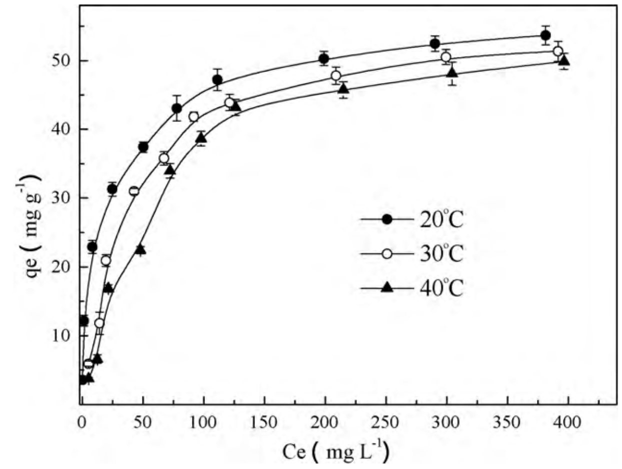

Fig. 6. Effect of temperature on sorption isotherm of phosphate by WR-AE (WR-AE dosage: 2 g L^{-1}; equilibrium pH: 4.53–4.61; shaker speed = 120 rpm). The error bar represents the standard deviation of duplicate results ($0.01 < p < 0.05$).

3.2.3. *Sorption equilibrium and thermodynamic parameters*

(1) Langmuir model

Ion exchange equilibria can be correlated by means of numerical quantities as the usual Langmuir relationship (Riegel, Tokmachev, & Hoell, 2008). Langmuir model is an indication of surface homogeneity of the exchangers and ion exchange phenomena (Wang, Gao, Yue, & Yue, 2007b). The maximum sorption capacity (Q_{max}) is evaluated by Langmuir isotherm equation in the linear form:

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}}\frac{1}{C_e} \tag{3}$$

where q_e is the amount of sorbed phosphate on the WR-AE (mg g^{-1}); C_e is equilibrium phosphate concentration in solution (mg L^{-1}); Q_{max} is the maximum sorption capacity (mmol g^{-1}); b is Langmuir constant (mg^{-1}).

The sorption isotherms of phosphate by WR-AE at 20, 30 and 40 °C are illustrated in Fig. 6. A slight decrease of the maximum sorption capacity with increasing temperature is observed in Fig. 6 and Table 1, which indicates an exothermic nature for sorption process. The high regression correlation coefficients (>0.998) observed in Langmuir isotherm for all temperatures indicate that Langmuir isotherm is applicable for describing sorption equilibrium of phosphate. The maximum sorption capacity (Q_{max}) is obtained at 20 °C, and the Q_{max} (1.80 mmol g^{-1}) of WR-AE is higher than some anion

Table 1
Langmuir and thermodynamic parameters for sorption of phosphate onto WR-AE.

T (°C)	Langmuir			
	Equation	Q_{max} (mmol g^{-1})[a]	b	R^2
20	$C_e/q_e = 0.0180C_e + 0.2628$	1.80 ± 0.06	0.0685 ± 0.0021	0.998
30	$C_e/q_e = 0.0182C_e + 0.3992$	1.76 ± 0.04	0.0456 ± 0.0011	0.999
40	$C_e/q_e = 0.0184C_e + 0.2960$	1.72 ± 0.04	0.0623 ± 0.0015	0.998
T (K)	Thermodynamic parameters			
	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K)	
293	−18.66 ± 0.86	−27.44 ± 0.98	−29.82 ± 1.12	
303	−18.27 ± 0.79			
313	−18.21 ± 0.85			

[a] Data are presented as the means of replicated samples ± standard deviation. Means with the same letter are not significantly different at the 5% level.

exchangers prepared from other agriculture residues such as rice hull (1.20 mmol g^{-1}), sugarcane bagasse (1.02 mmol g^{-1}), pine bark (1.06 mmol g^{-1}), coconut husk (0.89 mmol g^{-1}) and lauan sawdust (0.77 mmol g^{-1}), respectively (Orlando, Baes, & Nishijima, 2002). It is also shown that the Q_{max} of WR-AE is much higher than those of commercial anion exchange resins (0.45–1.36 mmol g^{-1}) and activated carbon (0.19 mmol g^{-1}); this indicates that anion exchanger prepared in this work can be considered as a more efficient and less costly material for phosphate removal in aqueous solution (Orlando et al., 2002; Park & Na, 2006).

(2) Thermodynamic parameters

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with sorption; the thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated to elucidate the process of sorption. The Langmuir isotherm was applied to calculate the thermodynamic parameters via Eqs. (4) and (5) (Huang, Hu, Chen, & Liu, 2007; Renbutsu et al., 2007):

$$\Delta G^0 = -RT\ln(K_L) \tag{4}$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{5}$$

where K_L is Langmuir equilibrium constant (L mol^{-1}), R is the universal gas constant, 8.314 J mol^{-1} K, T is the absolute temperature. The enthalpy change was determined by plotting ln K_L versus $1/T$ (Pan et al., 2008; Wu, 2007).

Table 1 also shows the thermodynamic parameters of ΔG^0, ΔH^0 and ΔS^0. The negative values of ΔG^0 indicate that the sorption of phosphate onto WR-AE is spontaneous and thermodynamically favorable (Li, Yue, Gao, Li, & Li, 2008). The decrease in the value of $-\Delta G^0$ with increasing temperature indicates that the sorption process is less favorable at higher temperature. The negative value of ΔH^0 validates the exothermic nature of the sorption of phosphate onto WR-AE. In addition, the negative value of ΔS^0 suggests a decrease in degree of freedom at the solid–liquid interface during sorption process, which reflects decreased randomness at the solid/solution interface and phosphate affinity to WR-AE (Kennedy, Vijaya, Sekaran, & Kayalvizhi, 2007).

3.2.4. *Desorption of phosphate*

In our previous work, WR-AE filter bed tests have been conducted by varying the conditions in the continuous system such as the influent concentrations, pH and flow rates. Results indicated that filter bed fed with WR-AE seemed to be suitable for the practical utilization in the removal of phosphate (Xu et al., 2009). In this work, desorption tests were carried out to evaluate the feasibility of regeneration property in WR-AE filter bed.

It is of practical and research interest to examine the regeneration behaviors of the WR-AE. Fig. 7 shows the original breakthrough curve of phosphate, and the q_{ed} is about 66.3 mg/g, with the curve showing an S-type mode. In general, it is observed that both NaCl and HCl solutions are adequate for almost complete desorption of the phosphate (Fig. 7). The results indicate that desorption of phosphate ions from the WR-AE is most probably through an reaction of ion exchange, i.e., the reverse of the reactions in Eq. (6) with Cl$^-$ from the NaCl or HCl solution displacing phosphate ions ($-\mathrm{N(CH_2CH_3)_3}^+\cdots\mathrm{H_2PO_4}^-$) from the WR-AE, i.e.:

$$\mathrm{R{-}(CH_2CH_3)_3}^+\cdots\mathrm{H_2PO_4}^- + \mathrm{Cl}^- \rightleftharpoons \mathrm{R{-}(CH_2CH_3)_3}^+\mathrm{Cl}^- + \mathrm{H_2PO_4}^- \tag{6}$$

To check the sorption efficiency of column, column was again reloaded with the phosphate solution. Although there are slight reductions in the sorption capacities with regeneration cycles (from initial about 66.3 to 59.8 mg/g after ten cycles for NaCl and from 66.3 to 58.9 mg/g for HCl), the regenerated WR-AE still possesses high sorption capacities and hence can be repeatedly used for the removal of phosphate from aqueous solution. This shows the great potential applications of WR-AE for the removal of phosphate in water supply.

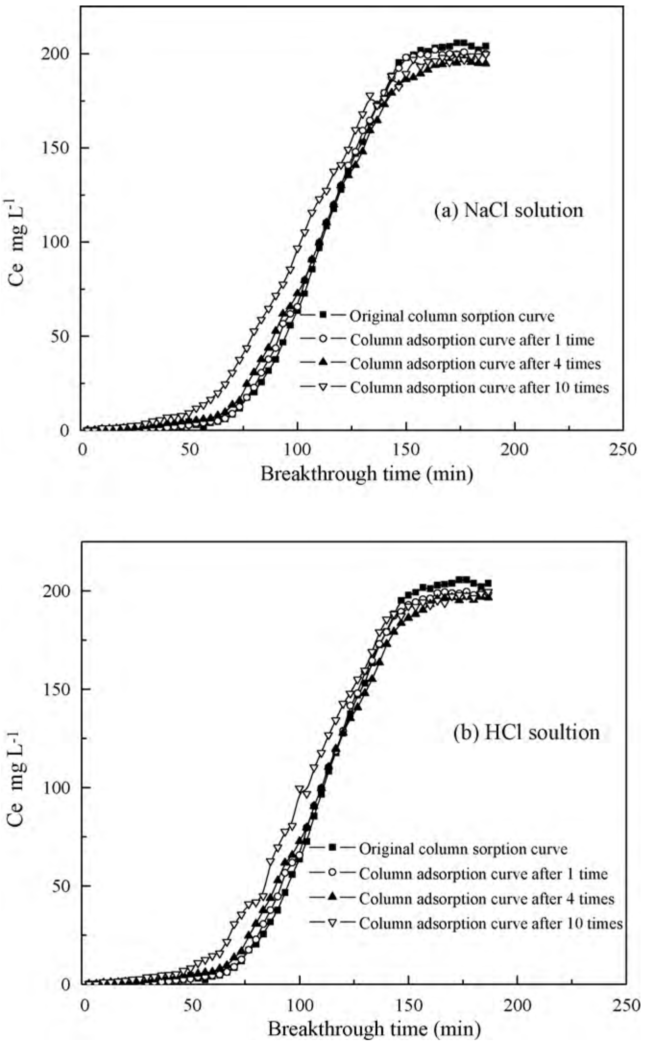

Fig. 7. Desorption efficiency of NaCl and HCl solutions after 10 times of desorption–sorption cycles (phosphate concentration: 200 mg L^{-1}; flow rate: 5 mL min^{-1}).

4. Conclusions

WR-AE was prepared from WR by epichlorohydrin and triethylamine in the presence of ethylenediamine and N,N-dimethylformamide. Chemical analysis indicated that amine groups were introduced into the framework of WR-AE. Results of batch sorption tests showed that WR-AE was efficient and an alternative used in an anion exchanger for phosphate removal in aqueous solutions.

The zeta potential and nitrogen content of WR-AE were −8.9 to +38.6 mV and 11.73 ± 0.02%, respectively. The optimal phosphate removal was obtained at 2 g L^{-1} of WR-AE dosage and pH 5.0–10.0, with negligible effect of temperature on sorption process.

Evaluation of equilibria was made by means of Langmuir approach. The maximum sorption capacity (Q_{max}) estimated by Langmuir isotherm was 1.80 mmol g^{-1}. The WR-AE with sorbed phosphate can be effectively regenerated in both NaCl and HCl solutions through an ion exchange mechanism and the regenerated WR-AE can be repeatedly used at least for ten times in the sorption–desorption cycles without any significant loss of the sorption capacities.

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