



Case Study

Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal

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ABSTRACT

To develop the agricultural by-product adsorbent that possesses anionic exchangeable function, the performance of a new anion exchanger prepared from wheat straw (WS) was evaluated in this study. Wheat straw anion exchanger (WS-AE) was prepared by the grafting of aminated intermediate onto WS. Results indicate that reaction time and temperature in the chemical modification process both affected the preparation of aminated intermediate and WS-AE. FTIR, nitrogen content, solid-state ^{13}C NMR and zeta potential data validated the existence of grafted amine group in the structure of WS-AE. The maximum sorption capacities of WS-AE for nitrate and phosphate were approximately 52.8 and 45.7 mg g^{-1} , respectively, which shows higher maximum capacity for phosphate and a similar capacity for nitrate in comparison with commercial anion resins. Regeneration studies and column adsorption tests were performed, and the excellent regeneration and column adsorption capacities provided strong evidence of the potential of WS-AE for the technological applications of phosphate and nitrate removal from aqueous solutions.

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1. Introduction

The adverse impacts of nutrient overloading in sensitive ecosystems are becoming increasingly noticeable with higher phosphorus and nitrogen contents in the domestic wastewater, agricultural effluent, livestock wastewater, etc. (Das et al., 2006; Ye et al., 2006). Despite the environmental benefits of limiting nutrient release, there is a continuous need to supply phosphorus and nitrogen to agriculture and industry. Thus, development of treatment methods that facilitate the removal of phosphorus and nitrogen from wastewaters prior to discharge into natural waters is required.

In wastewater treatment technology, various techniques including chemical and biological methods have been successfully applied, as reverse osmosis (Thörneby and Persson, 1999), biological de-nitrification (Uygur and Karg, 2004), electro-dialysis (Mohamed, 2002) and anion exchange (Fernandez-Olmo et al., 2007). Of all these, anion exchange is well recognized as one of the simplest and safest methods used for the removal of pollutants from wastewater. It is believed to have advantages that simultaneous removal of ionic substances such as nitrogen, phosphorus, heavy metals, etc. is possible while treatment efficiency is relatively constant regardless of environmental condition and influent quality (Wartelle and Marshall, 2006). Recently, numerous attempts have been made in

finding inexpensive and effective anion exchangers produced from agricultural by-products. Studies showed that many materials, such as sugarcane bagasse (Orlando et al., 2003), peanut hull (Gong et al., 2005), apple pomace (Robinson et al., 2002), sawdust (Ajmal et al., 1998), coconut husk (Manju et al., 1998) and pine bark (Orlando et al., 2003) could be modified into anion exchangers and utilized for this purpose. The agricultural by-product represents a potential alternative as an anion exchanger because of its particular properties such as its chemical stability and high reactivity, resulting from the presence of reactive hydroxyl groups in polymer chains.

Crosslinking agricultural by-products with epichlorohydrin is the most common method used in the preparation of agricultural by-products based anion exchangers (Orlando et al., 2003, 2002). In previous publications, agricultural by-products were first cross-linked with epichlorohydrin to form the epoxy ethers, and then the anion exchangers were produced after the graft of amine groups onto the epoxy ethers by amination reaction (Anirudhan and Unnithan, 2007; Xu et al., 2009; Gao et al., 2009). Results showed that these anion exchangers exhibited excellent sorption capacities for $\text{PO}_4\text{-H}$, NO_3^- , AsO_3^{2-} , AsO_4^{2-} and other anions removal from aqueous solutions. In this work, another new method for preparation of anion exchangers based on aminated intermediate (epoxypropyl triethylammonium chloride, ETC) is presented, which comprises first preparation of ETC by reaction of epichlorohydrin with triethylamine, then introduction of ETC into the agricultural by-products in the presence of a catalyst.

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The whole process may be illustrated as shown in Fig. 1.

2. Methods

2.1. Chemicals

All the chemicals used in this study were of analytical grade. The 1000 mg L⁻¹ of phosphate and nitrate stock solutions were prepared by dissolving required weighed quantities of KH₂PO₄ and KNO₃ (Deyang, China) in distilled water. All solutions for sorption and analysis were prepared by appropriate dilution of the freshly prepared stock solution. Epichlorohydrin, pyridine, methanol, triethylamine were obtained from Sinopharm, China.

Wheat straw (WS), a typical agricultural by-product, was used as the starting material in this work. The raw WS was obtained from Liao Cheng, Shandong, China. It was washed with distilled water, dried at 105 °C for 6 h and sieved into particles with diameters from 100 to 250 μm.

2.1.1. Preparation of wheat straw anion exchanger (WS-AE)

The synthesis process for WS-AE is divided into two steps, and aminated intermediate was synthesized in the first step. An aliquot of 78 ml (1 mol) of epichlorohydrin was reacted with 152 ml (1.1 mol) of triethylamine in 150 ml of 50/50 (v/v)% methanol solution at 30–65 °C. After stirred for 2–7 h, the intermediate was collected and used in the following reactions.

WS-AE was produced in the second synthesis process. 5 g of WS was reacted with 10–50 ml of intermediate and 5 ml of pyridine in a 250 ml three-neck round bottom flask for 1–4 h at 30–65 °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.

The structure of WS-AE is demonstrated in Fig. 1. Pyridine was used as a weak-base catalyst to open the strained ring of the epoxide group in base conditions (Orlando et al., 2002a). Because epichlorohydrin and triethylamine do not dissolve each other, methanol solution was used as an organic medium for the two-phase reaction between epichlorohydrin and triethylamine. As a result, intermediate obtained in the work actually was a mixture of ETC and unreacted reactants (epichlorohydrin and triethylamine).

2.2. Performance indicators of intermediate and WS-AE

2.2.1. Performance indicators of intermediate

Percent conversions of epichlorohydrin and epoxy values of intermediate were used as performance indicators of the intermediate (Liu and Wang, 2004; Bogdal and Gorczyk, 2003).

Percent conversions of epichlorohydrin reflect the synthesis efficiency of reaction between epichlorohydrin and triethylamine. The higher percent conversions observed in the reaction indicate the more epichlorohydrin introduced into the ETC.

Intermediate obtained in the work contained both ETC and unreacted epichlorohydrin. As a result, epoxy values of intermediate detected in this work actually consisted of not only the epoxy value of ETC, but also the epoxy value of unreacted epichlorohydrin. Theoretically, the increase in percent conversions of epichlorohydrin will decrease the epoxy value of unreacted epichlorohydrin and proportionally increase the epoxy value of ETC (Shi et al., 2005). While reaction conditions such as reaction time, temperature, etc. may also have an impact on the epoxy value of intermediate. Therefore, an integrative consideration was required in discussion of both the percent conversions of epichlorohydrin and epoxy values of intermediate to pursue the optimum values for the preparation of intermediate.

Percent conversions of epichlorohydrin were detected by the silver nitrate–potassium chromate titration method (Liu and Wang, 2004; Shi et al., 2005); epoxy values of intermediate were evaluated by the hydrochloric acid–thyme phenolphthalein titration method (Shi et al., 2005). All the titration experiments were replicated for three times.

2.2.2. Performance indicators of WS-AE

In this paper, the performance indicators of the final product WS-AE were determined through the data of nitrate and phosphate removal efficiency of WS-AE. The nitrate and phosphate removal experiments were operated as follows: A series of 125 ml flask were filled with WS-AE at mass loadings 2 g L⁻¹ for nitrate solution (60 mg L⁻¹) and phosphate solution (50 mg (P) L⁻¹) at room temperature (20 ± 1 °C). The conical flasks were then agitated in an orbital shaker at 120 rpm and liquid samples were taken out at a given time interval for nitrate and phosphate analyses with an UV–visible spectrophotometer (model UV754GD, Shanghai).

2.3. Characteristics of WS-AE

Specific 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 N₂, is 0.01 m² g⁻¹.

Zeta potential measurements were carried out using a micro-electrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd, China). To determine the zeta potentials of WS-AE and WS at different pH values, the samples' particles were dispersed into the distilled water with pH range of 2.0–12.0.

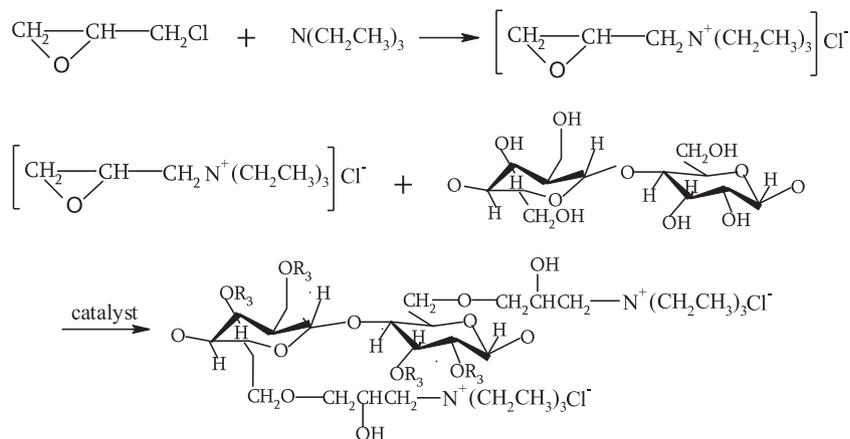


Fig. 1. Synthetic reactions of WS-AE.

The nitrogen content of WS–AE was measured by element analyzer (Elementar Vario EL III, Germany) to evaluate the grafted amine groups in the WS–AE.

Solid-state ^{13}C NMR spectra were acquired at room temperature on a Varian 400 Unity Inova spectrometer operating at 100.57 MHz and equipped with a 4 mm probe-head. All ^{13}C spectra were recorded under magic-angle spinning (MAS) conditions at a spinning speed of 14 kHz.

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

2.4. Desorption experiments

Desorption studies of the adsorbed phosphate and nitrate were carried out by shaking the spent WS–AE in 50 ml of 0.1 mol L^{-1} NaCl or HCl for a period of 2 h (Anirudhan and Unnithan, 2007). After complete recovery of the anions, the sorbent was filtered and washed with distilled water. The regenerated WS–AE sample was reused in the subsequent experiments. The sorption and regeneration cycles were repeated for four times, and a comparison of the value with those observed in the initial sorption step was used to compute the percentage recovery values.

2.5. Breakthrough column experiments

An organic-glass column with 200 mm length and 12 mm diameter filled with 1 g of WS–AE was fed with various concentrations of nitrate and phosphate solutions 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 residual concentrations in the effluent solutions.

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

$$q_{ed} = \frac{(c_0 V_0 - \sum c_n v_n)}{m} \quad (1)$$

where q_{ed} is the amount of anion sorption per gram WS–AE at saturation (mg g^{-1}), c_0 is the original concentration (mg L^{-1}), V_0 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 WS–AE (g).

2.6. Statistical analysis

All experiments (except desorption test and breakthrough column study) were replicated three times and only mean values

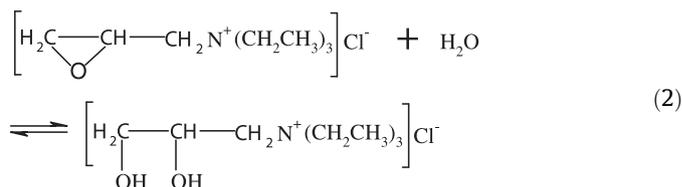
were presented. All data were processed by origin 7.5, and the regression and the analysis of variance (one-way ANOVA) were conducted using the statistical programs of SPSS V13.0 (SPSS Inc., Chicago, IL). Significant levels were set at $\alpha = 0.05$.

3. Results and discussion

3.1. Effect of reaction conditions on the preparation of intermediate

3.1.1. Effect of reaction temperature on the preparation of intermediate

The variation of the percent conversions of epichlorohydrin and epoxy values of intermediate at different reaction temperature is shown in Fig. 2(a). The percent conversions of epichlorohydrin first increase with increase in reaction temperature from 30 to 55 $^{\circ}\text{C}$, and then decrease with further increase in temperature. The epoxy values of intermediate are relatively high when the reaction temperature is 30 $^{\circ}\text{C}$, attribute to the large numbers of unreacted epichlorohydrin existing in the intermediate. As the temperature increases from 30 to 55 $^{\circ}\text{C}$, more epichlorohydrin is introduced into ETC, and the epoxy values of ETC will increase proportionally. However, a gradual decrease in the epoxy values of intermediate is observed in the reaction temperature range of 30–55 $^{\circ}\text{C}$ and the decrease trend sharpens at higher reaction temperature than 55 $^{\circ}\text{C}$. It is assumed that the ring-opening of epoxide rings in epichlorohydrin and ETC is induced by hydrolysis (Eq. (2)) as the reaction temperature increases, which will result in a decrease in the epoxy values of intermediate (Orlando et al., 2002b). Similar result was observed in the work of Shi for the synthesis of epoxypropyl triethyl ammonium chloride intermediate (Shi et al., 2005).



Based on the integrative consideration in both the percent conversions of epichlorohydrin and epoxy values of intermediate, it is evident a reaction temperature of 55 $^{\circ}\text{C}$ seems to be optimal value for such rational conversions and was, therefore, maintained for following experiment.

3.1.2. Effect of reaction time on the preparation of intermediate

Fig. 2(b) shows the effects of reaction time on the percent conversions of epichlorohydrin and epoxy values of intermediate. A

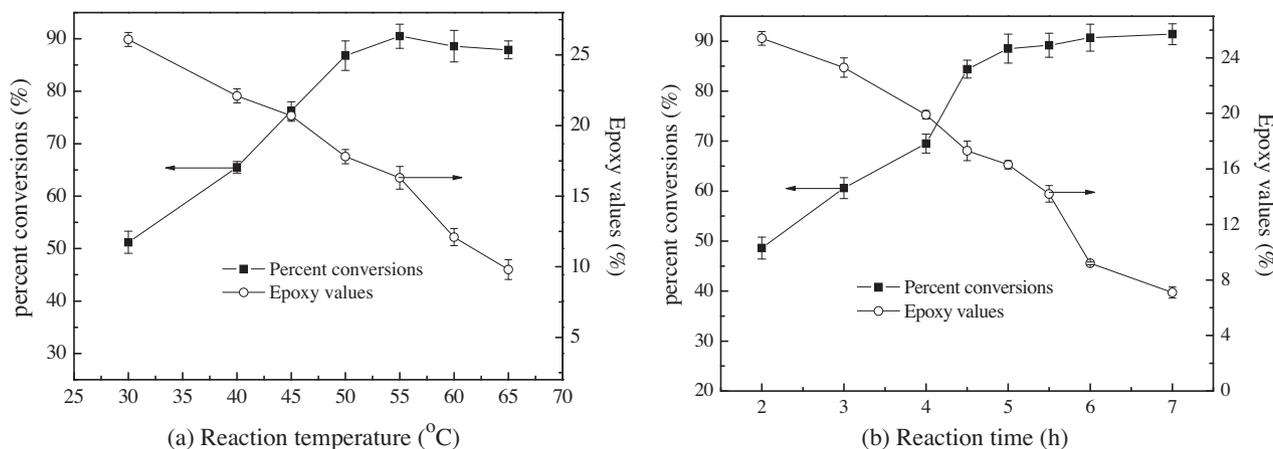
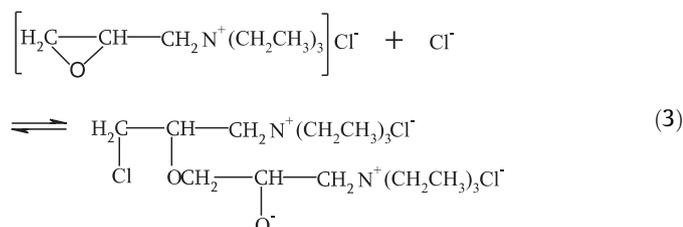


Fig. 2. Effect of reaction temperature and reaction time on the preparation of intermediate.

sharp increase in the percent conversions of epichlorohydrin is observed as the reaction time increases from 2 to 5 h and then the trend tends to gentle with further increase in reaction time, which suggests that a relatively longer reaction time will be favorable to the intermediate reaction process. Epoxy values of intermediate decrease as the reaction time increases, which may still result from the hydrolysis reactions occurred in the ETC and epichlorohydrin. Except for the hydrolysis reaction, another side reaction (Eq. (3)) caused by the crosslinking between the ETC will be induced by the increase in reaction time and results in a decrease in epoxy values (Bicak and Şenkal, 1996).



Based on the mentioned consideration, it is exhibited that 5 h could be selected as the optimal reaction time for the preparation of intermediate and used in the subsequent experiment.

3.2. Effect of reaction conditions on the preparation of WS-AE

3.2.1. Effect of reaction temperature on the preparation of WS-AE

Data of nitrate and phosphate removal efficiency were used as the performance indicators of the prepared WS-AE. Effect of reaction temperature on the preparation of WS-AE is shown in Fig. 3(a). As the reaction temperature increases from 30 to 55 °C, the percentages of nitrate sorbed onto the series of WS-AE increase from 47.5% to 72.5%. The removal efficiency of nitrate tends towards stability with further increase in reaction temperature from 55 to 65 °C; this result suggests that the effect of reaction temperature on the preparation of WS-AE tends to be maximized at 55 °C.

Fig. 3(a) also shows the phosphate removal efficiency of WS-AE prepared at different reaction temperature. Similar result is observed in comparison with the nitrate removal efficiency, and therefore, optimal reaction temperature for the preparation of WS-AE was selected at 55 °C in this work.

3.2.2. Effect of reaction time on the preparation of WS-AE

The effect of reaction time on the performance of prepared WS-AE is shown in Fig. 3(b). With the increase of reaction time

from 1 to 3 h, nitrate removal of WS-AE increases from 42.0% to 72.5%. It is found, however, a gently decrease is observed in the nitrate removal of WS-AE prepared in later period from 3 to 4 h. It is because the ring opening in epoxide group, caused by the hydrolysis and crosslinking reactions occurred in the intermediate (Eqs. (1) and (2)), will result in a decrease in epoxy values, which in turn weaken the performance of WS-AE. Similar result is observed in the phosphate removal experiments, and therefore, 3 h of reaction time was selected in the preparation of WS-AE.

Fig. 3(b) also shows the performance indicators of WS-AE prepared without the catalyst addition. The low removal efficiencies for both nitrate and phosphate indicate pyridine added as a catalyst is required in the synthesis of WS-AE.

3.2.3. Effect of intermediate dosage on the preparation of WS-AE

Fig. 4 illustrates the effect of intermediate dosage on the performance of prepared WS-AE. As the intermediate dosage increases from 10 to 35 ml, the nitrate removal of WS-AE increases from 37.0% to 72.5%, and the performance of WS-AE is almost constant with further increase in intermediate dosage from 35 to 50 ml. This indicates that 35 ml of intermediate is the optimal dosage for the preparation of WS-AE. A similar trend was observed in the case of phosphate sorption tests as shown in Fig. 4.

3.3. Characteristics of WS-AE prepared under the optimal conditions

The structural changes on WS-AE prepared under the optimal conditions were analyzed using specific surface area, zeta potential, nitrogen content, solid-state ¹³C NMR and FTIR techniques.

Specific surface areas of WS-AE and WS are 7.6 and 5.3 m² g⁻¹, respectively. In many reported work, there is no significant change in the specific surface areas between agricultural by-products and their modified products (specific surface areas range of 1.9–2.3 m² g⁻¹, Namasivayam and Sureshkumar, 2008). These modified products do not have the similar porous structure in activated carbon and other pore-structure adsorbents (specific surface area range of 500–2500 m² g⁻¹, Tamai et al., 2003), indicating the absence of surface adsorption in the potential sorption mechanism.

The new anion exchanger prepared from WS is used for the removal of anionic pollutant. As a result, it is significant to determine the change of surface charge of WS-AE in comparison with WS. Sample's zeta potentials were performed using electro-kinetic analyzer at pH range of 2–12 (Table 1). Results show that the zeta potentials of WS-AE are in the range of –28.2 to +32.4 mV in comparison with WS of –48.0 to +4.6 mV in designed pH range, indicating the existence of increased positive-charge functional

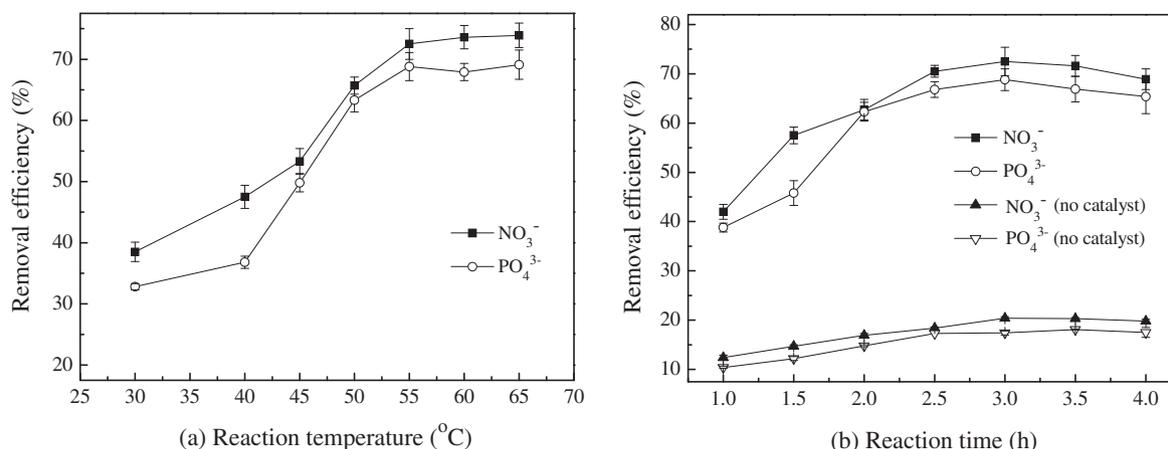


Fig. 3. Effect of reaction temperature and reaction time on the preparation of WS-AE.

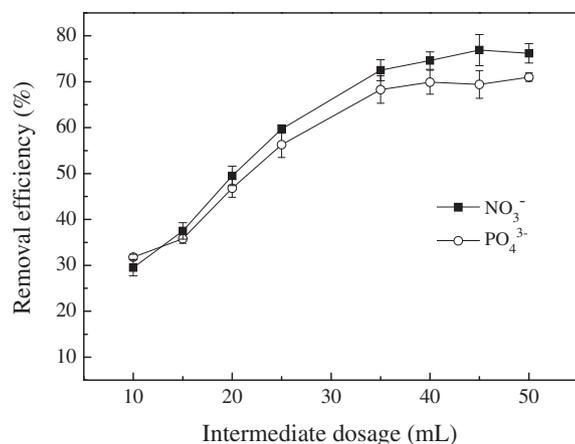


Fig. 4. Effect of intermediate dosage on the preparation of WS-AE.

groups on the WS-AE structure. It is also observed that the zeta potentials of WS-AE gradually decrease as the increase in pH from 2 to 12; this could be attributed to the hydroxyl and carboxyl groups existing in WS-AE, which will exhibit a greater negative charge when the pH is increased and result in the decrease in the positive charge. Similar behavior was observed in the work of Ong for the removal of basic and reactive dyes using ethylenediamine modified rice hull (Ong et al., 2007).

Table 2 displays the elemental changes of carbon, hydrogen and nitrogen in WS-AE in comparison with WS. The significant increase in nitrogen content (0.4–3.6%) of WS-AE indicates the reactions between WS and aminated intermediate proceed efficiently and quite a number of amine groups have been introduced into the WS-AE. Similar result was observed in the previous work of Orlando and Gao for the preparation of anion exchangers from coin, rice hull, pure alkaline lignin and sugarcane bagasse, which have the nitrogen contents in the range of 3.6%–5.8% (Orlando et al., 2002a, 2002b; Gao et al., 2009).

Solid-state ^{13}C NMR spectra were obtained using a cross-polarization contact time of 1000 μs , high-power proton decoupling and a magic-angle spinning frequency at a spinning speed of 14 kHz according to the procedure described by Smernik et al. (2006). The spectrum of WS is dominated by the set of resonances in the region between 60 and 120 ppm. In particular, the cellulose and hemicelluloses resonance signals are approximately 62–65, 72–74, 83–85 and 101–104 ppm. Intense amine carbon peaks are present in the spectra of WS-AE (30–60 ppm) as compared to the spectra of WS, which is the result of the presence of the carbons of $-\text{CH}_2\text{N}-$ and $-\text{NCH}_3$, where the central chemical shifts for these peaks are located at 52 and 35 ppm, respectively.

The IR spectrum of WS-AE and WS exhibits a sharp adsorption band in the region of 3600–3400 cm^{-1} , which corresponds to the presence of free hydroxyl groups. The bands at 2926 and 1625 cm^{-1} indicate the presence of ketone and aromatic in the WS, whereas in the case of WS-AE the bands obtained at 614 and 1337 cm^{-1} indicate the presence of chloroethane and amine

Table 2
Elemental change in WS-AE.

	N (%) ^a	C (%) ^a	H (%) ^a
WS	0.35 ± 0.00	41.13 ± 0.02	6.08 ± 0.02
WS-AE	3.57 ± 0.02	46.52 ± 0.04	6.21 ± 0.03

^a Values are means of triplicate determinations by element analyzer.

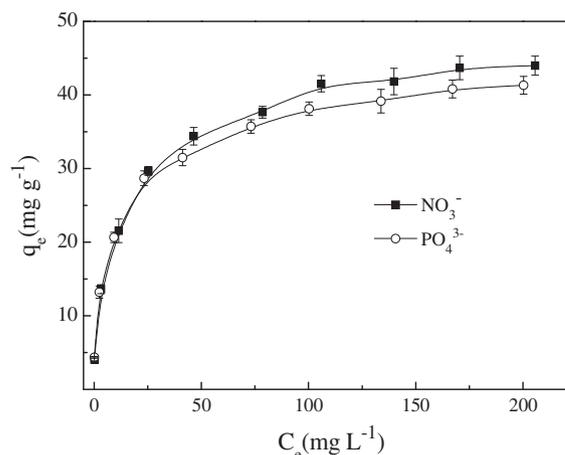


Fig. 5. Sorption capacities of NO_3^- and PO_4^{3-} vs equilibrium concentrations.

groups. Similar result was reported in our previous work, with grafted amine groups observed at the band of 1350 cm^{-1} (Xu et al., 2009).

Based on the characteristics of WS-AE mentioned above, it is evident that the grafted functional groups in WS-AE would be beneficial to the sorption of nitrate and phosphate ions from solution.

3.4. Sorption capacity of WS-AE

To evaluate the sorption capacities of WS-AE, batch sorption tests were conducted on the WS-AE for sorption of the nitrate and phosphate. The initial concentrations of nitrate and phosphate are selected in the range of 50 and 500 mg L^{-1} , respectively (Fig. 5). It is seen from Fig. 5 that the value of sorption capacity is higher for nitrate than phosphate, which suggests the more effective interaction between WS-AE and nitrate. The related parameters were analyzed with Langmuir model to evaluate the maximum nitrate and phosphate sorption capacities (Q_{max}). Langmuir type isotherm is an indication of surface homogeneity of the exchangers and ion exchange phenomena (Weber, 1972).

Langmuir isotherm equation in the linear form follows as:

$$\frac{1}{q_e} = \frac{1}{Q_{\text{max}}} + \frac{1}{bQ_{\text{max}}} \frac{1}{C_e} \quad (4)$$

where q_e is the amount of sorbed nitrate and phosphate on the WS-AE (mg g^{-1}); C_e is the equilibrium nitrate and phosphate

Table 1
Zeta potential change of WS-AE and WS as a function of pH.

	Zeta potential ^a at different pH						
	2.0	3.0	5.0	7.0	9.0	11.0	12.0
WS-AE	+32.4(±2.3)	+31.3(±1.9)	+19.8(±0.6)	+6.4(±0.3)	-5.7(±1.0)	-13.9(±0.5)	-28.2(±0.9)
WS	+4.6(±0.4)	-5.9(±0.3)	-24.6(±0.5)	-33.6(±1.2)	-36.7(±1.3)	-42.5(±0.9)	-48.0(±2.1)

^a Values are means of multifold determinations by microelectrophoresis apparatus.

Table 3
Parameters for Langmuir equations.

	Langmuir constants		R^2
	Q_{\max} (mg g ⁻¹) ^a	b ^a	
NO ₃ ⁻	52.8 ± 1.0	0.0634 ± 0.0035	0.997
PO ₄ ³⁻	45.7 ± 1.1	0.0546 ± 0.0042	0.998

^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.

Table 4
 Q_{\max} of NO₃⁻ and PO₄³⁻ in different exchangers.

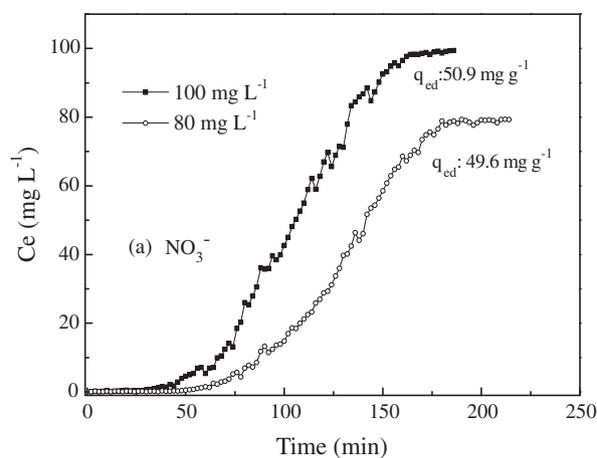
Exchangers	Q_{\max} /mg g ⁻¹		Reference
	NO ₃ ⁻	PO ₄ ³⁻ (P)	
WS-AE	52.8 ± 1.0	45.7 ± 1.1	This work
Activated carbon	5.8	6.8	Park and Na (2006)
Commercial anion exchange resins	36.0–71.6	13.8–42.1	Orlando et al. (2002); Park and Na (2006)
Amberlite IRA 400	65.36	–	Chabani et al. (2007)
Activated sepiolite	9.8	–	Öztürk and Bektaş (2004)
Mixed hydrous oxides	–	22.9	Chubar et al. (2005)
Modified zeolite	45.6	24.6	Ning et al. (2008)

Table 5
Desorption parameters of different desorption solvents.

Regeneration cycles	HCl		NaCl	
	q_e^a mg g ⁻¹	Desorption efficiency %	q_e^a mg g ⁻¹	Desorption efficiency %
<i>(Nitrate)</i>				
Original	21.5	–	21.5	–
1	21.1	98.4	20.6	96.1
2	20.7	96.5	19.8	92.3
3	19.8	92.1	19.5	90.7
4	19.4	90.5	18.9	88.1
<i>(Phosphate)</i>				
Original	17.6	–	17.6	–
1	17.1	97.5	16.7	95.4
2	16.5	94.2	15.8	90.1
3	16.1	91.5	15.7	89.5
4	15.3	87.4	15.1	86.6

^a No replicated.

concentrations in solution (mg L⁻¹); Q_{\max} is the maximum sorption capacity (mmol g⁻¹); b is the Langmuir constant (mg⁻¹).



The related parameters for the fitting of Langmuir equation are shown in Table 3. The Q_{\max} for nitrate and phosphate are 52.8 and 45.7 mg g⁻¹, respectively. Some commercially available anion exchange resins, activated carbon and reported modified adsorbents have been selected and evaluated their nitrate and phosphate adsorption capacities in some reported work (Orlando et al., 2002; Park and Na, 2006; Chabani et al., 2007; Öztürk and Bektaş, 2004; Chubar et al., 2005; Ning et al., 2008). The results are presented in Table 4 as comparing data to those of WS-AE. The phosphate sorption capacity of WS-AE (45.7 mg g⁻¹) is found to be much higher than those of commercial anion exchange resins (13.8–42.1 mg g⁻¹), activated carbon (5.8 mg g⁻¹) and reported modified adsorbents (22.9–24.6 mg g⁻¹). In the case of nitrate, the sorption capacity of WS-AE (52.8 mg g⁻¹) is similar to the commercial anion exchange resins (36.0–71.6 mg g⁻¹) but higher than the activated carbon (6.8 mg g⁻¹) and reported modified adsorbents (9.8–45.6 mg g⁻¹). Comparing these results with the Q_{\max} obtained from commercial anion exchange resin, activated carbon and other modified adsorbents, the prepared exchangers developed in this study can be considered as the alternative materials for nitrate and phosphate removal in aqueous solution.

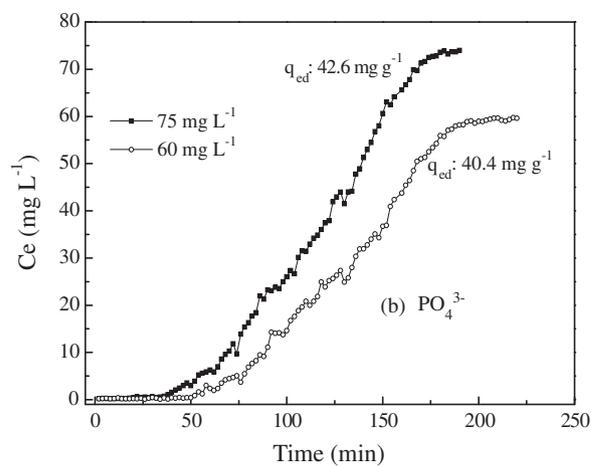
3.5. Desorption

Recovery of the adsorbed anions and repeated usability of the exchanger is important in reference to the practical applications of treatment of industrial effluent. The regeneration efficiency for WS-AE at different stripping liquids is shown in Table 5. Both HCl and NaCl demonstrate the excellent desorption capacities; this indicate that desorption of nitrate and phosphate ions from the WS-AE is most probably through an reaction of ion-exchange, i.e., the reverse of the reactions with Cl⁻ from the NaCl or HCl solution displacing nitrate and phosphate ions from the WS-AE.

After four times of adsorption–desorption cycles, the nitrate and phosphate sorption capacities are observed with only slight losses in their initial adsorption capacities. This indicates that WS-AE can be repeatedly used for the removal of nitrate and phosphate from aqueous solution.

3.6. Breakthrough column test

It is of practical and research interest to examine the column behaviors of the WS-AE. In this work, a column adsorption test was conducted by feeding the continuous system with two initial concentrations of nitrate (80 and 100 mg L⁻¹) and phosphate (60 and 75 mg L⁻¹).

**Fig. 6.** Breakthrough kinetic of WS-AE for NO₃⁻ and PO₄³⁻.

It is observed in Fig. 6 that the breakthrough curve shows an S-type mode and breakthrough time decreases as the concentrations of nitrate and phosphate increase. The column adsorption capacity q_{ed} of WS-AE for nitrate and phosphate are 49.6–50.9 mg g⁻¹ and 40.4–42.6 mg g⁻¹, respectively. A higher q_{ed} is observed at higher concentrations in both column tests for nitrate and phosphate removal, attribute to the concentration gradient which will enhance the adsorption process. Similar results were reported in the work of Goel for the adsorption of lead(II) by treated granular activated carbon and Han's work for methylene blue adsorption onto natural zeolite in fixed-bed column (Han et al., 2007; Goel et al., 2005).

Based on its regeneration and column behaviors, it is apparent that WS-AE could be considered as a potential anion exchange resin for the technological applications of nitrate and phosphate removal from aqueous solutions.

4. Conclusions

Optimal synthesis conditions for the preparation of WS-AE were determined and the characteristics of WS-AE prepared in optimal synthesis conditions were evaluated. It was observed that a number of amine group were grafted in the structure of WS-AE.

The maximum sorption capacities of WS-AE for nitrate and phosphate were 52.8 and 45.7 mg g⁻¹, respectively. The WS-AE with sorbed ions can be effectively regenerated in both HCl and NaCl solutions through an ion exchange mechanism and the regenerated WS-AE can be repeatedly use at least for four times in the sorption-desorption cycles without any significant loss of the sorption capacities.

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