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Removal of sulphate from aqueous solution using modified rice straw: Preparation, characterization and adsorption performance

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ABSTRACT

Rice straw as a lignocellulosic agricultural residue was chemically converted into a strong basic anion exchanger (RS-AE). Epoxy and amino groups were introduced into raw rice straw by reaction with epichlorohydrin and trimethylamine after it was treated in sodium hydroxide solution. The exchangers were characterized by element analysis, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The results showed that total exchanger capacity of rice straw was increased by 1.32 mEq/g, and quaternary amino groups were formed on its new fibrous surface after modification. Batch adsorption experiments suggested RS-AE exhibits a much higher sulphate maximum adsorption capacity (74.76 mg/g) in contrast to that of raw straw (11.68 mg/g). The equilibrium data were described by Langmuir and Freundlich isotherm models, respectively, and were found to agree very well with the former. RS-AE also showed a good performance in regeneration cycles and a high selectivity for sulphate ions.

1. Introduction

Sulphate is a major anion occurring in natural water and industrial effluent, such as inorganic chemical industry wastewater and acid mine drainage. Naturally, it mainly originates from the processes of chemical weathering of sulphur containing minerals and the oxidation of sulphides and sulphur. Sulphate is nontoxic, and sulphur is a necessary nutrient element for many kinds of living systems, however, high sulphate concentrations can cause unbalance of the natural sulphur cycle (Pol, Lens, Stams, & Lettinga, 1998), and also endanger human health when excessive ingestion.

Established methods for removal of sulphate from industrial effluents include chemical precipitation, biological treatment and adsorption technologies. Chemical precipitation, for example, to add barium or calcium salts, is rapid and effective, but it may produce another kind of pollution and secondary treatment for solid phase is necessary (Silva, Varesche, Foresti, & Zaiat, 2002). Removal of sulphate by sulphate-reducing bacteria is another alternative; however, the efficiency of biological treatment is susceptible to environmental conditions because the growth requirements of this microbial are relatively rigid (Muyzer & Stams, 2008). Adsorption method may be preferred for their rapid and high selectivity, and sulphur can be recovered. The commonly used zirconium loaded adsorbent is an efficient material to adsorb sulphate (Mulinari & Silva, 2008), but it is too expensive for consumption of the rare metal zirconium. So there is an interest to develop a low cost and effective anion adsorbent to remove sulphate from aqueous solution.

Recently, lignocellulosic agricultural residues such as banana stem and coconut coir pith (Anirudhan, Noeline, & Manohar, 2006; Anirudhan & Unnithan, 2007), wheat straw (Wang, Gao, Yue, & Yue, 2007a, 2007b), sugarcane bagasse and rice hull (Orlando, Baes, Nishijima, & Okada, 2002a, 2002b), corn stover (Wartelle & Marshall, 2006), soybean hull (Marshall & Wartelle, 2004) used as raw material to prepare anion exchangers have been intensively reported, which seems a potential way to obtain novel and low cost anion adsorbent. China has abundant lignocellulose agricultural resources, especially rice straw. World rice production in 2010/2011 is forecast to be 459.7 million tons, and 137.5 million tons will be harvested in China (USDA, 2010) thus the annual production of rice straw is very high.

Generally, to prepare anion exchanger, cationic groups such as amino groups need to be introduced into a starting material. In the earlier studies (Hwang & Chen, 1992; Laszlo, 1996; Orlando et al., 2002a, 2002b; Simkovic, 1999), two kinds of chemical conversion

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ideas to produce anion adsorbent from agricultural by-products had been proposed based on the reactivity of the primary alcoholic –OH mainly from cellulose contained in the materials. The first idea is to synthesize a complex cationic monomer in advance, commonly *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride or 3-bis (3-chloro-2-hydroxypropyl) imidazolium hydrogen sulphate, and then react with agricultural residues. The second is that agricultural residues are reacted with epichlorohydrin in the presence of pyridine and *N*,*N*-dimethylformamide, respectively, as catalyst and organic solvent, and then combined with amines to obtain lignocelluloses-based anion exchangers. The latter was widely adopted nowadays. For example, Anirudhan, Jalajamonya, and Suchithraa (2009), Anirudhan et al. (2006) and Anirudhan & Unnithan (2007) converted banana stem, coconut coir pith, and pure cellulose into anion exchangers to remove phosphate, arsenate, and chromate, respectively, from wastewater. Wang et al. (2007a, 2007b) prepared an anion exchanger from wheat straw to adsorb nitrate from aqueous solution. Gao, Xu, Wang, Yue, and Xu (2009) also obtained a quaternary amino anion exchanger from wheat straw through pyridine and *N*,*N*-dimethylformamide reaction system. However, the use of the catalyst and the organic solvent will inevitably impair the product's cost advantage promised by its abundant and renewable raw material.

In the present work, we focused our attention on using rice straw as a starting material to produce an anion exchanger for removal of sulphate. Although rice straw is a huge lignocellulosic resource both in China and the world, there has been few reports about rice straw based anion adsorbent. We also wanted to develop a low cost and effective procedure to prepare anion exchangers from lignocellulosic materials. Thus, rice straw was first treated with NaOH solution, followed by partially removal of water, and then reacted with epichlorohydrin and trimethylamine to prepare rice straw based anion exchanger (RS-AE). Element analysis, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) were employed to characterize the exchangers, and its adsorption performance for removal of sulphate, including adsorption isotherms, competitive adsorption and regeneration of spent adsorbent, were evaluated by batch adsorption experiments.

2. Materials and methods

2.1. Materials and chemicals

Raw rice straw was obtained from the suburb of Guangzhou, China. After washing with tap water and deionized water, the straw was milled into particles with size from 0.2 mm to 0.9 mm (mesh = 80–20), and then dried in an oven at 60 °C to constant weight for further treatment. The dried materials contain 34.6–36.3% cellulose determined by method of Soest (1967). Epichlorohydrin and 33% trimethylamine solution were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The stock sulphate solution was prepared by dissolving a certain weight of sodium sulphate anhydrous in deionized water. All other chemicals and reagents used in this study are analytical grade.

2.2. Preparation of RS-AE

The general procedure for preparation of RS-AE using cellulose contained in rice straw as starting material is shown in Fig. 1. Six grams of the above particles was treated with 200 ml 10% (w/w) NaOH solution for 2 h at room temperature to form sodium cellulose. After partially removal of water, the product was mixed with 60 ml pure epichlorohydrin. This mixture was stirred for 6 h at 65 °C to convert sodium cellulose into epoxypropyl-cellulose. The excess epichlorohydrin was separated and recovered from the reaction system through a gauze layer. Then 60 ml 33% trimethylamine solution was added to the reaction system and stirring for 3 h at 80 °C. The reaction product was collected and washed with 1:1 ethanol and 0.1 mol/L NaOH solution, and followed by 0.1 mol/L HCl to obtain anion exchangers in chloride resident form. The final product as RS-AE was washed with a large volume of deionized water until the eluted solution reached a neutral pH, and dried at 60 °C.

2.3. Exchangers characterization

Total nitrogen contents (*N*%) of raw rice straw and RS-AE were determined by Vario EL III element analyzer (Elementar Co., Ltd., Germany) with CHNS pattern. Total exchange capacity (TEC) can be evaluated from the nitrogen content incorporated to the final product with the following equation (Laszlo, 1996):

$$\text{TEC} \quad (\text{mEq} \quad \text{g}^{-1}) = \frac{N\%}{1.4} \tag{1}$$

The chemical structure of exchangers was characterized by a Fourier transform infrared spectrometer Nicolet NEXUS 670 (Nicolet Co., Ltd., USA), and the samples were prepared with KBr tablet method. The surface morphology of raw rice straw and RS-AE was probed using S-3700N scanning electron microscope (Hitachi Limited, Japan).

2.4. Sulphate adsorption studies

Adsorption experiments using raw rice straw and RS-AE were carried out in a 100 ml conical flask containing 50 ml sulphate solution. The flask was put into an orbital shaker at 150 rpm and 25 °C. The pH of sulphate solution used in all experiments was 6.4 which was the original value of deionized water. After shaking for 120 min, the supernatant liquid was separated from the adsorbents by filtration and the filtrate was collected as samples for chemical analysis. Sulphate concentration of the samples was measured by turbidimetric method using UV–vis adsorption spectra at wavelength of 420 nm (Mulinari & Silva, 2008). All the samples were at least duplicated. The term of sulphate adsorption efficiency appeared in this paper was tested using 50 ml 100 mg/L sulphate solution containing 0.1 g adsorbent.

To determine the adsorption isotherms, experiments were conducted at 25 °C with sulphate solution of different concentrations from 50 to 500 mg/L. 0.1 g adsorbent, raw rice straw or RS-AE was added into the sulphate solution, and shaken for 120 min. The maximum sulphate adsorption capacity was calculated by fitting the experimental plots with Langmuir adsorption isotherm model in the form of Eq. (2)

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{2}$$

where q_e is the amount of sulphate adsorbed onto the sorbent, mg/g; C_e is the sulphate concentration at equilibrium, mg/L; Q_{max} is in the place of the maximum adsorption capacity, mg/g; and b is the langmuir constant. The experimental data also were simulated with Freundlich adsorption equation in the following form:

$$q_e = K_f C_e^{1/n} \tag{3}$$

where q_e (mg/g) and C_e (mg/L) have the same meanings with those of Eq. (2); K_f (mg/g) and n are Freundlich equation constants.

2.5. Competitive adsorption and recovery of exchanger

Competitive adsorption experiment was designed to study the selectivity of RS-AE for sulphate ions. 0.1 g RS-AE was immersed

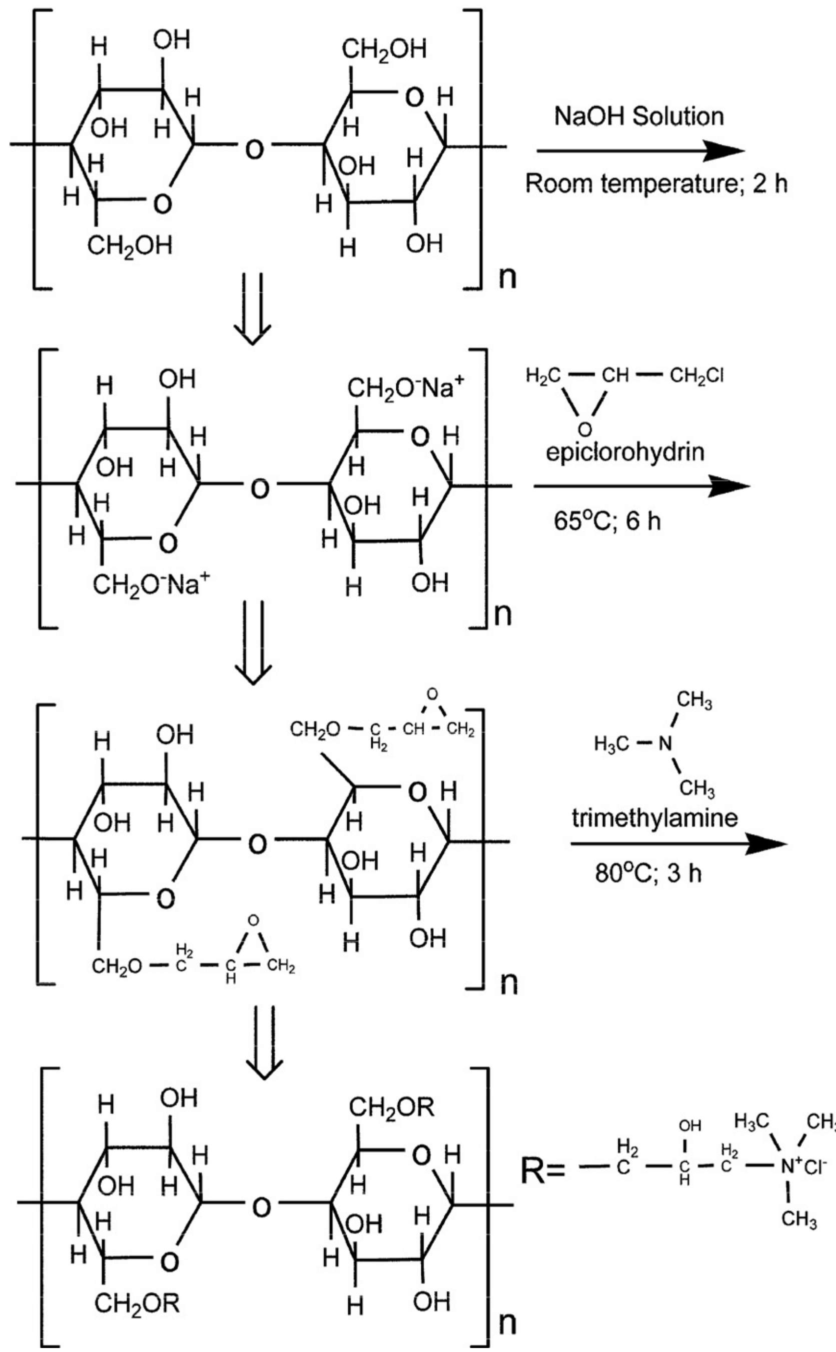

Fig. 1. The general procedure and reactions for preparation of RS-AE.

in 50 ml mixing anions solution containing Cl^-, NO_3^-, PO_4^{3-}, CrO_4^{2-} and SO_4^{2-}. The concentrations of different species anions were determined simultaneously by IC1000 ionic chromatography (Dionex Co., Ltd., USA).

Regeneration performance of RS-AE was tested for repeatedly use in practice applications. The spent RS-AE was immersed in 50 ml 0.1 M NaOH solution and shaken for 30 min to desorb the loaded sulphate ions. Then the exchanger was separated from the NaOH solution and washed with deionized water until the filtrate was up to a neutral pH. The regenerated RS-AE was used in the followed adsorption test to record its sulphate adsorption efficiency again. This adsorption and desorption cycle was repeated four times.

3. Results and discussion

3.1. Preparation of RS-AE

3.1.1. Effect of NaOH concentration

Alkaline treatment could remove part of lignin and hemicellulose from lignocellulosic materials, thus rendering the remaining cellulose more accessible to chemical reagent (Chu, Masyuko, Sweedler, & Bohn, 2010; Hendriks & Zeeman, 2009). Moreover, sodium cellulose exhibits a higher reactivity in contrast to cellulose itself (Kim & Yun, 2006; Laszkiewicz & Wcislo, 1990). In this study, NaOH solution with different concentrations was used to improve the reactivity of rice straw. As shown in Table 1, with the increase

Table 1
Effect of NaOH concentration on the performance of prepared exchangers.[a]

NaOH concentration (%)	Yield (%)	Sulphate adsorption efficiency (%)	Total nitrogen content (%)	Cellulose content of NaOH treated rice straw (%)
5	78.9	43.4 ± 2.6	1.75	47.5 ± 6.8
10	77.1	75.2 ± 1.7	2.75	61.4 ± 9.4
18	73.1	76.3 ± 2.5	2.95	68.7 ± 8.2
30	56.6	79.2 ± 3.1	3.05	77.9 ± 13.3

[a] The exchangers were obtained at quaternization temperature of 80 °C.

of NaOH concentration from 5% to 30% (w/w), total nitrogen content of the final product and its sulphate adsorption efficiency was enhanced from 1.75% to 3.05%, and 43.4% to 79.2%, respectively. On the contrary, the final product yield was reduced from 78.9% to 56.6%. The effect of NaOH treatment on adsorption capacity of final product can be explained by enhancement of the reaction between epichlorohydrin and cellulose, which allows more amino groups to be grafted onto final product so as to form effective adsorption sites. Moreover, cellulose content of the material was increased to 61% after NaOH treatment (10% NaOH solution and stirring for 2 h). It indicates that the lignin, hemicellulose and extractives contained in rice straw were partially destroyed and dissolved in strong basic solution. Taking yield into count, therefore, 10% is an appropriate NaOH concentration.

3.1.2. Crosslinking with epichlorohydrin

The crosslinking reaction between epichlorohydrin and cellulose or sodium cellulose was well studied by previous works (McKelvey & Benerito, 1967; McKelvey, Benerito, Berni, & Burgis, 1961; Orlando et al., 2002a, 2002b). It was found that aqueous medium is a disadvantage to this reaction. So before the sodium cellulose was reacted with epichlorohydrin, water was partially removed from the alkaline treated product by squeeze operation. Water content of this pressed product is approximately 60% (determined as weight loss after dried at 105 °C). On the other hand, this crosslinking reaction is always accompanied by some side reactions, for example, the self polymerization of epichlorohydrin and one epichlorohydrin molecular may reacts with two alkoxy groups supplied by sodium cellulose (Bai & Li, 2006; Chebli & Cartilier, 1998). In this context, it is important to notice that the excess epichlorohydrin can be easily recycled after filtration. The recoverable percentage is 65–75% confirmed by repeated experiments.

3.1.3. Optimization of quaternization temperature

Dimethylamine and triethylamine used as cationic groups to prepare anion exchangers from agricultural residues have been reported (Gao et al., 2009; Orlando et al., 2002a, 2002b). However, there is no information about trimethylamine as quaternization reagent to produce quaternary amino anion exchanger from the lignocellulose materials. In this work, rice straw was finally quaternized with trimethylamine. The optimization of quaterization temperature is shown in Fig. 2. With the rise of temperature from 65 to 80 °C, sulphate adsorption efficiency of RS-AE increases rapidly from 56.6% to 74.8%. While rising the temperature from 80 to 85 °C, only a slight increase was observed in the adsorption efficiency. It is different with sulphate adsorption efficiency that the product yield declined slowly with the quaternization temperature. This may be due to that amine is a weak base and delignification might occur along with the increase of temperature. As a result, the optimal quaternization temperature is 80 °C.

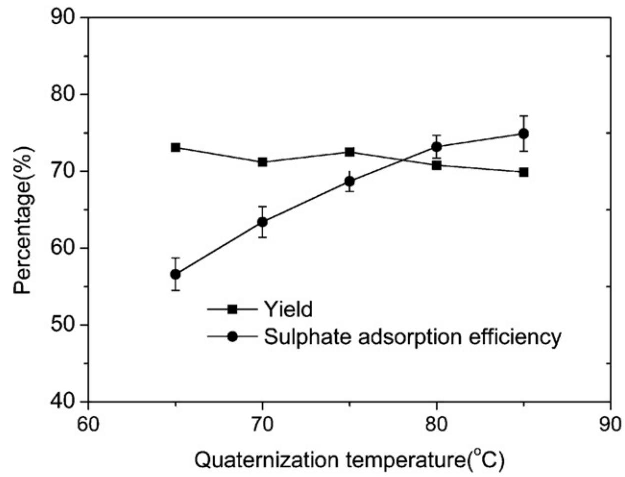

Fig. 2. Optimization of quaternization temperature (raw rice straw was treated with 18% NaOH solution).

3.2. Characterization of exchangers

3.2.1. Total exchange capacity

Element analysis results showed that total nitrogen contents of raw rice straw and RS-AE were 0.45% and 2.75%, respectively. According to the increased N content, total exchange capacity of RS-AE was theoretically calculated as 1.64 mEq/g using Eq. (1). For the raw rice straw, it also can be computed using its original *N*% instead, and the result is 0.32 mEq/g. The comparison of total exchange capacity suggested RS-AE has a much higher potential in adsorption ability.

3.2.2. Fourier transform infrared spectrum

The FT-IR spectra of raw rice straw and RS-AE are shown in Fig. 3. The broad adsorption peak around 3440 cm^{-1} is attributed to the stretching of H-bonded hydroxyl groups. The other adsorption at 2920 cm^{-1} relates to the C–H stretching. The band at 1640 cm^{-1} is assigned to the bending mode of the adsorbed water (Liu et al., 2006). The peak observed at 899 cm^{-1} in raw rice straw corresponds to the glycoside linkages deforming with ring vibration and OH bending (Zheng et al., 2010). In contrast to raw rice straw,

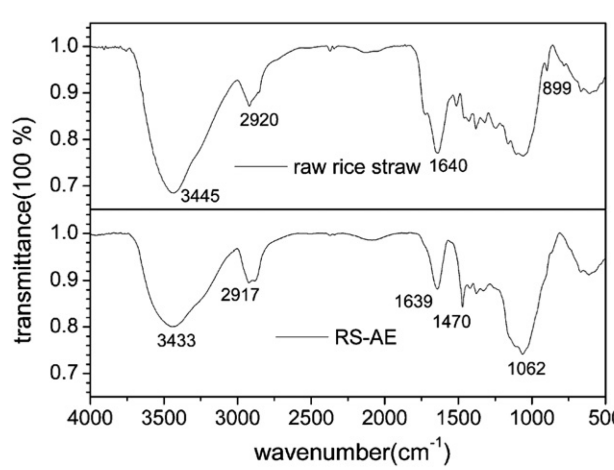

Fig. 3. The FT-IR spectra of raw rice straw and RS-AE.

there is a sharp adsorption peak of the stretching vibration of C–N bond at 1470 cm^{-1}, and a broad band of the skeletal vibration of quaternary ammonium salt (Anirudhan et al., 2006) at 1062 cm^{-1} in RS-AE. It indicated that a large number of amino groups have been introduced into RS-AE structure after chemical conversion, which is also can be confirmed by the increase of nitrogen content (*N*%). Furthermore, the characteristic adsorption of OH group at 3440 cm^{-1} was relatively weaker in RS-AE. The possible reason for this decrease in intensity is that OH groups were partially consumed in the crosslinking reaction with epichlorohydrin.

3.2.3. Surface morphology of exchangers

Scanning electron micrographs of raw rice straw and RS-AE were obtained at an amplification of 500×, represented in Fig. 4a and b. From the surface of raw rice straw (Fig. 4a), it can be clearly observed a large number of heterogeneous pores and aggregate particles. The pores may be originated from intercellular gaps (Anirudhan et al., 2006), and the particles observed on raw rice straw possibly are silica residues (Flogeac, Guillon, Marceau, & Aplincourt, 2003). The component of these aggregate particles determined by energy dispersive X-ray spectroscopy (EDX) contains O 64.79%, C 20.21%, Si 7.72%, K 5.22%, P 0.9%, Cl 0.89% and Mg 0.59%. This suggests these silicon containing materials may be related to the earth in which the rice was planted. After chemical modification, a significant change was observed in surface morphology of the exchangers. As shown in Fig. 4b, the prepared exchanger RS-AE appears to have a smoother surface with lots of homogenous cellulose fibers instead of porous structure. The diameter of the fibers is ranged from 5 to 10 μm, which agrees with the observation result from the literature (Lim, Son, Lee, Park, & Cho, 2001). Comparing the two micrographs, we can infer that cellulose fiber structure was well exposed by alkaline treatment and it was the main location for chemical modification reactions and the formation of quaternary amino groups as active adsorption sites.

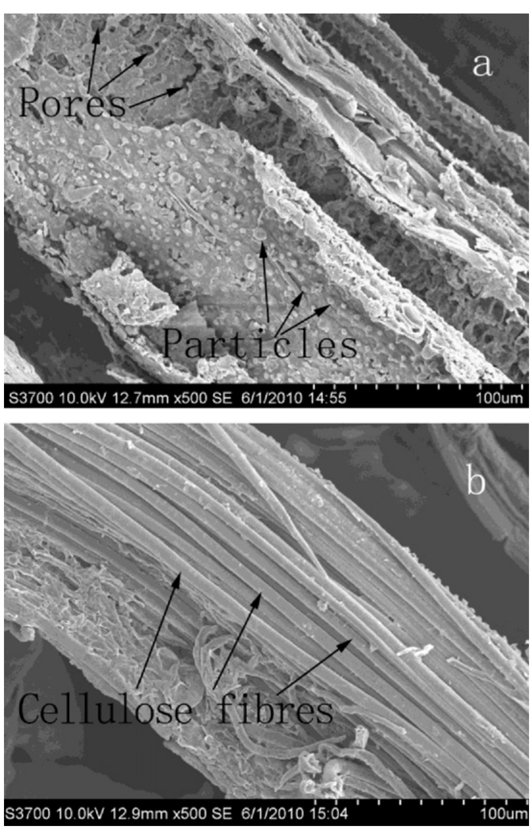

Fig. 4. The scanning electron micrographs of raw rice straw (a) and RS-AE (b).

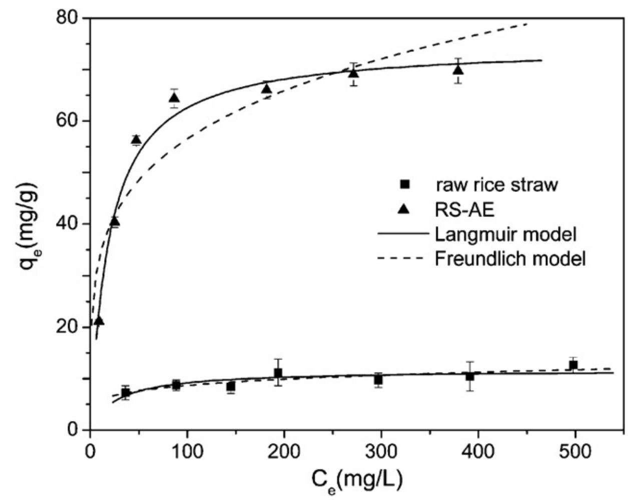

Fig. 5. Adsorption isotherm of sulphate by raw rice straw and RS-AE (temperature: 25 °C; shaker speed: 150 rpm; contact time: 120 min; pH: 6.4).

3.3. Adsorption isotherms and maximum adsorption capacity

The adsorption isotherms of sulphate by raw rice straw and RS-AE were plotted in Fig. 5, and the experimental data were fitted with Langmuir and Freundlich equations. As shown, the adsorption isotherm of RS-AE ascended very fast at lower sulphate concentrations. As the concentration of sulphate in solution is increased, the amount of sulphate adsorbed finally reached a limiting value. This suggested there is a strong affinity between sulphate ions and exchanger. On the contrary, the isotherm of raw rice straw is much lower than that of RS-AE, and almost like a horizontal line. It demonstrated that raw rice straw was not effective enough to adsorb sulphate ions.

The related parameters of Langmuir and Freundlich models were evaluated by non-linear regression analysis and the results are shown in Table 2. The comparison of R^2 value for Langmuir model and Freundlich model showed that the Langmuir adsorption model are fitted better for the adsorption of sulphate ions onto RS-AE. The equilibrium data from raw rice straw did not agree well with both of these models. The maximum adsorption capacities of raw rice straw and RS-AE for sulphate were obtained using the parameter Q_{max} in Langmuir equation. The Q_{max} values for RS-AE and raw rice straw are 74.76 mg/g and 11.68 mg/g, respectively. It is clear that RS-AE is more effective than raw rice straw for removal of sulphate from aqueous solution.

3.4. Competitive adsorption

Adsorption of sulphate ions separately and in the presence of other anions onto RS-AE was conducted. In the presence of other anions, the removal percentage of sulphate was reduced from 71.8% (separately) to 34.5%. This decrease is due to the competition for adsorption sites by other species anions. Compared with other species anions, sulphate was recorded the highest removal percentage, which is most likely because of its divalent property (Orlando

Table 2
Langmuir and Freundlich equation constants and correlation coefficients for adsorption of sulphate by raw rice straw and RS-AE.

	Langmuir equation			Freundlich equation		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Raw rice straw	11.68	0.037	0.65	3.70	5.38	0.74
RS-AE	74.76	0.051	0.98	20.45	4.53	0.82

Table 3
Comparison of RS-AE with other adsorbents.

Starting materials	Target contaminants	Q_{max} (mmol/g)	References
Rice hull	Nitrate	1.21	Orlando et al. (2002a)
Corn stover	Phosphate	0.66	Wartelle and Marshall (2006)
Coconut coir pith	Arsenic(V)	0.14–0.18[a]	Anirudhan and Unnithan (2007)
Cellulose	Chromate	1.09[a]	Anirudhan et al. (2009)
Amberlite IRA-900	Nitrate	1.2	Orlando et al. (2002a)
Rice straw	Sulphate	0.78	This study

[a] The original data were 10.42–13.57 mg/g for arsenic(V) and 126.7 mg/g for chromate.

et al., 2002b). Furthermore, the RS-AE exhibited a selectivity in the order $SO_4^{2-} > CrO_4^{2-} > NO_3^{-} > PO_4^{3-} > Cl^{-}$.

3.5. *Recovery of exchanger*

For consideration of practical applications, the spent RS-AE was regenerated by 0.1 M NaOH solution. After four cycles of adsorption and regeneration, the sulphate adsorption efficiency of RS-AE decreased less than 10% (from 74.7% to 66.2%). It is necessary to point out that the weight loss of the sorbent after four cycles is less than 2%, which proved that RS-AE could keep stable in diluted alkaline solution. The recovery performance indicates the potential of RS-AE for repeatedly use in the removal of sulphate ions from waste water.

3.6. *Comparison with other adsorbents*

Comparison between the RS-AE in this study and other lignocellulose based anion adsorbents and a commercial anion exchanger (Amberlite IRA-900) in the literature was made. The related data and references were summarized and listed in Table 3. The RS-AE represents a comparable adsorption capacity with other similar anion adsorbent. And the more important is that RS-AE was prepared in absence of pyridine and *N*,*N*-dimethylformamide in contrast with the widely used method (Anirudhan et al., 2009; Anirudhan et al., 2006; Anirudhan & Unnithan, 2007; Gao et al., 2009; Orlando et al., 2002a, 2002b; Wang et al., 2007a, 2007b). This gave advantages in terms of chemical costs and a closer relation to the concept of environmental friendly material.

4. Conclusions

Rice straw was converted into a strong basic anion exchanger by reaction with NaOH, epichlorohydrin, and trimethylamine. NaOH treatment has a remarkable effect on the performance of exchangers, and the proper concentration of NaOH is 10% (w/w). Characterization results show that RS-AE with amino groups has a higher TEC (1.64 mEq/g) than raw rice straw (0.32 mEq/g), and it appears to have a fibrous surface with many homogenous cellulose fibers. RS-AE exhibits a good sulphate adsorption performance and a higher selectivity and it can be recovered with a slight loss of adsorption capacity.

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