Preparation and utilization of wheat straw anionic sorbent for the removal of nitrate from aqueous solution

WANG Yu[1,2], GAO Bao-yu[1,*], YUE Wen-wen[1], YUE Qin-yan[1]

1. School of Environmental Science and Engineering, Shandong University, Jinan 250100, China. E-mail: wy@sdein.gov.cn
2. Environmental Monitoring Center of Shandong Province, Jinan 250013, China

Abstract

In order to reduce the impact of eutrophication caused by agricultural residues (i.e., excess nitrate) in aqueous solution, economic and effective anionic sorbents are required. In this article, we prepared anionic sorbent using wheat straw. Its structural characteristics and adsorption properties for nitrate removal from aqueous solution were investigated. The results indicate that the yield of the prepared anionic sorbent, the total exchange capacity, and the maximum adsorption capacity were 350%, 2.57 mEq/g, and 2.08 mmol/g, respectively. The Freundlich isotherm mode is more suitable than the Langmuir mode and the adsorption process accords with the first order reaction kinetic rate equation. When multiple anions (SO_4^{2-}, $H_2PO_4^-$, NO_3^-, and NO_2^-) were present, the isotherm mode of prepared anionic sorbent for nitrate was consistent with Freundlich mode; however, the capacity of nitrate adsorption was reduced by 50%. In alkaline solutions, about 90% of adsorbed nitrate ions could be desorbed from prepared anionic sorbent. The results of this study confirmed that the wheat straw anionic sorbent can be used as an excellent nitrate sorbent that removes nitrate from aqueous solutions.

Key words: adsorption; anionic sorbent; nitrate; thermodynamic adsorption; adsorption kinetics; raw wheat straw (RWS); modified wheat straw (MWS)

Introduction

Wheat straw is a common organic residue that is readily available in several areas of intensive agriculture. The total annual production of various straws, including wheat, rice, corn, is approximately 700 million tons in China (Li, 1998). Wheat straw production accounts for 15.2% of this total, amounting over one hundred million tons annually. Wheat straw can be used as (1) an industrial material, where it is mainly used in paper making (2.3%); (2) as feedstock (24.0%); and (3) as a biomass energy source (31.5%). The remaining part of the unused wheat straw is either incinerated or abandoned as waste. There has been an increasing interest in processing such agricultural residues for use as anionic sorbents. Materials such as sugarcane bagasse (Orlando *et al.*, 2002b), peanut hull (Gong *et al.*, 2005), apple pomace (Robinson *et al.*, 2002), sawdust (Ajmal *et al.*, 1998), coconut husk (Manju *et al.*, 1998), orange peel (Namasivayam *et al.*, 1998), banana pith (Namasivayam *et al.*, 1996) and pine bark (Orlando *et al.*, 2002b) have been utilized for such purposes. However, there has been no report on the use of processed wheat straw as an anionic sorbent.

The main components of wheat straw are cellulose (32.1%), hemi-cellulose (29.2%), lignin (16.4%), ash (4.8%) and other components (17.5%). Cellulose (Laszlo, 1996), lignin (Funaoka *et al.*, 1995) and other active components (Papatheofanous *et al.*, 1998) are often used in the preparation of anionic sorbents. This article details the preparation of an anionic sorbent from wheat straw and its subsequent characterization of the product. The kinetics and thermodynamics of nitrate absorption in aqueous solution were investigated. This study demonstrates the use of wheat straw as an effective anionic sorbent material. It offers a solution to the reduction of waste output of this material, potentially curtailing its adverse environmental impacts. The high anion-absorbing capacity of this product apparently suggests that it can be widely used in the treatment of wastewater.

1 Materials and methods

1.1 Materials and instruments

To chemically modify the wheat straw, we followed the procedure as described in the literature (Orlando *et al.*, 2002a). Commercial chemicals of analytical reagent, including: N,N-dimethylformamide, dimethylamine, epichlorohydrin, sodium nitrate, sodium nitrite,

sodium sulfate, and sodium phosphite, were used to prepare the solution for wheat straw treatment. Air-dried raw wheat straw was obtained from Liaocheng, Shandong.

During the entire course of this experiment, the following analytical instruments were used. Total C, N, O and H of the wheat straw were analyzed using Vario EL III Elementar (Elmentar company, Germany). The chemical structure and functional groups of the chemically modified wheat straw were determined using AVATAR370 FT-IR (Nicolet company, American). The resolution was ± 2 cm^{-1}, the spectral range was from 4800 to 200 cm^{-1}, and the optical grade potassium bromide (KBr) was used as a background material. S-520 SEM (Hitachi, Japan) was used to examine the micrographs of wheat straw. The samples were mounted on metal grids and coated with gold under vacuum before observation, the accumulation voltage and current were 25 kV and 20 A, respectively. The concentrations of anions were detected using 752 UV-Vis spectrophotometer (Shanghai Instrument Company, China) and PIC-8 Ion Chromatograph (Qingdao Puren Company, China), respectively.

1.2 Preparation

The raw material was rinsed with water, and then dried at 60°C for 48 h. The oven-dried materials were ground, and allowed to pass a fine-mesh sieve (150 to 250 μm). Finally, wheat residue (raw wheat straw (RWS)) was crosslinked with epichlorohydrin and dimethylamine (Orlando *et al.*, 2002a). The detailed procedure is as follows: an aliquot of 5 g of wheat residue was dispersed in 60 ml N, N-dimethylformamide (DMF) in a 500 ml 3-necked round bottom flask. A 50 ml aliquot of epichlorohydrin was added and the mixture was stirred for 1 h at 100°C. Next, 20 ml pyridine catalyst was added and the mixture was stirred for 1 h at 100°C. Finally, 75 ml 33% (w/w) dimethylamine was added and stirred for 3 h at 100°C. The product was washed until the eluent reached neutrality and then the modified wheat residue (MWS) was dried at 60°C in a vacuum drier. electrokinetic analyzer EKA (JS94H) was used to determine the zeta potential. The zeta potential of RWS and MWS were –35 mV and +40 mV, respectively.

1.3 characterizations of the sorbent

The yield of sorbent (Y) was determined gravimetrically using the following quation:

$$Y(\%) = m_1/m_0 \times 100 \tag{1}$$

where, m_1 and m_0 are the dry weight of RWS and MWS, respectively.

We used elementar to determine the content of N (N%) of RWS and MWS, respectively. The total exchange capacity (TEC) was calculated using the following equation (Orlando *et al.*, 2002a).

$$\text{TEC} = \frac{\text{N}\%}{1.4} \tag{2}$$

where, TEC is the total exchange capacity (mEq/g) of MWS, N% is the total nitrogen of MWS, and 1.4 is the correction coefficient.

The infrared spectrum of RWS and MWS was determined by AVATAR370 FT-IR.

SEM analysis was carried out to examine the appearance of RWS and MWS as well as the changes that occurred after nitrate was adsorbed onto the surface of MWS.

1.4 Adsorption experiment

Static adsorption experiment was carried out to determine the adsorption equilibrium and the maximum adsorption capability, nitrate concentrations of 50–500 mg NO$_3^-$-N/L, with an interval of 50 mg/L, were prepared using KNO$_3$. An aliquot of 0.2 g of MWS was added to 50 ml KNO$_3$ solution, and was then shaken for 90 min in a thermostat. The MWS was separated from the nitrate solution by filtration on a vacuum. The filtrate was collected and diluted with de-ionized water to 50 ml (unless otherwise specified) for further analysis. The concentration of nitrate was determined colormetrically using a UV-Vis 752 spectrophotometer. This experiment was triplicated.

Competitive adsorption experiment was conducted to determine the selectivity of the MWS for different anions. We first prepared a mixed solution that contained nitrate, nitrite, sulfate and phosphate. We used commercial analytical grade of KNO$_3$, KNO$_2$, K$_2$SO$_4$ and KH$_2$PO$_4$ to prepare the desired concentrations of mixed anions. A concentration gradient of 10, 20, 30, 40 and 50 mg/L of the anions was obtained. An aliquot of 0.2 g of MWS was added to 50 ml mixed solution, and then shaken for 90 min in a thermostat. The MWS was separated from the mixed solution by filtration in vacuum. The filtrate was collected and diluted with de-ionized water to 50 ml (unless otherwise specified) for further analysis. The concentrations of different anions were determined using Ion Chromatograph.

Desorption and reuse experiment were done to determine the desorption ratio and reusability of MWS. An aliquot of 0.2 g adsorbed MWS was eluted with different volumes of 0.1 mol/L NaOH (ranging from 5 to 35 ml), and was then shaken for 30 min in a thermostat. The eluted MWS was separated by filtration in vacuum, and the concentration of nitrate released into the filtrate was determined colormetrically using a UV-Vis 752 spectrophotometer. Furthermore, the regenerated MWS was washed with de-ionized water for 3 times and again added to nitrate containing solution for the next adsorption–desorption cycles. The desorption ratio (r) was calculated using the following equation:

$$r\ (\%) = \frac{A_{\text{desorbed}}}{A_{\text{adsorbed}}} \times 100 \tag{3}$$

where, r is the desorption ratio, A_{desorbed} is the amount of nitrate ions desorbed, A_{adsorbed} is the amount of nitrate ions adsorbed.

2 Results and discussion

2.1 Characterization of the sorbent

2.1.1 Analysis of MWS yield (%)

The MWR yield was calculated with the ratio between MWS and RWS, using Eq.(1). The result showed that MWS yield was as high as 350%. The reason is that the cellulose and lignin in RWS contain a large amount of easily accessible hydroxyl groups which could be used for the attachment of epichlorohydrin and dimethylamine , and formed tertiary amino sorbent, and thus these can enhance the yield of MWS.

2.1.2 TEC analysis

The results of chemical analysis showed that the total N contents of RWS and MWS were 0.35% and 3.6%, respectively. According to Eq.(2), the total N content divided by a factor of 1.4 provides the total exchange capacity (TEC) of MWS. The TEC of RWS and MWS were simply calculated as 0.25 and 2.57 mEq/g, respectively. This represents a 10-fold increase as compared to the raw wheat straw.

2.1.3 FT-IR analysis

The FT-IR spectra of RWS and MWS are shown in Fig.1. It shows that the spectrum for RWS is very similar that for MWS, indicating that the main structure of RWS is not altered, but some of the associated functional groups had been modified. For example, the appearance of a conspicuous peak at 1360 cm^{-1} for RWS, which is associated with tertiary amino group (νC–N-stretching vibration), clearly demonstrates the modification of functional groups. The zeta potential of RWS was –35 mV, whereas that of MWS was +40 mV. This indicates that a significant increase in the zeta potential of wheat straw after chemical treatment can greatly enhance the anion adsorption capacity.
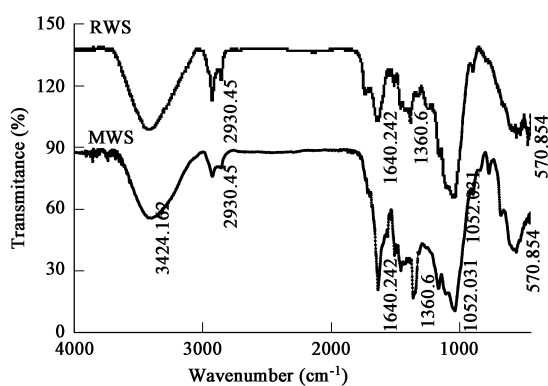

Fig. 1 FTIR spectrum of RWS and MWS.

2.1.4 SEM analysis

The results of the scanning electronic microscopic measurements of the structure of RWS and MWS are shown in Figs.2a and 2b. It is obvious that the surface of MWS is smoother than that of RWS, which indicates that the order of cellulose was improved after removing the hemicellulose, lignin, ash and extractives during the process of synthesis. Fig.2c shows the SEM structure of MWS after reaction with KNO$_3$ for 90 min. It is clear that the absorbed nitrate anions were aggregated on the surface of MWS, indicating that MWS is very effective in the adsorption of nitrate.

2.2 Adsorption equilibrium and maximum adsorption capacity

At room temperature (23±2°C), the adsorption equilibrium for nitrate of RWS and MWS are shown in Fig.3. The data in Fig.3 were fitted by the Freundlich and Langmuir isotherm mode.

The Langmuir model is written as Eq.(4):

$$q_e = \frac{bQ_{max}C_e}{1 + bC_e} \tag{4}$$

where, C_e presents the equilibrium concentration of nitrate in the solution (mmol/L); q_e is the adsorbed amount of nitrate (mmol/g); Q_{max} represents the maximum amount of adsorbed nitrate (mmol/g); and b is a constant related to the energy of adsorption (L/mmol).

The Freundlich model is written as Eq.(5):

$$q_e = KC_e^{1/n} \tag{5}$$

where, K is the proportionality constant, which is indicative of bond strength (mmol$^{(1-1/n)}$L$^{1/n}$/g), and n is a dimensionless exponent related to bond energies between nitrate ion and the adsorbents.

The result is shown in Table 1. It was found that the maximum adsorption capacity of RWS and MWS were 0.144 mmol/g and 2.08 mmol/g, respectively, which indicates that MWS was more effective than RWS. From the correlation coefficients, it can been seen that the MWS data fit the-Freundlich isotherm and the Langmuir isotherm, but the Freundlich isotherm mode is more suitable than the Langmuir mode, which can also be interpreted by the heterogeneous of the surface of MWS. On the contrary, the RWS data did not fit the Freundlich isotherm and the Langmuir isotherm well, which demonstrates that RWS
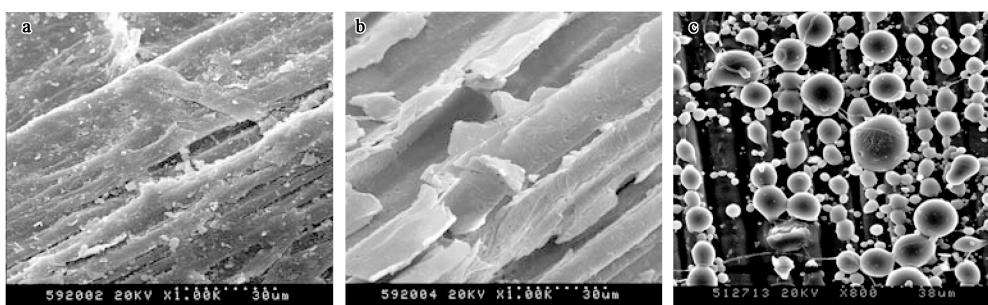

Fig. 2 SEM micrographs of raw wheat straw (a), modified wheat straw (b), and adsorbed wheat straw (c).

Table 1 Parameters for Langmuir and Freundlich equations

	Langmuir			Freundlich		
	Q_{max} (mmol/g)	B (L/mmol)	R^2	K ((mg$^{(1-1/n)}$ · L$^{1/n}$)/g)	n	R^2
RWS	0.144	0.00283	0.452	0.121	1.63	0.858
MWS	2.08	0.28	0.966	2.69	1.73	0.995

Q_{max}: maximum adsorption capacity; b: energy of adsorption, K: proportionality constant, n: dimensionless exponent.
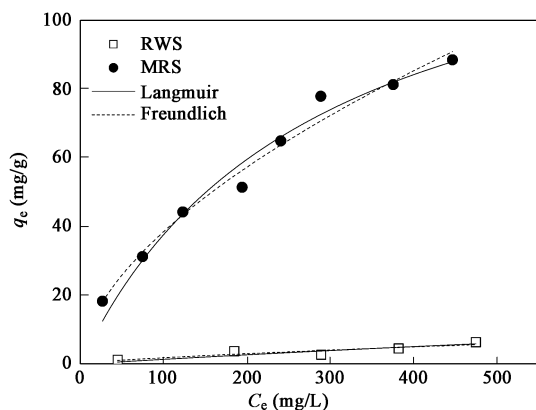

Fig. 3 Isothermal curve of nitrate adsorption by RWS and MWS. pH: 6.8; shaker speed: 120 r/min; sorbent dose: 2.5 g/L; contact time: 150 min.

was not sufficiently effective in the adsorption of nitrate. Orlando *et al*. (2002b) reported the maximum adsorption capacities of several anionic sorbents obtained by treating rice hulls, pine barks and other organic residues with the same chemical compounds as used in this study (Table 2). Our results clearly demonstrated that MWS had the highest adsorbed amount (Q_{max}), and it can be used to effectively remove the nitrate in aqueous solutions.

Table 2 Parameters of Langmuir model of different anionic sorbents for the nitrate adsorption

Sorbent	Q_{max} (mmol/g)	b (L/mmol)	R^2	Reference
MWS	2.08	0.28	0.966	This study
RWS	0.02	0.00283	0.452	This study
Coconut husk	0.89	1.65	0.9929	Orlando *et al*., 2002b
Rice hull	1.20	2.65	0.9924	Orlando *et al*., 2002b
Pine bark	1.06	1.48	0.9763	Orlando *et al*., 2002b
Sugarcane baggasse	1.02	1.6	0.9878	Orlando *et al*., 2002b

2.3 Adsorption kinetics

The adsorption kinetics of nitrate of different initial concentration by MWS are shown in Fig.4. The curves of the different initial concentration (100, 300, 500 mg/L) have similar trends. The curves can be divided into three parts. In the first part, when contact time $t < 10$ min, the slopes were sharp and about 80% adsorption occurred in 10 min. The instantaneous increase of C_t may be because of chemical sorption of nitrate by MWS. In the second part (10 min $< t < 20$ min), the slopes became gentle and about 20% adsorption occurres. The gradual increase of C_t may be because of a thorough utilization of active position in the MWS. In the third part ($t > 20$ min), C_t no longer changes, and the adsorption reached equilibrium.
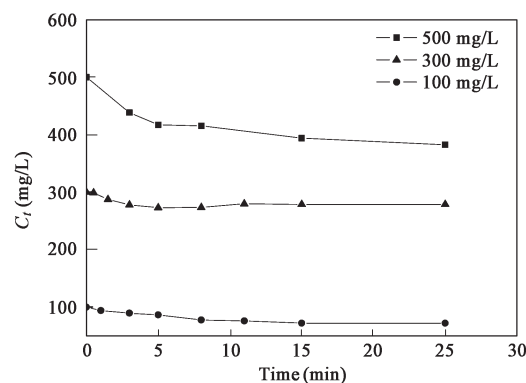

Fig. 4 Adsorption kinetic graph of series concentration of nitrate. pH: 6.8; shaker speed: 120 r/min; sorbent dose: 2.5 g/L; contact time: 150 min.

The data in Fig.4 were fitted by the first order reaction kinetic rate according to Eq.(6). The results in Fig.5 and Table 3 show that this adsorption process accords with the first order reaction kinetic rate equation; the kinetic rate constants for nitrate concentrations at 100, 300, and 500 mg/L were 0.01759, 0.01925 and 0.03059 min^{-1}, respectively and the kinetic rate constant increased with the increasing concentrations of nitrate.

$$\ln C_t = \ln C_0 - kt \tag{6}$$

where, C_0 is the initial concentration, C_t is the concentration at t min, k is the reaction kinetic rate constant (min^{-1}),

Table 3 First order reaction kinetic rate equation and the reaction parameter of the series concentration of nitrate

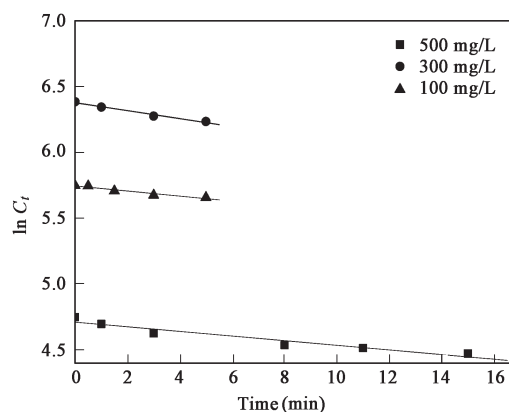| NO$_3^-$ (mg/L)	Equation	k (min^{-1})	R^2
100	$\ln C_t = 4.711 - 0.01759t$	0.01759	0.9628
300	$\ln C_t = 5.746 - 0.01925t$	0.01925	0.9672
500	$\ln C_t = 6.380 - 0.03059t$	0.03059	0.9896

Fig. 5 First order reaction kinetic graph of series concentration of nitrate. pH: 6.8; shaker speed: 120 r/min; sorbent dose: 2.5 g/L; contact time: 150 min.

and t is the adsorption time (min).

2.4 Competitive adsorption

The isotherms with different anions co-exist in the solution are shown in Fig.6. The isotherm equations of different anions are shown in Table 4. From Fig.6, it was found that the adsorption capacity of MWS was the strongest for sulfate and weakest for nitrite, and nitrate and phosphate were in between. Table 4 shows the isotherms of sulfate, phosphate, and nitrate, all in accord with the Freundlich isotherm mode. Next, from the value of K, in the presence of a mixed anion solution, the preferential absorption of the anions follows the following order, $SO_4^{2-} > H_2PO_4^- > NO_3^- > NO_2^-$, which confirms that the absorption ability is associated with anion valence number; the bigger valence number, the better is the absorption ability. If the anion valence numbers are the same, the one with a bigger atomic number will have better absorption ability. However, in the presence of a mixed anions solution, the capacity of nitrate absorption is reduced by 50%.

2.5 Desorption and reuse

The desorption ratio with different volumes of 0.1 mol/L NaOH is shown in Table 5. It was found the desorption ratio was changed with different volumes of 0.1 mol/L NaOH. About 90% of adsorbed nitrate ions could be desorbed from MWS anionic sorbent using 30 ml 0.1 mol/L NaOH, which indicated that the MWS anionic sorbent had higher regeneration efficiency at alkaline solutions. Furthermore, the reusability of MWS anionic sorbent was tested (Fig.7). The adsorption-desorption cycle was repeated twelve times. The results showed that the static adsorption capacities of MWS anionic sorbent did not change obviously and only decreased slightly at

Table 4 Freundlich isotherm equation of different anions

Anions	Equation	n	K	R^2
NO_3^-	$\lg q_e = 0.4261 \lg C_e + 0.1183$	2.35	1.31	0.9468
NO_3^-*	$\lg q_e = 0.5774 \lg C_e + 0.4296$	1.73	2.66	0.9949
HPO_4^{2-}	$\lg q_e = 0.3916 \lg C_e + 0.1947$	2.55	1.56	0.9883
SO_4^{2-}	$\lg q_e = 1.0032 \lg C_e + 0.7048$	1	5.06	0.9635
NO_2^-	– –		–	–

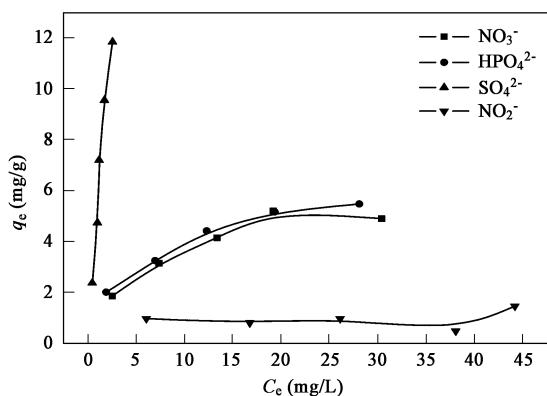NO_3^-*: nitrate adsorbed without other anions.

Fig. 6 Isotherm of different anions co-exist. pH: 6.8; agitate speed: 120 r/min; sorbent dose: 2.5 g/L; contact time: 150 min.

Table 5 Desorption ratio of nitrate

Volume (ml)	Desorption ratio (%)	Volume (ml)	Desorption ratio (%)
5	62	25	83
15	71	30	90
20	77	35	90

Adsorption conditions: initial nitrate concentration: 50 mg/L; amount of MWS: 0.2 g; pH: 6.8; temperature: 25°C; desorption reagent: 0.1 mol/L NaOH solution.
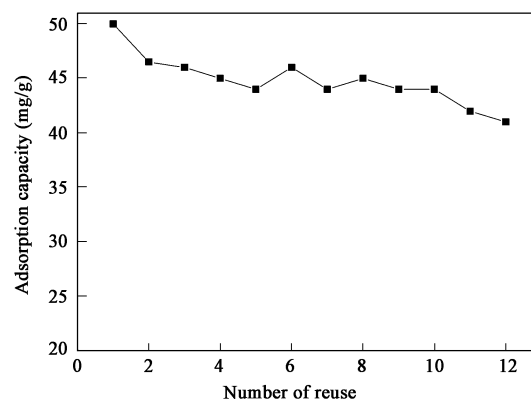
Fig. 7 Number of MWS reuse. pH: 6.8; nitrate concentration: 50 mg/L; amount of MWS: 0.2 g; temperature: 25°C; desorption reagent: 0.1 mol/L NaOH solution.

eleventh cycle. From the parameters of desorption ratio and reusability, it demonstrated that the MWS anionic sorbent had higher practical value in treatment of nitrate pollution.

3 Conclusions

The yield of MWS anionic sorbent and the total exchange capacity of 350% and 2.57 mEq/g represent a 10-fold increase as compared to the raw wheat straw. FTIR analysis indicated the presence of tertiary amino groups. The zeta potential of MWS anionic sorbent was +40 mV, representing the advantages for use as an anionic sorbent in aqueous solutions. SEM micrographs show that the absorbed nitrates formed particulate matter on the surface of the MWS.

The kinetics and thermodynamics study indicated that the absorption equilibrium of the MWS anionic sorbent fits the Freundlich isotherm mode with a maximum capacity of 2.08 mmol/g (RWS: 0.02 mmol/g), and the absorption process obeys the first order kinetic rate equation. The rate constants increased with the increasing concentration of the nitrates. In the presence of a mixed ion solution, the preferential absorption of the anions was in the following order, $SO_4^{2-} > H_2PO_4^- > NO_3^- > NO_2^-$, and the isothermal absorption followed the Freundlich mode. However, the capacity of nitrate absorption was reduced by 50%. At desorption and reuse experiment, about 90% of adsorbed nitrate ions could be desorbed from MWS anionic sorbent using 30 ml of 0.1 mol/L NaOH. The static adsorption capacities of MWS anionic sorbent did not change obviously and only decrease slightly at the eleventh cycle.

Acknowledgements

References

Ajmal M, Khan A H, Ahmad A, 1998. Role of sawdust in the removal of copper(II) from industrial wastes[J]. Water Res, 32(10): 3085–3091.

Funaoka M, Matsubara M, Seki N, 1995. Conversion of native lignin to a highly phenolic functional polymer and its separation from lignocellulosics[J]. Biotechnol Bioeng, 46(6): 545–552.

Gong R M, Ding Y, Li M et al., 2005. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution[J]. Dyes Pigments, 64: 187–192.

Laszlo J A, 1996. Chemical strategies for producing anion exchangers from ligncellulosic residues to be used for removing textiles dyes from wastewater[M]. In: Ion exchange dvelopments and application (Greig J. A., ed.). Proc. IEX'96, 128–130. SCI, Cambridge..

Li J J, 1998. The evaluation of available biomass in China[M].

Beijing: Chinese Environmental Science Press. (7) 17–18.

Manju G N, Raji C, Anirudhan T S, 1998. Evaluation of coconut husk carbon for the removal of arsenic from water[J]. Wat Res, 32(10): 3062–3070.

Namasivayam C, Muniasamy N, Gayatri K, 1996. Removal of dyes from aqueous solutions by cellulosic waste orange peel[J]. Bioresour Technology, 57: 37–43.

Namasivayam C, Prabha D, Kumutha M, 1998. Removal of direct red and acid brilliant blue by adsorption onto banana pith[J]. Bioresour Technology, 64: 77–79.

Orlando U S, Baes A U, Nishijima W, 2002a. A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials[J]. Bioresource Technology, 83: 195–198.

Orlando U S, Baes A U, Nishijima W, 2002b. Preparation of agricultural residue anion exchangers and its nitrate maximum adsorption capacity[J]. Chemosphere, 48: 1041–1046.

Papatheofanous M G, Billa E, Koullas D P, 1998. Optimizing multisteps mechanical-chemical fractionation of wheat straw components[J]. Industrial Crops and Products, 7: 249–256.

Robinson T, Chandran B, Nigam P, 2002. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw[J]. Wat Res, 36: 2824–2830.