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Removal of nitrate and phosphate from aqueous solution by modified corn straw: characteristics and mechanism

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ABSTRACT

This study investigated the removal of NO_3^- and PO_4^{3-} from eutrophic water by a new sorbent of modified corn straw which is low-cost and environmentally safe. The sorbent was characterized using element analyzer, spectrum and scanning electron microscopy, ^{13}C nuclear magnetic resonance and Fourier transform infrared. Results suggest that the quaternary amino group and hydroxyl group are the main functional groups on the fibrous surface of the sorbent. The effects of contact time, initial concentration and pH on the removal of NO_3^- and PO_4^{3-}, as well as adsorption isotherms at different temperature were investigated. Results showed that the adsorption of NO_3^- and PO_4^{3-} by this sorbent can reach equilibrium within 10 min, which was highly efficient. The adsorption process could fit well with the pseudo-second-order reaction kinetic rate equation and the adsorption rate is positively correlated to the square of the adsorption process driving force. The equilibrium data fitted well with Langmuir adsorption model and the maximum NO_3^- and PO_4^{3-} adsorption capacities at neutral pH were 19.9 and 0.164 mg/g at 30°C, respectively. A stability test was operated for three cycles. Results demonstrate that the adsorption capacity of this sorbent only loses 14.0%, indicating that the sorbent has good potential for reuse and recycle.

Keywords: Nitrate; Phosphate; Eutrophic water; Corn straw; Agricultural waste modification

1. Introduction

In the agricultural countries, the disposal of numerous agriculture wastes has aroused wide interest in scientific community. In China, the output of agriculture residues can reach 900 million tons each year [1], but most of the agriculture residues are burned without recycle and reuse. It is not only a waste of resources but also a source of air pollution. Consequently, numerous studies have focused on the comprehensive utilization of agriculture residues.

With the development of industry and agriculture, more and more nitrate and phosphate was accumulated in water and resulted in the eutrophication of lakes, reservoirs, estuaries and inland seas [2]. Accordingly, increasing attention has been focused on the removal of nitrates and phosphorus from industrial water over the past decades. At present, common techniques for nitrate and phosphorus removal include electrodialysis [3], reverse osmosis [4,5], biological

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denitrification [6] and ion exchange [7,8]. Among these techniques, ion exchange has the best adsorption property, but commercial ion exchangers are too expensive to be widely used in the treatment of eutrophic water bodies.

Therefore, there is an urgent need to develop a flexible and effective adsorbent from agricultural wastes that are actually abundant. Recently, increasing studies have developed the low-cost absorbent materials from agriculture residues, such as banana stem, sugarcane bagasse [9,10], peanut hull [11], coconut husk [12] and corn stalk [13]. Among all these biosorbents, plant stalks (such as bagasse, rice straw, and corn stalk) are mainly composed of organic cellulose, hemicellulose, lignin and inorganic silicon dioxide [14]. The corn straw may be preferred for their high components of cellulose (>30%) and abundance [15], which could facilitate the adsorption of anion.

Furthermore, surface modification is a promising technique to improve the adsorption capacity. Many techniques of modifications such as the access of amine groups, protonation and heat treatment have been reported [16,17]. Some scientists have used *N*,*N*-dimethylformamide (DMF) and pyridine as solvent and catalyst, combined tertiary amino groups to the hydroxyl group of the cellulose unit with epichlorohydrin and dimethylamine [18]. By this method of modification, the maximum adsorption capacity for NO_3^- of adsorbent can be improved from 0.02 to 2.08 mmol/g [19].

However, both DMF and pyridine are costly and toxic, which greatly limit their widely use in reality. This paper reports a preparation of a cheap and environmentally safe adsorbent (modified corn straw [MCS]) from corn straw by means of chemical modification of cross-linking with epichlorohydrin and trimethylamine. NaOH solutions were used to replace DMF and pyridine, which is an effective basic anion exchanger which could increase the possibility to deal with the large quantities of corn residues and, at the same time, reduce the nitrate and phosphate pollution from aqueous solutions. The anion adsorbent was environmentally safe and can make full use of agricultural wastes. The adsorption performance was investigated by testing its efficiency to remove NO_3^- and PO_4^{3-} in water solution.

2. Experimental section

2.1. Materials

Raw corn straw (RCS) was obtained from the local area in Guangzhou, China. The straw was rinsed with tap water for three times to remove dirt on the surface of the straw, and then dried at 60°C in a drying oven for 48 h. The dried materials were ground and sieved into particles ranging from 0.2 to 0.9 mm particles (80–20 mesh). Through the above steps the clean RCS was obtained. The analytical grade epichlorohydrin, trimethylamine water solution, potassium nitrate (KNO_3) and monopotassium phosphate (KH_2PO_4) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). The stock solution of NO_3^- and PO_4^{3-} was prepared by dissolving defined amount of dried KNO_3 and KH_2PO_4. In the study, in order to investigate the effect of pH on nitrate and phosphate removal, we use solutions of 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) to adjust the pH of the medium. Deionized water was used in the whole experimental process.

2.2. Adsorbent preparation

10.0 ± 0.2 g of RCS particles (80–20 mesh) were treated with 10% (w/v) NaOH solution for 2 h to remove most of the lignin in order to expose cellulose and form sodium cellulose. After the removal of water, sodium cellulose was mixed with 100 mL epichlorohydrin in a three-neck round-bottom flask. This mixture was stirred at 65°C for 6 h to obtain epoxypropyl cellulose. To remove the excess epichlorohydrin, 100 mL trimethylamine water solution was added and the mixture was stirred at 80°C for 3 h. The product was then collected and rinsed with 50% ethanol, 0.1 M NaOH solution and 0.1 M HCl solution, sequentially, to convert it into chloride loaded form. The final product was washed with deionized water until the eluent reached neutrality and the MCS was dried in a vacuum drying oven to a constant weight [17].

2.3. Characterization

Element analyzer (elementar vario EL III, German) was employed to determine the *N*% of RCS and MCS, respectively. Nitrogen adsorption–desorption experiments for surface and porosity quantification were performed with Chemisorption Surface Area Analyzer (ASAP 2010, Micromeritics, USA). The surface areas were estimated by using the Brunauer–Emmett–Teller method. The microstructure of the adsorbents' external surface was investigated by a field emission scanning electron microscopy (SEM; S-3700N, Hitachi Limited, Japan). The functional groups of raw rice straw and prepared anion exchangers were analyzed by using Fourier transform infrared spectrometer (FTIR) Nicolet (NEXUS 670, Nicolet Co., Ltd., USA) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy. Samples for FTIR were prepared with potassium bromide (KBr). The concentration of nitrate or phosphate in the solution remaining after filtration was determined using a UV–visible spectrophotometer (UV2550-SHIMADZU, Japan). The concentration of Cl^- and SO_4^{2-} left was determined by ion chromatography (IC 90, Dionex Co., Ltd., USA).

2.4. Adsorption experiment

Adsorption studies were carried out with synthetic NO_3^- and PO_4^{3-} solutions to investigate the performance of the adsorbents. The experiments were performed in a 100-mL conical flask containing several MCS as sorbent and 50 mL NO_3^- or PO_4^{3-} solution with different concentrations. The flasks were shaken in a thermostat orbital shaker at rate of 150 rpm at the desired temperatures. The initial pH was varying from 2.0 to 11.0 with NO_3^- concentration of 50 mg/L and PO_4^{3-} concentration of 2 mg/L at 30°C.

To investigate the effect of initial NO_3^- concentration and contact time on removal of NO_3^-, time intervals (0.5, 1, 2, 5, 10, 20, 30, 40, 50, 60, 75 and 90 min) were adopted in adsorption experiments with different initial NO_3^- concentrations (25, 50 and 100 mg/L).To investigate the effect of initial PO_4^{3-} concentration and contact time on removal of PO_4^{3-}, time intervals (0.5, 1, 3, 10, 20, 40, 60 and 90 min) were adopted in adsorption experiments with different initial PO_4^{3-} concentrations (2, 4 and 10 mg/L).

The adsorption isotherms were obtained by changing initial NO_3^- and PO_4^{3-} concentrations at neutral pH. After 120 min of contact, the supernatant liquid was separated from the sorbent by filtration, and the filtrate was collected for chemical analyses. The adsorption capacity, q_e (mg/g), was calculated from the mass balance Eq. (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where C_0 (mmol/L) and C_e (mmol/L) represent the initial and equilibrium concentration; V (L) is the volume of solution and m (g) is the mass of sorbent.

In order to investigate the competitive adsorption of the co-existing anions from water, 0.2 g MCS was immersed in 50 mL mixing anions solution containing nitrate, phosphate, chloride and sulfate at 30°C. The initial concentration of nitrate, phosphate, chloride and sulfate were all 10 mg/L. To investigate the effect of dissolved organic matter (DOM), 0.2 g of MCS was added to 50 mL mixed solution at 30°C for 2 h. The initial concentration of nitrate, phosphate and humic acid (HA) were all 10 mg/L.

Desorption and reuse experiments were performed to determine desorption and regeneration of MCS. The adsorbed MCS was eluted with 0.1 M NaOH for 2 h. The regeneration was repeated three times.

All flask experiment was triplicated.

3. Results and discussion

3.1. Characterization of the sorbent

3.1.1. The TEC of adsorbent

The total exchange capacity (TEC) was calculated by the following Eq. (2):

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

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

As analyzed by element analyzer, nitrogen contents (N%) of RCS and MCS were 0.46% and 1.92%. According to Eq. (2), the TEC of RCS and MCS were 0.33 and 1.37 mEq/g. This indicated that the TEC of corn straw was greatly increased after chemical treatment which suggests that the chemical modification could greatly enhance the anion adsorption capacity.

3.1.2. SEM analysis

The scanning electron micrographs of RCS and MCS taken at magnitude of 50 times and 1,000 times are presented in Fig. 1. RCS, as shown in Figs. 1(a) and (b), appeared to be long and straight, with several gaps on the surface, which might originally exist in the corn straw as intercellular gaps [20] or resulted from the grinding process.

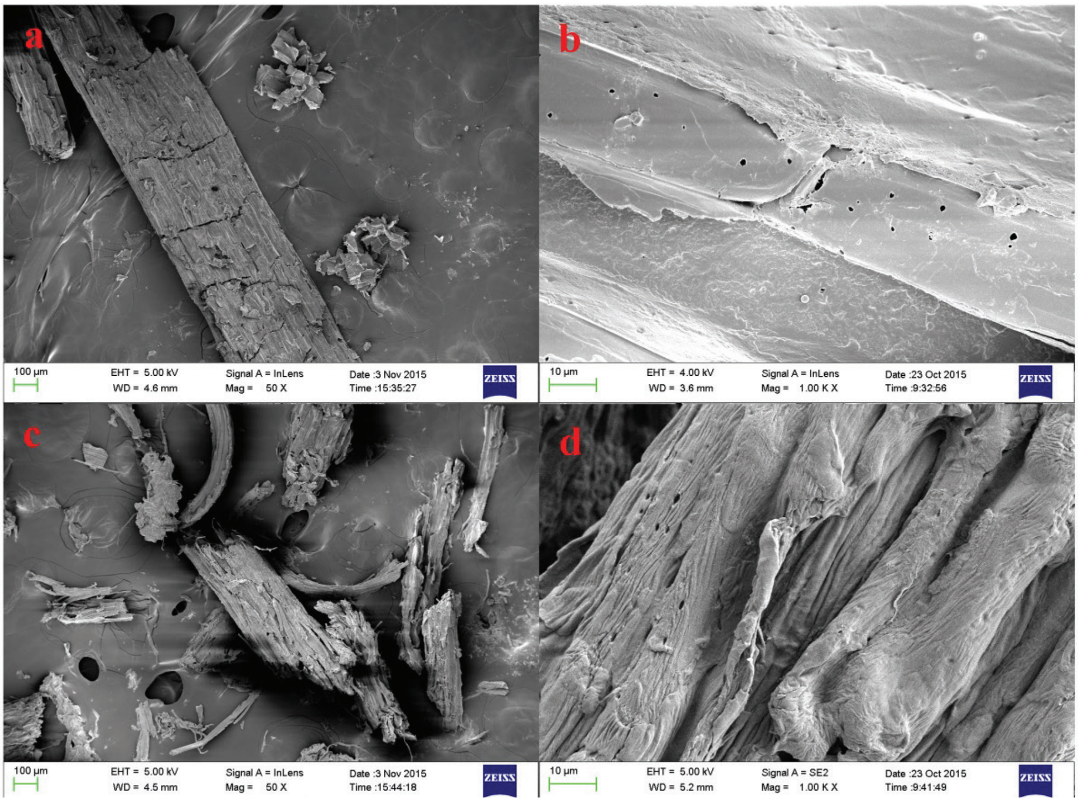

Fig. 1. SEM images of RCS and MCS. (a) RCS, 50×; (b) RCS, 1,000×; (c) MCS, 50× and (d) MCS, 1,000×.

MCS, as shown in Figs. 1(c) and (d), appeared to be broken and twisted on account of string and alkaline pretreatment. Furthermore, some cellulose fibrous can be found on the MCS surface in Fig. 1(d). The diameter of these fibrous was about 5–10 μm, which is consistent with the results in the literature [21]. Numerous studies showed that the alkali solution is a good swelling agent for lignocellulosic materials and can remove most lignin and part of hemicelluloses at the same time. Therefore, through the chemical modification, especially the pretreatment of 0.1 M NaOH, the cellulose structure in corn straw was well exposed and more accessible to modifying agents [22,23].

3.1.3. FTIR analysis

The FTIR spectra of RCS and MCS are shown in Fig. 2. The strong adsorption band around 3,433 cm^{-1} was attributed to the stretching vibration of hydrogen-bonded hydroxyl groups (–OH) from the cellulose structure and polyphenol structure of lignin. The peak at 2,920 and 1,379 cm^{-1} were the C–H stretching and bending from CH_2– groups [24]. The band at 899 cm^{-1} was believed to arise from the β-(1,4)-glycosidic linkages [25]. These above peaks at 3,433, 2,920, 1,379 and 899 cm^{-1} were all typical peaks of native cellulose [24]. It is obvious that the spectrum of MCS was very similar to that of RCS, suggesting that the main structure of both RCS and MCS was native cellulose. However, there were still some associated functional groups was modified. For example, compared with RCS, the MCS has a sharp peak of the stretching vibration of the C–N bond at 1,467 cm^{-1} and a broad band of the skeletal vibration of quaternary ammonium salt at 1,062 cm^{-1} [25]. These changes clearly indicated that a large amount of quaternary amino groups were introduced into the corn straw after modifications.

3.1.4. ^{13}C NMR analysis

The ^{13}C NMR spectra of RCS and MCS are shown in Fig. 3. The chemical shifts around 60–70, 80–90 and 98–110 ppm were associated with C6, C4 and C1 from the cellulose structure, respectively. The peak around 70–80 ppm was the appearance signal of C2, C3 and C5, of which the signal are difficult to distinguish and usually appeared as shoulder peak acromion in the spectrogram. Obviously, the chemical shifts of C1 to C6 were consistent to the study of the physicochemical characterization of cellulose [25–27].

The spectra of RCS and MCS exhibit an obvious difference. Specifically, the MCS has a sharper peak in the vicinity of 56 ppm than that of RCS, which is attributed to the C6 that connected to the quaternary amino groups [28,29]. This result indicated that quaternary amino groups were successfully introduced to the corn straw by chemical modification.

3.2. Effect of initial pH

The effect of initial pH on the adsorption of NO_3^- and PO_4^{3-} by MCS is illustrated in Fig. 4.The optimal pH range for NO_3^- removal was 3–9, under which the adsorption capacity can reach to 7.38 mg/g. At the same time, the optimal pH range for PO_4^{3-} was 4–9 and the adsorption capacity can reach to 0.112 mg/g. The adsorption capacity decreased slowly with the increase of pH. The effect of pH on adsorption can be explained by surface protonation of the functional groups of the sorbent [30,31]. The functional group on the surface of MCS is the quaternary amino group, which can be easily protonated in the solution [32,33]. Protonation is usually impaired by the increase of pH. The protonation of amino groups led to a positively charged sorbent surface, thus enabling the adsorption of anions to occur through electrostatic attraction. Besides, in strongly acidic solution, most of the nitrate and phosphate are in the form of [HNO_3] and [H_3PO_4] because of the high concentration of H$^+$. It can significantly reduce the adsorption of nitrate and phosphate by the sorbent. The decrease on removal of NO_3^- and PO_4^{3-} at higher pH was apparently due to the higher concentration of OH$^-$ ions, presented in the reaction mixture which competes with the NO_3^- and PO_4^{3-} ions for the adsorption sites of MCS.

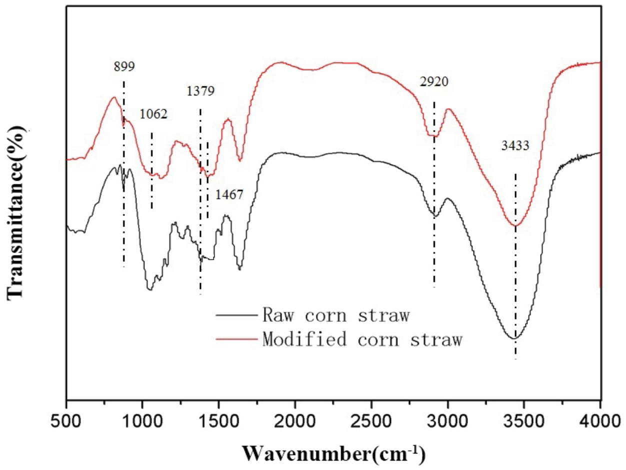

Fig. 2. FTIR spectra of RCS and MCS.

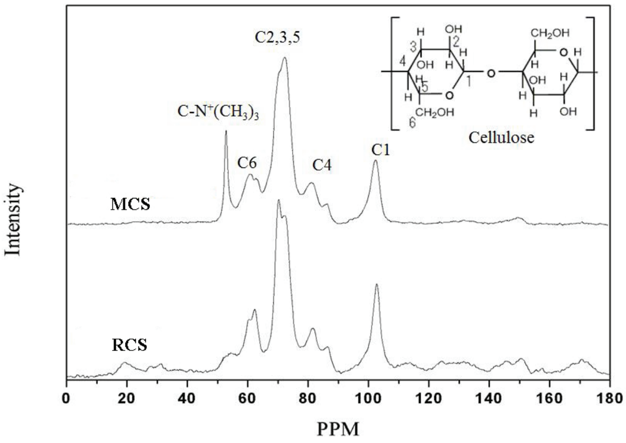

Fig. 3. ^{13}C NMR spectra of RCS and MCS.

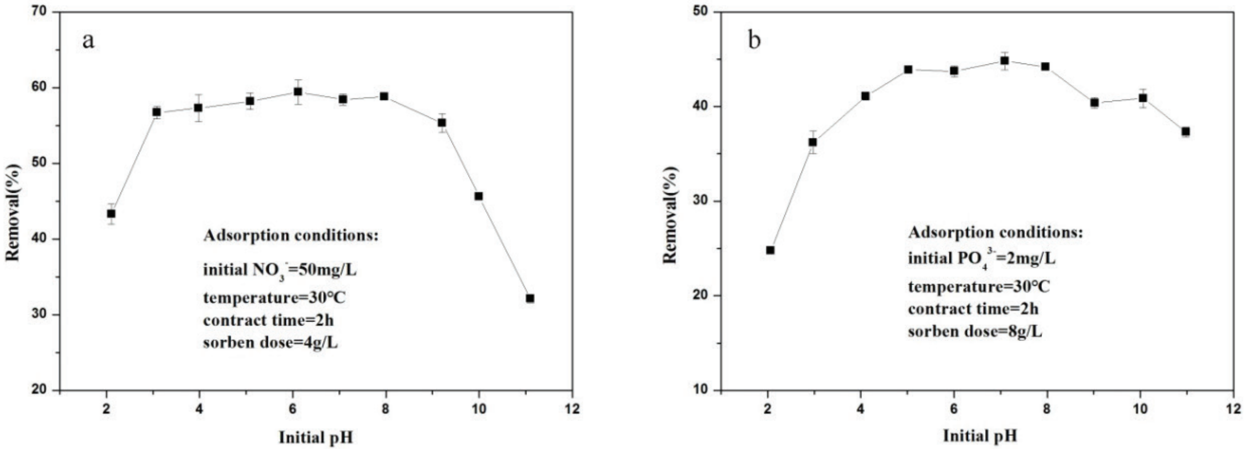

Fig. 4. Effect of initial pH on the adsorption of NO_3^- and PO_4^{3-} by MCS (a) NO_3^- and (b) PO_4^{3-}.

3.3. Removal of NO_3^-

3.3.1. Adsorption equilibrium and maximum adsorption capacity

The adsorption equilibrium for nitrate of MCS at different reaction temperature (10°C, 20°C and 30°C) is shown in Fig. 5, which indicated that the nitrate adsorption capacity increased when the temperature rose from 10°C to 30°C. This implied that the adsorption of NO_3^- onto MCS was an endothermic process and the capacity of adsorption was enhanced at higher temperature.

The data in Fig. 5 were fitted by the Freundlich and Langmuir isotherm model.

The Langmuir model is written as follows:

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

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

The Freundlich model is written as follows:

$$q_e = KC_e^{1/n} \tag{4}$$

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

The result is shown in Table 1. By comparison of correlation coefficient, we found that the Langmuir adsorption equation fitted better for the adsorption of NO_3^- onto MCS. Such result supported our hypothesis that the adsorption of NO_3^- by MCS was a monomolecular layer adsorption. The maximum adsorption capacities can be obtained from the parameter $Q_{\max}$ in the Langmuir adsorption model. The $Q_{\max}$ values for the adsorption of NO_3^- on MCS at 10°C, 20°C and 30°C were 17.9, 19.7 and 19.9 mg/g, respectively.

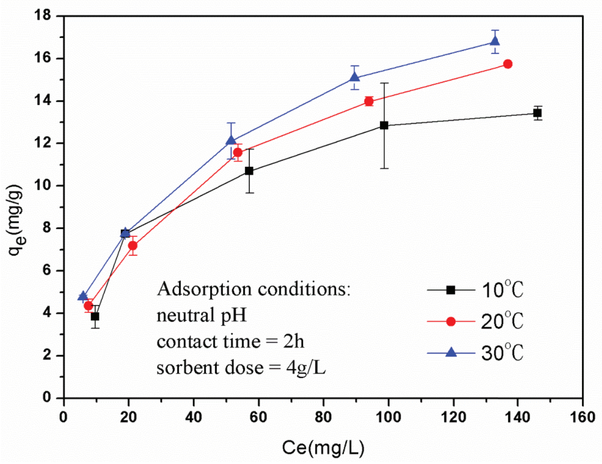

Fig. 5. Adsorption equilibrium for nitrate of MCS.

Table 1
Parameters of Langmuir and Freundlich adsorption models for NO_3^- adsorption at different temperature

T (°C)	Langmuir model			Freundlich model		
	$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K (mg/g)	n	R^2
10	17.9	0.030	0.976	1.74	2.32	0.904
20	19.7	0.043	0.995	1.80	2.22	0.913
30	19.9	0.033	0.999	2.32	2.43	0.907

3.3.2. Adsorption kinetics

The adsorption kinetics of nitrate of different initial concentration by MCS is shown in Fig. 6. The curves of the different initial concentration (25, 50, 100 mg/L) have similar trends. The curves can be divided into two phases. In the first 10 min, the slopes were sharp and most adsorption occurred quickly. The instantaneous increase of C_t may be attributed to the chemical sorption of nitrate by MCS. After 10 min, the increase slowed down until the adsorption reached equilibrium.

The data in Fig. 6 were fitted by the pseudo-first-order model and pseudo-second-order model. The pseudo-first-order rate expression is defined by Eq. (5) and the integrated form is given in Eq. (6).

$$\frac{dq_t}{dt} = k_{pl}(q_e - q_t) \tag{5}$$

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_{pl}}{2.303}t \tag{6}$$

The pseudo-second-order rate expression is defined by Eq. (7) and the integrated form is given in Eq. (8).

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{7}$$

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \tag{8}$$

where k_{p1} is the pseudo-first-order rate constant (min^{-1}), k is the pseudo-second-order rate constant (g/mg min), and q_e and q_t are the amount of nitrate adsorbed at equilibrium and at time t, respectively.

The result is shown in Table 2. The pseudo-first-order kinetics equation was not suitable for the whole process of adsorption. Only the adsorption data from the first 20 min can obtain a high correlation coefficient from 0.965 to 0.982. However, the amount of nitrate adsorbed at equilibrium ($q_{e,\mathrm{Cal}}$) calculated from the pseudo-first-order model was not conform to the experimental results ($q_{e,\mathrm{Exp}}$). Table 2 shows that this adsorption process accords with the pseudo-second-order reaction kinetic rate equation, it suggested that the adsorption rate is proportional to the square of the adsorption process driving force ($q_e - q_t$).

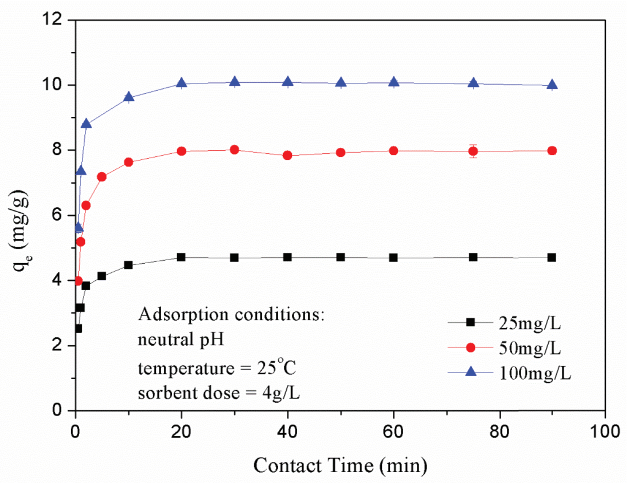

Fig. 6. Adsorption kinetics of nitrate of different initial concentration by MCS.

3.4. Removal of PO_4^{3-}

3.4.1. Adsorption equilibrium

Fig. 7 presents the experimental adsorption isotherm for phosphate removal when the initial concentration of phosphate was 2 mg/L at 30°C. The Langmuir and Freundlich isotherm models were used to describe the equilibrium data. The correlation coefficient obtained from the Langmuir and Freundlich equations were 0.994 and 0.979, respectively, indicating the equilibrium data agreed better with the Langmuir model than with Freundlich model. The values of $Q_{\max}$ and b were found to be 0.164 mg/g and 0.364 L/mg, respectively. The values of K and $1/n$ were found to be 0.0559 and 0.371, respectively.

3.4.2. Adsorption kinetics

The adsorption kinetics of phosphate of different initial concentration by MCS is shown in Fig. 8. The curves of the different initial concentration (2, 4 and 10 mg/L) have similar trends. The slopes were sharp and most adsorption occurred in the first 10 min, and after that it failed to exert an obvious change. The increase in PO_4^{3-} concentration from 2 to 4 mg/L leads to an obvious enhancement in the adsorption capacity (0.101–0.119 mg/g). However, when the initial PO_4^{3-} concentration was enhanced to 10 mg/L, only a small increase was observed in the uptake of phosphate. The most reasonable explanation was that the amount of adsorbed PO_4^{3-} was dependent on the number of active adsorption sites provided by MCS at high PO_4^{3-} concentration. Therefore, the equilibrium adsorption capacity cannot be infinitely increased with the increase of initial concentration of PO_4^{3-}.

The data in Fig. 8 were fitted by the pseudo-first-order model (data from the first 20 min) and pseudo-second-order model, which is shown in Table 3. The adsorption process accords with the pseudo-second-order reaction kinetic rate equation, it suggested that the phosphate adsorption rate was proportional to the square of the adsorption process driving force ($q_e - q_t$).

Table 2
Parameters of pseudo-first-order and pseudo-second-order kinetics for NO_3^- adsorption by MCS at different initial NO_3^- concentration

C_0 (mg/L)	$q_{e,\mathrm{Exp}}$ (mg/g)	Pseudo-first-order equation			Pseudo-second-order equation		
		$q_{e,\mathrm{Cal}}$ (mg/g)	k_{p1} (1/min)	R^2	$q_{e,\mathrm{Cal}}$ (mg/g)	k (g/(mg·min))	R^2
25	4.71	2.14	0.263	0.980	4.69	0.478	0.992
50	8.03	3.23	0.214	0.982	8.01	0.243	0.998
100	10.1	3.40	0.215	0.965	10.2	0.245	0.995

3.5. Competitive adsorption

The competitive adsorption of the co-existing anions from water by MCS is shown in Table 4. In the presence of other anions, the adsorption capacity of nitrate was reduced from 2.35 mg/g (separately) to 1.12 mg/g. The adsorption capacity of phosphate was reduced from 0.128 to 0.060 mg/g. Due to the competition for adsorption sites by other anions, the removal efficiency of nitrate and phosphate has decreased. Moreover, the concentration of chloride was increased after the competitive adsorption which attributed to that the corn straw was converted into chloride loaded form. The chloride loaded on the MCS exchanged with other anions in the solution in the process of adsorption. As a consequence, the MCS showed selectivity among the anions was in the following order: SO_4^{2-}> NO_3^-> PO_4^{3-}> Cl^-.

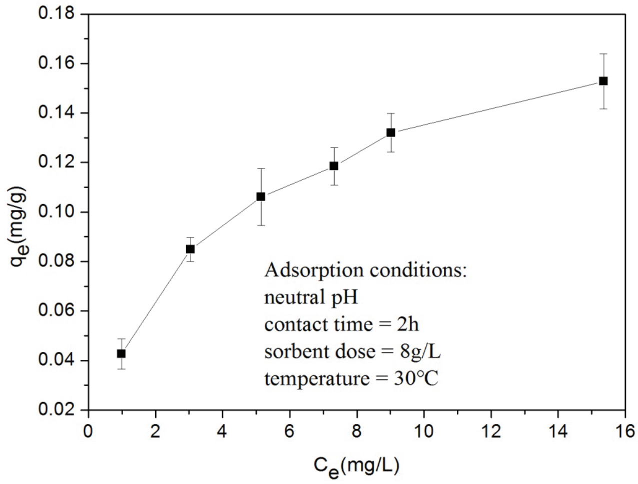

Fig. 7. Adsorption equilibrium for phosphate of MCS.

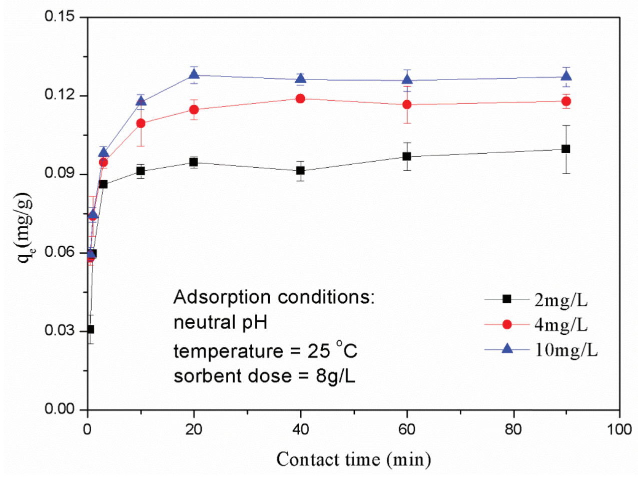

Fig. 8. Adsorption kinetics of phosphate of different initial concentration by MCS.

The effect of DOM on the adsorption of heavy metals by soil has been frequently reported. However, the effect on anion removal was rare. Wang et al. [34] showed that the effect of DOM on nitrate removal followed the trend: HA > gallic acid (GA) > tanic acid (TA). Since the order of electronegativities of these acid was HA > GA > TA, electrostatic interaction may be the dominant effect of DOM on the selective nitrate removal.

In the presence of DOM, the adsorption quantity reduced from 2.35 mg/g (separately) to 1.47 mg/g. At the same time the adsorption quantity reduced from 0.128 mg/g (separately) to 0.079 mg/g. The decrease in adsorption was probably caused by non-specific adsorption interactions between MCS, nitrate, phosphate and DOM.

3.6. Recovery of modified corn straw

The spent MCS was regenerated by using 0.1 M NaOH solution. In order to investigate the reusability of MCS, the regeneration was repeated three times. As shown in Fig. 9, after three cycles, the nitrate adsorption capacity of MCS was decreased by about 14% (from 8.02 mg/g at the first cycle to 6.93 mg/g at the end). This result showed that MCS could be successfully regenerated by NaOH solution with small loss in adsorption capacity, which makes the exchanger applicable for a continuous adsorption process. The small amount of nitrate that was not recovered from the spent MCS represents the nitrate that was bound to adsorbent through strong interactions, and as a result, the

Table 4
Competitive adsorption of the co-existing anions from water by MCS

Anions	C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	q (mg/g)[a]
NO_3^-	10.0	5.52	1.12	2.35
PO_4^{3-}	10.0	9.76	0.060	0.128
SO_4^{2-}	10.0	5.35	1.16	–
Cl^-	10.0	14.4	–	–

[a] The adsorption capacity of nitrate or phosphate separately.

Table 3
Parameters of pseudo-first-order and pseudo-second-order kinetics for PO_4^{3-} adsorption by MCS at different initial PO_4^{3-} concentration

C_0 (mg/L)	$q_{e,\mathrm{Exp}}$ (mg/g)	Pseudo-first-order equation			Pseudo-second-order equation		
		$q_{e,\mathrm{Cal}}$ (mg/g)	k_{p1} (1/min)	R^2	$q_{e,\mathrm{Cal}}$ (mg/g)	k (g/(mg·min))	R^2
2	0.101	0.0387	0.111	0.751	0.105	8.59	0.955
4	0.119	0.0478	0.119	0.923	0.116	16.6	0.991
10	0.128	0.0657	0.171	0.992	0.123	14.5	0.980

decrease in adsorption capacity was observed in the regeneration cycles.

3.7. Comparison with other adsorbents

Comparison between the MCS and other adsorbents and commercial anion exchangers were summarized and listed in Table 5. MCSs adsorption capacity of nitrate was higher than activated carbon and anion exchange resin Purolite A 520E [35,36]. Adsorption capacity in this study was slightly lower than other techniques listed in Table 5, but the costs of other adsorbents were 4–14 times more expensive than MCS. In addition, most of the modification of agricultural residues were followed the method reported by Orlando et al. [10], which used DMF and pyridine as solvent and catalyst. Both DMF and pyridine are highly toxic and may pose environmental risk to human beings. In contrast, the materials in this study were environmentally friendly.

3.8. Adsorption mechanism

The adsorption of nitrate and phosphate by MCS was greatly affected by the introduction of quaternary amino groups. FTIR and ^{13}C NMR analysis indicated the presence of quaternary amine groups. The quaternary amino groups showed electropositive and adsorbed anions by electrostatic attractions. In the modification process, we have converted the corn straw into chloride loaded form. The chloride loaded on the MCS exchanged with other anions in the solution in the process of adsorption.

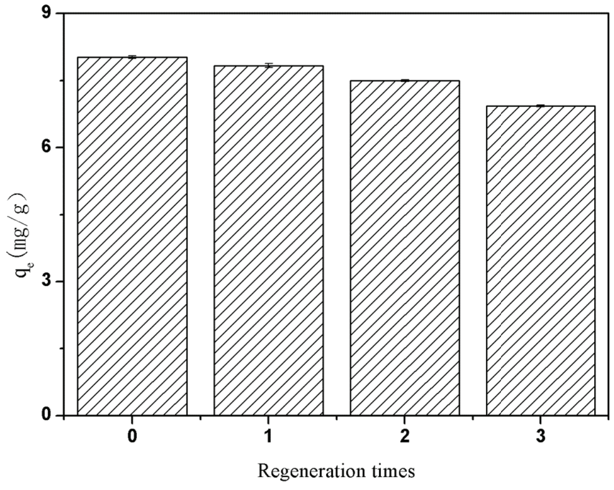

Fig. 9. Recovery of modified corn straw.

At the same time, through physical broken and chemical modifications, the MCS have lager specific surface area and can provide more adsorption sites. SEM micrographs showed that the structure in corn straw was well exposed. Besides, the TEC of MCS was 1.37 mEq/g, indicating that the TEC of corn straw after treatments was greatly increased.

4. Conclusion

MCS derived from corn straw could effectively remove NO_3^- and PO_4^{3-} from aqueous solution. The TEC and SEM micrographs showed that the MCS have larger relative surface than RCS. FTIR and ^{13}C NMR analysis indicated the quaternary amino groups were successfully introduced on the corn straw. The adsorption capacity of NO_3^- and PO_4^{3-} by the sorbent is fast, and it is dependent to pH values in solution. The adsorption isotherms were better fitted with the Langmuir model than with Freundlich models. The maximum adsorption capacities of NO_3^- and PO_4^{3-} at neutral pH were 19.9 and 0.164 mg/g while the reaction temperature was 30°C. The absorption process obeys the pseudo-second-order reaction kinetic rate equation, suggesting that the nitrate and phosphate adsorption rate are both proportional to the square of the adsorption process driving force ($q_e - q_t$). After three recovery cycles, the nitrate adsorption capacity of MCS was only decreased by about 14%.

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Table 5
Comparison of MCS with other anion sorbents

Materials	Q_{max} (mg/g)	Cost ($/kg)	Reference
Rice hull	81.8 (nitrate)	83.2	Orlando et al. [10]
Banana peel	62.7 (phosphate)	25.5	Anirudhan et al. [37]
Corn straw	73.08 (chromate)	39.9	Wartelle and Marshall [38]
Amberlite IRA-900	74.4 (nitrate)	111.7	Orlando et al. [9]
Purolite A 520E	10.9 (nitrate)	4.34	Song et al. [35]
Activated carbon	0.84–1.73 (nitrate)	1–3	Mahmudov and Huang [36]
MCS	19.9 (nitrate) 0.164 (phosphate)	6.06	This study

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