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Uptake of perchlorate from aqueous solutions by amine-crosslinked cotton stalk

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ABSTRACT

Virgin cotton stalk was produced into an effective biosorbent for perchlorate adsorption. Surface analysis including BET surface area and SEM illustrated the reduction of porous structure in amine-crosslinked cotton stalk (AC-CS). Elemental and zeta potential analysis validated the graft of some positively charged amine groups on surface of AC-CS. Spectra analysis (XPS, FTIR and Raman spectra) suggested that interaction between AC-CS and ClO_4^- should be based on electrostatic attraction. The maximum adsorption capacity (q_{max}) of AC-CS for perchlorate at different pHs (3.0, 6.0, 9.0 and 11.0) were calculated as 29.6, 42.6, 41.0 and 33.0 mg/g, respectively. The saturated perchlorate uptakes in column were in range of 25.0–38.1 mg/g at different pHs. In addition, the exhausted AC-CS column was regenerated by 0.5 mol/L of NaCl solution, which was adequate for almost complete desorption of the perchlorate.

1. Introduction

Perchlorate (ClO_4^-) was widely used in manufactures of rocket propellants, fireworks, weapons, automobile airbags, batteries and analytical chemistry products (Tan et al., 2012; Yoon, Meng, et al., 2009). The major sources of perchlorate pollution are linked to military use, because of its rich oxygen content and highly oxidized form of chlorine (Atikovic, Suidan, & Maloney, 2008; Kucharzyk, Crawford, Cosens, & Hess, 2009). As an emergent environmental contaminant, perchlorate has been detected in soil, public groundwater and surface water systems. This form of contamination has been reported at numerous locations in Unites States, China and some other countries (Kosaka, Asami, Matsuoka, Kamoshita, & Kunikane, 2007; Theodorakis et al., 2006; Tikkanen, 2006). Perchlorate has also been detected in plants; food products, cow's milk and human breast milk (Yoon, Meng, et al., 2009). Perchlorate is of concern because it can inhibit the iodide uptake by the thyroid gland and therefore, the presence of perchlorate in drinking water can cause thyroid ailments as well as other medical problems (Tan et al., 2012). USEPA included perchlorate in the Contaminants Candidate List (CCL) with a reference dose of 0.7 μg/kg/day; this corresponds to the equivalent level of 24.5 μg/L in drinking water. As a result, a new drinking water standard of 24.5 μg/L for perchlorate was adopted in 2005.

Perchlorate, although thermodynamically unstable, is kinetically non-reactive at the low concentrations typically found in contaminated ground and surface water. In addition, perchlorate salts have high solubility and low tendency to form complexes in water. So perchlorate is a bit difficult to be removed from water.

Many technologies including biological and chemical reduction, adsorption, electrochemical reduction, membrane filtration and integrated technologies have been applied for perchlorate (Baidas, Gao, & Meng, 2011; Lee et al., 2008, 2011; Song & Logan, 2004; Tan et al., 2012; Wang, Lippincott, & Meng, 2008; Ye, You, Yao, & Su, 2012; Yoon, Meng, et al., 2009; Yoon, Amy, et al., 2009). Perchlorate treatment using biological and chemical reduction is currently being practiced but they have some disadvantages such as the low reaction rate, sensitivity to pH, temperature and salinity changes as well as introduction of metals with chemical treatment (Baidas et al., 2011; Tan et al., 2012; Ye et al., 2012). Membrane filtration using reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membranes plays an important role in removing perchlorate from drinking water. However, this technology has a big hindrance to its application in large scale system; perchlorate is just removed from one stream to another stream, the reject stream needing further treatment (Ye et al., 2012; Yoon, Meng, et al., 2009; Yoon, Amy, et al., 2009). Electrodialysis may be more effective than conventional membrane filtration for perchlorate but its operation costs are very high. Adsorption technology is widely used for water treatment due to its simplicity, high capacity, and capability of operating at a relatively high flow rate with a small treatment unit (Ye et al., 2012). However, in spite of the good affinity toward perchlorate,

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a major problem of adsorption is its cost. Another challenge associated with using adsorption technology is regeneration of spent resins since perchlorate on most anion exchange resins is difficult to displace with chloride (Baidas et al., 2011).

In this research, perchlorate was removed from aqueous solution by cotton stalk based biosorbent. The cotton stalk based biosorbent was prepared by introducing some amine groups onto cotton stalk, forming the amine-crosslinked cotton stalk (AC-CS). Physicochemical properties of AC-CS were elucidated by the Raman spectra, FTIR, X-ray photoelectron spectroscopy (XPS), elemental analysis, SEM, BET surface area analysis and zeta potential analysis. Maximum adsorption capacity (q_{max}) of AC-CS for perchlorate was evaluated after isotherm tests. In addition, a fixed-bed column with length of 20 cm and diameter of 1.2 cm was employed for column adsorption and desorption tests.

2. Materials and methods

2.1. Characteristics of AC-CS

AC-CS was prepared as our previous method in a lab-scale system with chemical composition as $-CH_2CHOHCH_2NHCH_2CH_2NHCH_2OHCHCH_2N(CH_2CH_2)_3{}^+Cl^-$ (Xu, Gao, Yue, Zhong, & Zhan, 2010; Xu, Gao, Tang, et al., 2011). The compositions of cellulose, hemicellulose and lignin in virgin cotton stalk are about 23.6%, 25.9% and 25.3%; the high content of holocellulose (including cellulose and hemicellulose) made it easy for cross-linking reaction. Ten grams of virgin cotton stalk was mixed with 20 mL of epichlorohydrin and 15 mL of N,N-dimethylformamide in a 500 mL three-neck round bottom flask at 85 °C for 60 min. An aliquot of 5 mL of ethylenediamine was added by dropwise and the solution was stirred for 45 min at 85 °C. Thereafter, 15 mL of 99% triethylamine (w/w) was added and the mixture was stirred for 120 min at 85 °C. The product was washed with some distilled water, dried at 60 °C for 12 h and then used in all the subsequent experiments.

Physicochemical properties of AC-CS, virgin cotton stalk as well as perchlorate loaded AC-CS were measured by the BET surface area analysis, elemental analysis, SEM, zeta potential analysis, Raman spectra, FTIR and XPS.

Specific surface area of AC-CS and virgin cotton stalk were measured with an automatic BET surface area analyzer (Model F-Sorb 2400, Beijing Jinaipu Technical Apparatus Co., Ltd., China). The detection limit of this instrument is 0.01 m^2/g (N_2). SEM micrographs of the three samples (virgin cotton stalk, AC-CS and perchlorate loaded AC-CS) were obtained by JEOL JSM-6480LV scanning electron microscope. The samples were coated with platinum before the SEM micrograph was obtained. The grafted amine groups in the AC-CS were evaluated by element analyzer (Elementar Vario EL III, Germany).

In the Raman analysis, AC-CS (0.1 g) was placed in 50 mL of perchlorate solution (10 g/L) and stirred for 24 h. The AC-CS, perchlorate loaded sample and perchlorate solution (10 g/L) were analyzed by Raman spectroscopy (Nicolet Almega XR Dispersive Raman, Thermo Electron Corporation, USA). The laser wavelength used in Raman measurement was 1050 nm.

The surface binding state and elemental speciation of virgin cotton stalk, AC-CS and perchlorate loaded AC-CS were analyzed by XPS. The measurements were performed by a spectrometer (ESCALAB 250) with Mg$K\alpha$ irradiation (1486.71 eV of photons) as X-ray source. The perchlorate loaded AC-CS was prepared by mixing AC-CS (0.1 g) with 50 mL of perchlorate solution (1000 mg/L) for 24 h.

The functional groups in virgin cotton stalk, AC-CS and perchlorate loaded AC-CS were investigated by using the FTIR technique (Perkin-Elmer "Spectrum BX" spectrometer). The spectrum was scanned from 400 to 4000 cm^{-1}. The saturated sample was prepared by mixing the adsorbent with solution containing 1000 mg/L of perchlorate.

A microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) was used to determine the zeta potentials of AC-CS and virgin cotton stalk. The AC-CS or virgin cotton stalk samples were prepared in 25 mL of distilled water containing 0.1 g of samples and shaken for 15 min at 20 °C. In addition, the perchlorate loaded AC-CS samples were prepared by maintaining the suspensions contained with 0.1 g of AC-CS and 100 mg/L perchlorate.

2.2. Isotherm, column adsorption and desorption tests

Isotherm tests were performed to determine the q_{max} for perchlorate at different pH conditions. The saturated uptake of perchlorate in column was determined in batch fixed-bed column tests. The results were evaluated by the Thomas model so as the maximum column adsorption data (q_0) were calculated and compared with the q_{max} obtained in isotherm tests. Thereafter, regeneration of the spent AC-CS was conducted in the column by eluting NaCl (0.5 mol/L) solution.

In the isotherm tests, AC-CS (0.1 g) was mixed with 50 mL of solutions in 125 mL Erlenmeyer flasks containing different concentrations of perchlorate. The suspensions were stirred for 6 h and the pH values were monitored at 3.0, 6.0, 9.0 and 11.0. After adsorption, the equilibrium pH was obtained at 3.4, 5.2, 5.8 and 7.1.

A fixed-bed column with 200 mm length and 12 mm diameter was used in the column adsorption/desorption tests. The bed depth of AC-CS in the column is 2.4 cm (AC-CS weight: 1.0 g) with flow rate of 10 ml/min and influent perchlorate concentration of 100 mg/L. Four sets of experiments were conducted to evaluate the effect of influent pH (3.0, 6.0, 9.0 and 11.0) on perchlorate adsorption. The effluent solutions were collected, and every 10 ml was selected as a sample to determine the residual concentrations in the effluent solutions. The saturated column adsorption capacity (q_{ed}) was calculated by the Eq. (1) expressed as:

$$q_{ed} = \frac{9C_0V_0 - \sum c_n v_n}{m} \quad (1)$$

where q_{ed} is the amount of perchlorate per gram AC-CS at saturation (mg/g), c_0 is the original concentration of perchlorate (mg/L), V_0 is the total volume of the influent solutions (L), c_n is the concentration of sample n (mg/L), and v_n is the volume of sample n (L), m is the amount of AC-CS (g).

Regeneration of the AC-CS was achieved by eluting NaCl (0.5 mol/L) solution through the exhausted column (from top to bottom) with flow rate 10 ml/min. The eluted perchlorate and regeneration capacities were calculated.

3. Results and discussion

3.1. Characteristics of AC-CS

3.1.1. BET surface area and elemental analysis

The elemental compositions and surface area of AC-CS and virgin cotton stalk are listed in Table 1. The virgin cotton stalk contained large numbers of C (41.34%), O (44.56%), H (6.70%) element and little N (0.32%) element. After the amine crosslinking reaction, an extent of amine groups was grafted on the framework of holocellulose so as N element (3.24%) in AC-CS was increased. As expected, the BET specific surface areas of AC-CS and virgin cotton stalk was quite small with a range of 4.56–8.82 m^2/g; this was consistent with our previous work (Xu, Gao, Tang, et al., 2011; Xu, Gao, Gao, et al., 2011) as well as the results reported by Chergui, Kerbachi,

Table 1
Elemental compositions and surface area of AC-CS and virgin cotton stalk.

Biosorbent	Specific surface area (m^2/g)	Micropore volume (cm^3/g)	Elemental compositions (%)			
			C	O	H	N
Virgin cotton stalk	8.82	0.947	42.34	48.46	8.16	0.32
AC-CS	4.56	0.768	41.09	47.48	7.14	3.74

and Junter (2009) and Namasivayam and Sureshkumar (2008). The BET specific surface area of AC-CS was decreased as compared with that of virgin cotton stalk; it may be ascribed to the amine reactions occurred on surface of virgin cotton stalk, leading to a constriction of pore channels in internal framework of AC-CS. This result was also validated by the decreased micropore volume in AC-CS (0.768 cm^3/g) as compared with that in virgin cotton stalk (0.947 cm^3/g).

3.1.2. Zeta potential analysis

Zeta potentials of virgin cotton stalk, AC-CS and perchlorate loaded AC-CS as a function of pH was shown in Fig. 1. Zeta potentials of all selected samples were decreased as increase in pHs. The pH-dependent functional groups, such as hydroxyl and carboxyl groups, were the basic groups in these samples. These pH-dependent groups exhibited a greater negative charge at higher pH range, resulting in the decrease in the zeta potentials. The zeta potentials of AC-CS were in range of +34.6 to −19.4 mV at different pHs (3.0–11.0), extremely higher than those of virgin cotton stalk (+2.1 to −43.2 mV); this indicated the incorporation of cross-linked amine groups into virgin cotton stalk increased the surface potential of AC-CS.

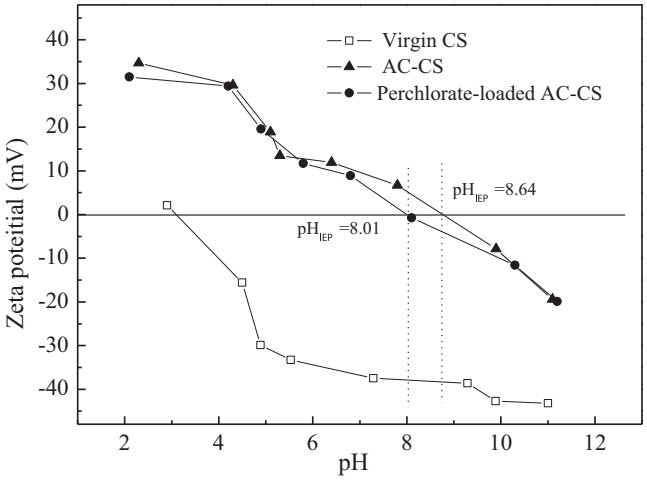

Fig. 1. Zeta potentials of CS, AC-CS and perchlorate-loaded AC-CS as a function of pH.

Addition of perchlorate was found to cause a gradual decrease in zeta potentials of AC-CS (Fig. 1). It was suggested by Baidas that the decrease was the result of neutralization of the positive functional groups by adsorbed perchlorate (Baidas et al., 2011). The point of zero charge pH (pH_{PZC}) of perchlorate loaded AC-CS was located at 8.01, slightly lower than that of clean AC-CS (8.67). An insignificant shift (less than 0.7 pH units) observed in the pH_{PZC} value between perchlorate loaded AC-CS and clean AC-CS suggested that interactions between AC-CS and ClO_4^- were largely electrostatic attraction (Baidas et al., 2011). These findings are in agreement with published data (Baidas et al., 2011; Xu et al., 2010; Xu, Gao, Tang, et al., 2011; Yoon, Meng, et al., 2009).

3.1.3. SEM analysis

SEM observations were carried out to elucidate the surface morphology of virgin cotton stalk and clean AC-CS. An SEM micrograph of virgin cotton stalk was shown in Fig. 2(a), and indicated the fibrous structure of the biomass. After the modifying procedure, almost all ash and extractives were removed so as the surface of AC-CS got smooth; in addition to this, no porous structures were observed on this surface. This phenomenon validated the results obtained by BET surface area tests, which showed the decrease trend of specific surface area and micropore volume.

This structural feature of AC-CS may be important because it illustrated the absence of porous adsorption in potential adsorption mechanism. SEM photograph was also obtained for AC-CS after biosorption procedure with perchlorate (Fig. 2c). No remarkable difference was observed on surface of perchlorate-loaded biosorbent.

3.1.4. FTIR analysis

FTIR spectra of virgin cotton stalk, clean AC-CS and perchlorate loaded AC-CS were shown in Fig. 3. In FTIR spectra of virgin cotton stalk and clean AC-CS, the predominant peaks at 3418.96 and 3405.29 cm^{-1} was assigned to hydroxyl groups (—OH) of macromolecular association in cellulose, hemicellulose, pectin, etc. (Ofomaja & Naidoo, 2010; Reddy, Seshaiah, Reddy, & Lee, 2012).

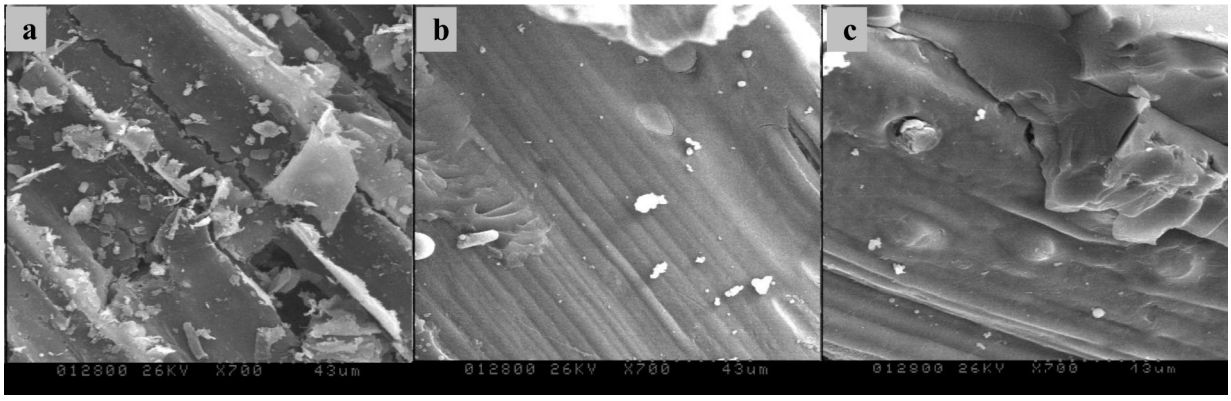

Fig. 2. SEM of virgin cotton stalk (a), clean AC-CS (b) and perchlorate loaded AC-CS (c).

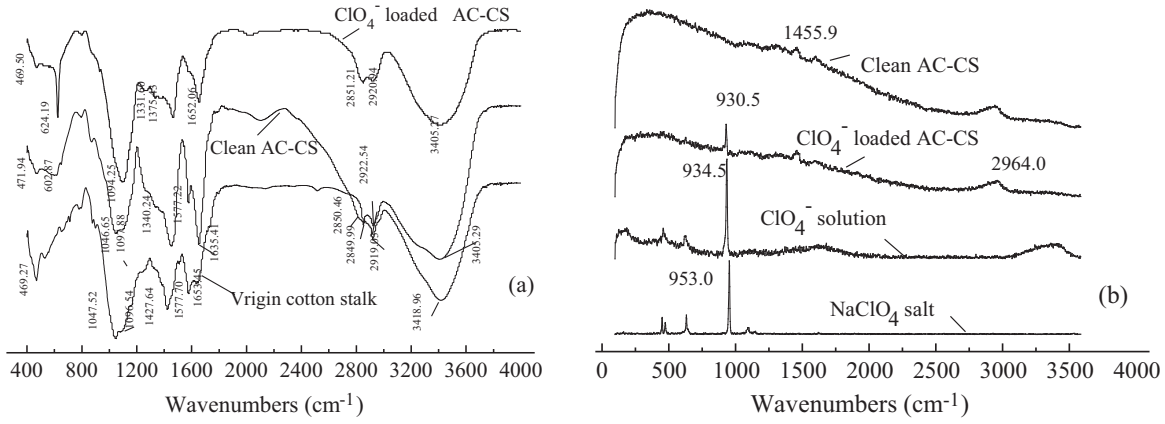

Fig. 3. FTIR (a) and Raman spectra (b) of selected samples.

Two bands in the region of 2940 and 2860 cm^{-1} were assigned to the symmetrical and asymmetrical —CH— vibrations. The adsorption bond at the location 1040–1100 cm^{-1} corresponded to the —COC— group vibrations in the cyclic structures of carbohydrates. After modification, the appearance of band at 602.87 cm^{-1} corresponded to the stretching vibration of the C—Cl bond, which was obtained from the grafted chemical reagent of epichlorohydrin. The new but insignificant bands between 1340.24 and 1380.0 cm^{-1} were observed in spectrum of clean AC-CS corresponding to the —CN stretching vibrations; this was in accordance with the work of Sundaraganesan, who reported the C—N stretching vibrations in the region 1334–1453 cm^{-1} (Sundaraganesan, Kalaichelvan, Meganathan, Joshua, & Cornard, 2008).

After adsorption of perchlorate onto AC-CS, the special vibration at 602.87 cm^{-1} disappeared. In contrast, an intense peak at 624.19 cm^{-1} was observed in spectrum of perchlorate loaded AC-CS which was absent in the spectrum of clean AC-CS. This might be ascribed to the adsorbed perchlorate replacing the Cl^- on surface of biosorbent.

3.1.5. Raman spectra

Interactions between perchlorate and AC-CS were evaluated by the Raman spectra of aqueous and solid forms of perchlorate. Raman spectra of solid sodium perchlorate and aqueous perchlorate were shown in Fig. 3b. The Raman peak of solid sodium perchlorate was detected at 953.0 cm^{-1}; this was in accordance with the perchlorate peak (951 cm^{-1}) in $NaClO_4$ salt observed by Yoon, Meng, et al. (2009). Selvasekarapandian et al. also reported the perchlorate peak of 945 cm^{-1} for salt of $LiClO_4$ and our groups detected a peak at 941 cm^{-1} in $KClO_4$ salt (Selvasekarapandian, Baskaran, Kamishima, Kawamura, & Hattori, 2006; Tan et al., 2012). These peaks for solid perchlorate salts corresponded to ($Na^+\cdots ClO_4\cdots Na^+$, $Li^+\cdots ClO_4^-\cdots Li^+$ and $K^+\cdots ClO_4^-\cdots K^+$) trimers, tetramers, or higher-order structures (Selvasekarapandian et al., 2006; Tan et al., 2012; Yoon, Meng, et al., 2009). A Raman peak for 10 g/L $NaClO_4$ solution occurred at 934.5 cm^{-1}, ascribed to the strong Cl—O bonds of the tetrahedral perchlorate ions (Yoon, Meng, et al., 2009).

Raman spectra of perchlorate loaded AC-CS and clean AC-CS indicated the characteristic peaks of AC-CS at 1455.9 and 2964.0 cm^{-1} (Fig. 3b). Additionally, a new peak at 930.5 cm^{-1} was observed in Raman spectrum of perchlorate loaded AC-CS as compared with that of clean AC-CS; this confirmed the adsorbed perchlorate on surface of AC-CS. The same band position of the soluble (934.5 cm^{-1}) and adsorbed perchlorate (930.5 cm^{-1}) was ascribed to the symmetric (ν_1) vibration of the perchlorate anion (Selvasekarapandian et al., 2006; Yoon, Meng, et al., 2009). The ν_1 symmetric stretching mode of the anion was sensitive to ion association and ion–ion interaction; this indicated that the adsorbed perchlorate was existed as free anions on surface of AC-CS. As a result, perchlorate adsorbed onto the AC-CS was suggested through electrostatic attraction between the perchlorate ions and the positively cross-linked amine groups.

3.1.6. XPS analysis

The XPS analyses of virgin CS, clean AC-CS and perchlorate loaded AC-CS were performed (Fig. 4). The N1s spectrum of the clean AC-CS surface can be curve-fitted with two peak components. The dominant peak component at the binding energy of 399.0 eV was assigned to the nitrogen atoms in neutral amine (—N). The minor peak at the binding energy of 401.8 eV was attributed to positively charged nitrogen in protonated amine ($—N^+$) (Wei, Zheng, & Paul Chen, 2011; Yu, Kang, & Neoh, 2004). The new peak at 197 eV was ascribed to the Cl^- binging with $N^+(CH_2CH_3)_3$ groups (Fig. 4d). After adsorption with perchlorate, an obvious peak at 208 eV was observed in Cl2p photoelectron spectrum of perchlorate loaded AC-CS (Fig. 4e), indicating strong attachment of perchlorate onto the surface of biosorbent. The ratio of $—N^+$ to —N was 0.78 on spectrum of AC-CS (Fig. 4b), and it was decreased to 0.25 (Fig. 4c) after adsorption of perchlorate; this result indicated that the tertiary amine group played the main role in uptake of perchlorate by electrostatic attraction.

3.2. Isotherm, column adsorption and desorption tests

3.2.1. Isotherm tests

In this work adsorption isotherms are represented by a q_e *vs* C_e plot, where C_e is the perchlorate concentration at equilibrium (mg/L) and q_e is the adsorption capacity, expressed as the mass of adsorbed perchlorate per mass unit of AC-CS (mg/g). Langmuir isotherm model was analyzed in order to achieve the q_{max} of perchlorate by AC-CS. Langmuir model was developed on the assumption that a single specie of the sorbate will adsorb on the sorbent in a monolayer to homogeneous adsorption sites. It can be expressed using Eq. (2).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{maw}K_L}\right)\frac{1}{C_e} \quad (2)$$

where q_{max} is the monolayer capacity of the sorbent (mg/g); K_L is the Langmuir constant (L/mg).

The q_e *vs* C_e as a function of pH was shown in Fig. 5a, where curves fitted with Langmuir model was represented. The q_e was increased as the pH increased from 3.0 to 6.0 and then the q_e almost kept constant at pH range of 6.0–9.0; thereafter, the q_e was

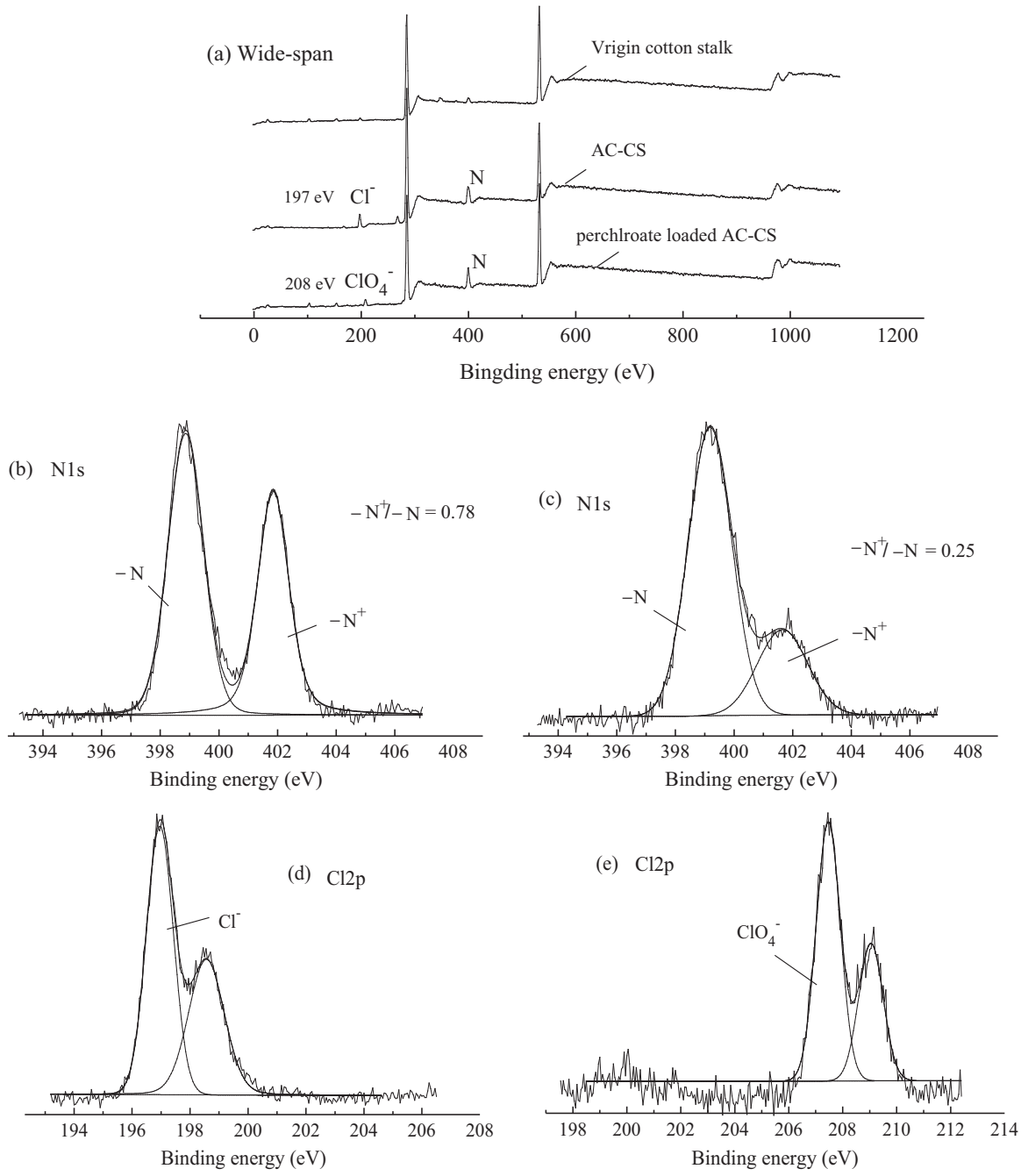

Fig. 4. XPS of (a) wide-scan of virgin CS, clean AC-CS and perchlorate loaded AC-CS; (b) N1s of clean AC-CS; (c) N1s of perchlorate loaded AC-CS; (d) Cl2p of clean AC-CS; (e) Cl2p of perchlorate loaded AC-CS.

decreased with the further increase in pH. As shown in Fig. 5a, the Langmuir isotherm provided a good fit with a high coefficient of determination ($R^2 > 0.982$) for all pH conditions. Parameters obtained for the regression of Langmuir adsorption model were summarized in Table 2. The Langmuir equilibrium constants (K_L) increased with increase in pH. Although the Langmuir model did not provide any mechanistic understanding of the adsorption phenomena, the model was conveniently used to estimate the

Table 2
Parameters obtained by Langmuir model (a) and Thomas model (b).

pH	Langmuir model (isotherm adsorption)				Thomas model (column adsorption)			
	Q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_{TH} (mL/min mg)	q_0[a] (mg/g)	q_{ed}[b] (mg/g)	R_2
3.0	29.6	0.040	<0.71	0.982	2.79	23.9	25.0	0.984
6.0	42.6	0.045	<0.69	0.983	2.06	39.2	38.1	0.988
9.0	41.0	0.049	<0.67	0.997	2.24	36.0	36.9	0.993
11.0	33.0	0.060	<0.63	0.991	2.46	28.8	28.5	0.995

[a] Predicted data.
[b] Experimental data.

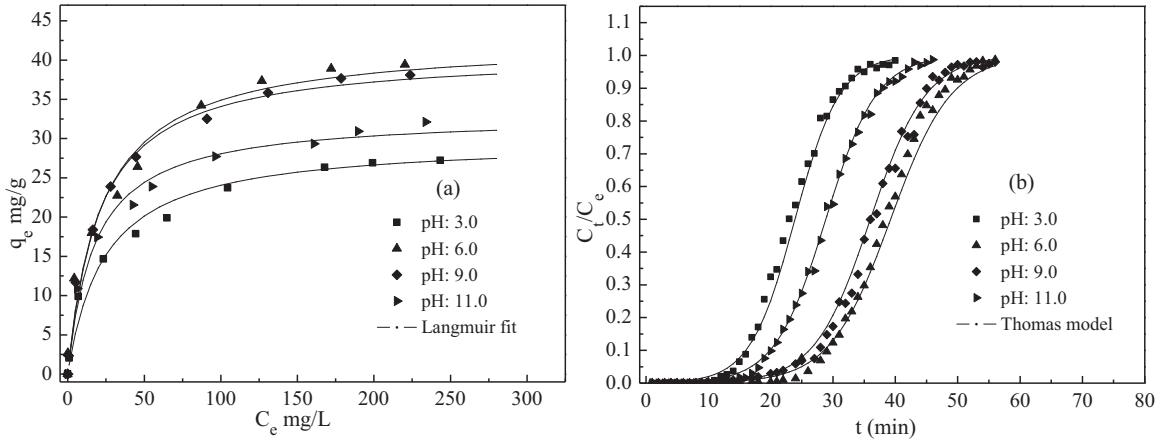

Fig. 5. The pH effect on isotherm (a) and column adsorption (b) (a, temperature: 20 °C; dosage: 2 g/L) (b, temperature: 20 °C; flow rate: 10 ml/min, perchlorate concentration: 100 mg/L, mass of AC-CS: 1.0 g).

maximum perchlorate uptake from the experimental data. As shown in Table 2, the q_{max} at different pHs (3.0, 6.0, 9.0 and 11.0) were calculated as 29.6, 42.6, 41.0 and 33.0, respectively (capacity of virgin cotton stalk for perchlorate was <1 mg/g). The q_{max} of perchlorate onto AC-CS at pH 6.0–9.0 was 1.3–1.4 times higher that at pH 3.0; this indicated that a neutral or weakly alkaline condition was optimal for the adsorption procedure.

After adsorption, the equilibrium pH was obtained at 3.4, 5.2, 5.8 and 7.1. It showed a neutral trend for all the pH values after adsorption of perchlorate by AC-CS; this will be beneficial to the improvement of effluent pH for basic wastewaters.

The essential feature of the Langmuir isotherm can be expressed by means of a dimensionless constant separation factor or equilibrium parameter R_L, which is calculated using Eq. (3).

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where C_0 is initial concentration (mg/L). The values of R_L calculated as above equation are incorporated in Table 2. The R_L values obtained at all pH conditions were in the range of 0–1, which confirmed the favorable uptake of perchlorate by AC-CS.

3.2.2. Column adsorption

The appropriate design of column requires a good prediction of the breakthrough curve for the effluent. Thomas equation is one of the most general models that are often used to describe the performance theory of the adsorption process in fixed-bed column. This model assumes that adsorption process follows Langmuir kinetics of adsorption–desorption and also obeys second-order reversible reaction kinetics (Futalan, Kan, Dalida, Pascua, & Wan, 2011; Kavianinia, Plieger, Kandile, & Harding, 2012). The linearized form of Thomas model is ascribed as:

$$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} q_0 m}{Q} - K_{Th} C_0 t \tag{4}$$

where k_{Th} (mL/min mg) is the Thomas rate constant, q_0 is the maximum solid phase concentration (mg/g), m is the mass of AC-CS (g) and Q is the flow rate of solution (mL/min).

Perchlorate uptakes by AC-CS at different influent pH were shown in Fig. 5b. The saturated perchlorate uptakes in column (q_{ed}) were 25.0 (pH 3.0), 38.1 (pH 6.0), 36.9 (pH 9.0) and 28.5 (pH 11.0) mg/g. It was apparent that the perchlorate adsorption capacity was optimum at neutral condition, and decreased at acidic and alkalic influents.

The predicted curves fitted by Thomas model were also shown in Fig. 5b. The column adsorption procedure corresponded well to the Thomas model (Table 2). It was observed that the q_0 predicted by the Thomas model were 23.9, 39.2, 36.0 and 28.8 mg/g at pH 3.0, 6.0, 9.0 and 11.0, respectively; they were very close to the experimental data (25.0, 38.1, 36.9 and 28.5 mg/g) with coefficient parameters (R^2) between 0.984 and 0.997. The Thomas rate constant obtained at different influent pH (3.0, 6.0, 8.0 and 11.0) were 2.79, 2.04, 2.24 and 2.46, respectively.

3.2.3. Desorption procedure in column

A desorption test was carried out to evaluate the feasibility of regenerating the exhausted AC-CS column. The perchlorate concentrations in the effluent elution solutions as well as the desorption capacities were determined. For each adsorption–desorption procedure, the pH of the influent perchlorate solution was constant at 6.0 and eluent (0.5 mol/L of NaCl solution) was conducted at 10 ml/min.

The elution curves from cycles 1–4 showed a very similar unsymmetrical shape, with a rapid perchlorate concentration increased, followed by a flatter diminution (figure was not given). As shown in Fig. 6, the perchlorate capacity of AC-CS in column was about 38.3 mg/g after one adsorption–desorption cycle, even higher than the original capacity (38.1 mg/g). After 4 cycles of adsorption–desorption, the capacities were decreased to 97%; this result indicated that NaCl solution was adequate for almost complete desorption of the perchlorate. It was suggested that desorption of perchlorate ions from the AC-CS was most probably through an reaction of ion exchange, i.e., the reverse of the reaction

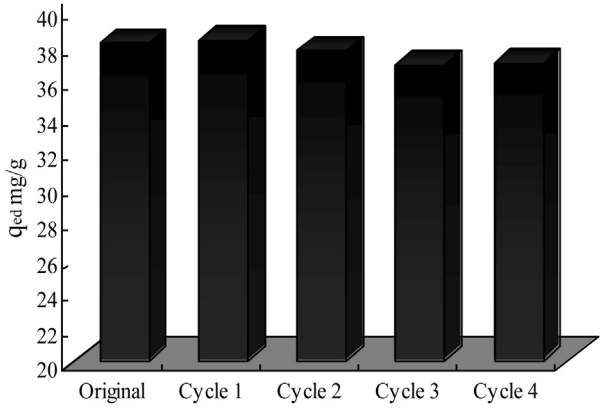

Fig. 6. Adsorption capacity of AC-CS for perchlorate during 4 cycles of desorption–adsorption.

with Cl^- from the NaCl solution displacing perchlorate ions from the cross-linked amine groups.

4. Conclusion

A new amine-crosslinked biosorbent was prepared from cotton stalk after amination reaction. Surface analysis (BET surface area analysis, elemental analysis, SEM, zeta potential analysis) indicated large amounts of amine groups were grafted on surface of AC-CS. BET surface area and micropore volume of AC-CS were decreased as compared with virgin cotton stalk due to the constriction of pore channels in internal framework of AC-CS. Spectra analysis (XPS, FTIR and Raman spectra) suggested that interactions between AC-CS and ClO_4^- were largely electrostatic attraction. The q_{max} of AC-CS for perchlorate at different pHs (3.0, 6.0, 9.0 and 11.0) were calculated as 29.6, 42.6, 41.0 and 33.0, respectively. A neutral or weakly alkaline condition was optimal for the adsorption procedure. The saturated perchlorate uptakes in column were in range of 25.0–38.1 mg/g at different pHs. Additional, desorption test indicated NaCl solution was adequate for almost complete desorption of the perchlorate.

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References

Atikovic, E., Suidan, M. T., & Maloney, S. W. (2008). Anaerobic treatment of army ammunition production wastewater containing perchlorate and RDX. *Chemosphere*, *72*(11), 1643–1648.

Baidas, S., Gao, B., & Meng, X. (2011). Perchlorate removal by quaternary amine modified reed. *Journal of Hazardous Materials*, *189*(1/2), 54–61.

Chergui, A., Kerbachi, R., & Junter, G.-A. (2009). Biosorption of hexacyanoferrate (III) complex anion to dead biomass of the basidiomycete Pleurotus mutilus: Biosorbent characterization and batch experiments. *Chemical Engineering Journal*, *147*(2/3), 150–160.

Futalan, C. M., Kan, C.-C., Dalida, M. L., Pascua, C., & Wan, M.-W. (2011). Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite. *Carbohydrate Polymers*, *83*(2), 697–704.

Kavianinia, I., Plieger, P. G., Kandile, N. G., & Harding, D. R. K. (2012). Fixed-bed column studies on a modified chitosan hydrogel for detoxification of aqueous solutions from copper (II). *Carbohydrate Polymers*, *90*(2), 875–886.

Kosaka, K., Asami, M., Matsuoka, Y., Kamoshita, M., & Kunikane, S. (2007). Occurrence of perchlorate in drinking water sources of metropolitan area in Japan. *Water Research*, *41*(15), 3474–3482.

Kucharzyk, K. H., Crawford, R. L., Cosens, B., & Hess, T. F. (2009). Development of drinking water standards for perchlorate in the United States. *Journal of Environment Management*, *91*(2), 303–310.

Lee, C., Batchelor, B., Park, S. H., Han, D. S., Abdel-Wahab, A., & Kramer, T. A. (2011). Perchlorate reduction during electrochemically induced pitting corrosion of zero-valent titanium (ZVT). *Journal of Hazardous Materials*, *197*, 183–189.

Lee, S., Quyet, N., Lee, E., Kim, S., Lee, S., Jung, Y. D., et al. (2008). Efficient removals of tris(2-chloroethyl) phosphate (TCEP) and perchlorate using NF membrane filtrations. *Desalination*, *221*(1–3), 234–237.

Namasivayam, C., & Sureshkumar, M. V. (2008). Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent. *Bioresource Technology*, *99*(7), 2218–2225.

Ofomaja, A. E., & Naidoo, E. B. (2010). Biosorption of lead(II) onto pine cone powder: Studies on biosorption performance and process design to minimize biosorbent mass. *Carbohydrate Polymers*, *82*(4), 1031–1042.

Reddy, D. H. K., Seshaiah, K., Reddy, A. V. R., & Lee, S. M. (2012). Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified Moringa oleifera leaves powder. *Carbohydrate Polymers*, *88*(3), 1077–1086.

Selvasekarapandian, S., Baskaran, R., Kamishima, O., Kawamura, J., & Hattori, T. (2006). Laser Raman and FTIR studies on Li^+ interaction in PVAc–$LiClO_4$ polymer electrolytes. *Spectrochimica Acta: Part A*, *65*(5), 1234–1240.

Song, Y., & Logan, B. E. (2004). Effect of O_2 exposure on perchlorate reduction by *Dechlorosoma* sp. KJ. *Water Research*, *38*(6), 1626–1632.

Sundaraganesan, N., Kalaichelvan, S., Meganathan, C., Joshua, B. D., & Cornard, J. (2008). FT-IR, FT-Raman spectra and ab initio HF and DFT calculations of 4-N,N′-dimethylamino pyridine. *Spectrochimica Acta: Part A*, *71*(3), 898–906.

Tan, X., Gao, B., Xu, X., Wang, Y., Ling, J., Yue, Q., et al. (2012). Perchlorate uptake by wheat straw based adsorbent from aqueous solution and its subsequent biological regeneration. *Chemical Engineering Journal*, *211/212*, 37–45.

Theodorakis, C., Rinchard, J., Anderson, T., Liu, F., Park, J.-W., Costa, F., et al. (2006). Perchlorate in fish from a contaminated site in east-central Texas. *Environmental Pollution*, *139*(1), 59–69.

Tikkanen, M. W. (2006). Development of a drinking water regulation for perchlorate in California. *Analytica Chimica Acta*, *567*(1), 20–25.

Wang, C., Lippincott, L., & Meng, X. (2008). Kinetics of biological perchlorate reduction and pH effect. *Journal of Hazardous Materials*, *153*(1/2), 663–669.

Wei, Y.-T., Zheng, Y.-M., & Paul Chen, J. (2011). Enhanced adsorption of arsenate onto a natural polymer-based sorbent by surface atom transfer radical polymerization. *Journal of Colloid and Interface Science*, *356*(1), 234–239.

Xu, X., Gao, B.-Y., Tang, X., Yue, Q.-Y., Zhong, Q.-Q., & Li, Q. (2011). Characteristics of cellulosic amine-crosslinked copolymer and its sorption properties for Cr(VI) from aqueous solutions. *Journal of Hazardous Materials*, *189*(1/2), 420–426.

Xu, X., Gao, B.-Y., Yue, Q.-Y., Zhong, Q.-Q., & Zhan, X. (2010). Preparation, characterization of wheat residue based anion exchangers and its utilization for the phosphate removal from aqueous solution. *Carbohydrate Polymers*, *82*(4), 1212–1218.

Xu, X., Gao, Y., Gao, B., Tan, X., Zhao, Y.-Q., Yue, Q., et al. (2011). Characteristics of diethylenetriamine-crosslinked cotton stalk/wheat stalk and their biosorption capacities for phosphate. *Journal of Hazardous Materials*, *192*(3), 1690–1696.

Ye, L., You, H., Yao, J., & Su, H. (2012). Water treatment technologies for perchlorate: A review. *Desalination*, *298*, 1–12.

Yoon, I.-H., Meng, X., Wang, C., Kim, K.-W., Bang, S., Choe, E., et al. (2009). Perchlorate adsorption and desorption on activated carbon and anion exchange resin. *Journal of Hazardous Materials*, *164*(1), 87–94.

Yoon, J., Amy, G., Chung, J., Sohn, J., & Yoon, Y. (2009). Removal of toxic ions (chromate, arsenate, and perchlorate) using reverse osmosis, nanofiltration, and ultrafiltration membranes. *Chemosphere*, *77*(2), 228–235.

Yu, W. H., Kang, E. T., & Neoh, K. G. (2004). Functionalization of hydrogen-terminated Si(1 0 0) substrate by surface-initiated RAFT polymerization of 4-vinylbenzyl chloride and subsequent derivatization for photoinduced metallization. *Industrial and Engineering Chemistry Research*, *43*(17), 5194–5202.