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Column adsorption of perchlorate by amine-crosslinked biopolymer based resin and its biological, chemical regeneration properties

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ABSTRACT

Column adsorption of perchlorate by amine-crosslinked biopolymer based resin was investigated by considering the bed depth, stream flow rate and influent pH. The empty bed contact time (EBCT) increased with the growth of bed depths, meanwhile rising flow rate at constant bed depth (3.4 cm) decreased the breakthrough time. It was observed that perchlorate adsorption capacity was optimum at neutral condition (pH: 6.0, 170.4 mg/g), and decreased at acidic (pH: 3.0, 96.4 mg/g) or alkalic (pH: 12.0, 72.8 mg/g) influents. The predominant strains of the acclimated sludge for resin biological regeneration were the β-subclass of Proteobacteria. Biological regeneration of the saturated amine-crosslinked biopolymer based resin with mixed bacteria have shown its merit with regeneration and biological perchlorate destruction simultaneously, although its regeneration efficiency was only 61.2–84.1% by contrast to chemical regeneration with efficiency more than 95%.

1. Introduction

As an alarming contaminant in groundwater and surface water, perchlorate (ClO_4^-) has become widespread in the United States and China causing rising public health attention (Lee et al., 2011; Yoon et al., 2009). The perchlorate salts have rendered their extensive use for producing solid propellants, highway safety flares, automotive air bags, fireworks, batteries, and analytical chemistry products, which become the major sources of perchlorate pollution (Lee et al., 2011; Wang, Lippincott, & Meng, 2008b).

Perchlorate is toxic to humans because it can compete with iodide associated with its exposure, which results in the inhibition of iodine uptake in the thyroid gland, affecting/altering the production of thyroid hormones and possibly causing mental retardation in fetuses and infants (Srinivasan & Sorial, 2009; Yoon et al., 2009). The United States Environmental Protection Agency (USEPA) has established an official reference dose (OFD) of 0.0007 mg/kg/day for perchlorate, which corresponds to a drinking water equivalent level (DWEL) of 24.5 μg/L in 2005 (Srinivasan & Sorial, 2009; Wang et al., 2008b).

Various treatment technologies including adsorption, ion exchange, membrane filtration, biological treatment, and chemical/catalytic reduction have been developed for perchlorate removal (Baidas, Gao, & Meng, 2011; Dudley, Salamone, & Nerenberg, 2008; Mahmudov & Huang, 2010; Park, Batchelor, Lee, Han, & Abdel-Wahab, 2012; Song & Logan, 2004; Srinivasan & Sorial, 2009). Substantial advances in perchlorate treatment such as biological and chemical reduction have many limitations in wastewater treatment and drinking water purification due to either low reaction rate or the use of huge amount of metals as in the case of chemical reduction (Park et al., 2012; Song & Logan, 2004). Membrane filtration technologies have been proved to be expensive and require the innocuous disposal for concentrated perchlorate wastes (Srinivasan & Sorial, 2009). Among all alternatives for perchlorate removal, adsorption is apparently the most efficient method, due to its simplicity, high capacity, and capability of operating (Baidas et al., 2011; Lin, Chen, Cheng, & Li, 2013; Mahmudov & Huang, 2010; Tan et al., 2012). However, a problem of adsorption is the innocuous disposal of the spent adsorbent and desorbed perchlorate solutions after regeneration. Traditionally, the brine desorption technique was commonly used for the adsorbent regeneration (Srinivasan & Sorial, 2009). The concentrated perchlorate in the spent brine is more toxic, which requires a suitable final treatment. Recently,

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direct bio-regeneration method has been attempted for decomposing the perchlorate from the spent adsorbent (Sharbatmaleki & Batista, 2012; Tan et al., 2012; Venkatesan, Sharbatmaleki, & Batista, 2010; Wang, Lippincott, & Meng, 2008a; Wang, Lippincott, Yoon, & Meng, 2009). It accomplished adsorbent regeneration and biological perchlorate destruction simultaneously.

In this work, an amine-crosslinked biopolymer based resin prepared by our previous method was employed for the perchlorate uptake from solution (Xu et al., 2009, 2011, 2013a). The amine-crosslinked biopolymer based resin was packed in a column for perchlorate concentration. The concentrated perchlorate on the amine-crosslinked biopolymer based resin was then reduced by mixed perchlorate-reducing bacteria in a closed container. The mixed and heterotrophic bacteria were cultivated from anaerobic sludge which was collected from the wastewater treatment plant. Adsorption and bio-regeneration cycle was conducted for two times. Additional, brine desorption technique using HCl as eluent was also employed as control experiment.

2. Materials and methods

2.1. Biopolymer and reagents

The amine-crosslinked biopolymer based resin was prepared as our previous method with some minor modifications (Xu et al., 2010, 2011). Ethylenediamine and triethylamine was introduced onto the biopolymer obtained from wheat stalk, forming the positively quaternary amine group $-CH_2CHOHCH_2NHCH_2CH_2NHCH_2OHCHCH_2N(CH_2CH_2)_3^+$ with nitrogen content of 8.45% which was 0.35% in virgin wheat stalk.

The chemicals used in the tests were all analytical grade. Ethylenediamine, triethylamine, ethylenediamine, alcohol, triethylamine, hydrochloric acid, sodium hydroxide, sodium perchlorate, sodium acetate, dipotassium phosphate, ammonium sulfate, magnesium sulfate were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Column adsorption

2.2.1. Batch column adsorption tests

The perchlorate in the solution should be concentrated on the amine-crosslinked biopolymer based resin before biological reduction. Adsorption in fixed-bed column has shown relatively higher uptake as compared with other adsorption procedures (Song, Zou, Bian, Su, & Han, 2011; Xu et al., 2013a,b). As a result, a column with 20 cm in length and 1.8 cm in diameter was conducted in this test for the perchlorate concentration process. A sintered glass filter was placed in the bottom of column to maintain the adsorbent particles. To determine the influences of bed depth, pH and flow rate on perchlorate concentration uptake, different experiments were performed. Perchlorate concentration in the stream was conducted at 200 mg/L in all column tests. In the bed depth test, a down-flow perchlorate solution stream with pH value of 6.0 was pumped by a peristaltic pump (BT-100, Baoding Lange Co., Ltd.) to the columns with different bed depths (1.5 cm, 3.4 cm and 5.1 cm) at a flow rate of 10 mL/min. Three flow rates with 6, 10 and 25 mL/min were employed and the pH test was conducted at pH range of 3.0–12.0. The samples were collected at different time intervals in the bottom of column and detected by ion chromatograph (ICS-900, Dionex) with an Ion-Pac® AS20 column (4 mm × 250 mm, Dionex).

2.2.2. Column data analysis

The performance of column is usually evaluated with the concept of breakthrough curve. The effluent volume (V_{eff}, mL) is calculated from the following equation:

$$V_{eff} = Qt_{total} \quad (1)$$

Total mass of perchlorate, q_{total} (mg), adsorbed at specific column parameters, maximum capacity of the column or equilibrium perchlorate uptake per unit mass of resin, $q_{eq(exp)}$ (mg/g), total amount of perchlorate passing from the column (m_{total}) and total removal percentage of perchlorate (Y %) are calculated from the following equations::

$$q_{total} = \frac{Q}{1000}\int_0^{t_{total}} C_{ad}\,dt = \frac{Q}{1000}\int_0^{t_{total}} (C_0 - C_t)\,dt \quad (2)$$

$$q_{eq(exp)} = \frac{q_{total}}{M} \quad (3)$$

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \quad (4)$$

$$Y\ (\%) = \frac{q_{total}}{m_{total}} \times 100 \quad (5)$$

where Q is the volumetric flow rate (mL/min), C_0 is the influent perchlorate concentration (mg/L), t_{total} is the total flow time (min), C_{ad} is adsorbed perchlorate concentration (mg/L). The integral in Eq. (2) is equal to the area in the breakthrough curve. M is the dry weight of biopolymer based resin packed in the column (g). The empty bed contact time (EBCT) in the column is described as:

$$\text{EBCT}\ \ (\text{min}) = \frac{\text{bed volume (mL)}}{\text{flow rate (mL/min)}} \quad (6)$$

2.2.3. Mathematical models

Modeling of data available from column studies facilitates scale-up potential. To describe the column breakthrough curves obtained at different conditions (bed depths, flow rates and pH), two models represented as Adams–Bohart and Thomas were used.

Adams–Bohart model (Han et al., 2008; Quintelas, Fernandes, Castro, Figueiredo, & Tavares, 2008; Xu et al., 2013a,b):

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{F} \quad (7)$$

Thomas model (Han et al., 2009; Song et al., 2011):

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} q_0 m}{Q} - K_{Th} C_0 t \quad (8)$$

where k_{AB} is the kinetic constant (L/mg min), N_0 is the saturation concentration (mg/L), Z is the bed depth of column (cm) and F is the linear velocity (cm/min) and can be calculated by dividing the flow rate to the column section area. The values of k_{AB} and N_0 can be obtained from a plot of $\ln(C_t/C_0)$ versus t. The 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 adsorbent (g) and Q is the flow rate of solution (mL/min).

2.3. Biological regeneration

2.3.1. Cultivation and enrichment of perchlorate-reducing mixed bacteria

The gravity-settled anaerobic sludge collected from Chenning pulp and paper wastewater treatment plant (Zibo, Shandong Province) was used as the seed of heterotrophic perchlorate-reducing bacteria in a sealed container. They have been cultivated in a double organic-glass cylinder with effective volume of 4 L which is shown in Fig. 1 (Tan et al., 2012). The mixed bacteria were stored in a refrigerator at 4 °C and cultivated again for 35 days before treated by the procedures previously described (Tan et al., 2012).

The fresh culture medium for the cultivation was adjusted to pH 7.1 ± 0.1 by NaOH and HCl and then was kept anoxic by purging with oxygen-free nitrogen. The basal medium contained the required salts (per liter) as: 1.44 g NaH_2PO_4, 0.1 g $(NH_4)_2SO_4$, 0.1 g $MgSO_4$, 4.0 mg $FeSO_4$, 0.6 mg $Na_2MoO_4{\cdot}2H_2O$, 1.0 mg $NaSeO_3$,

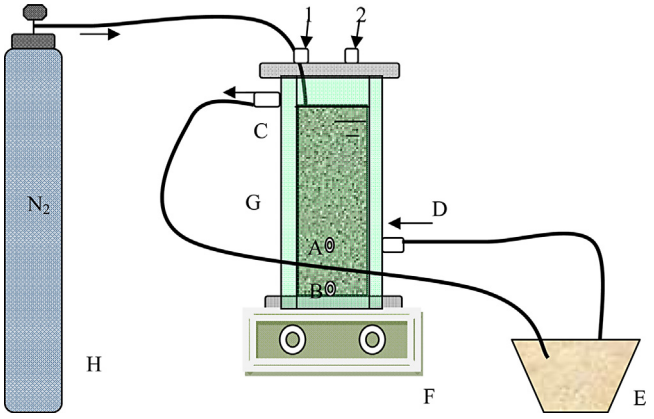

Fig. 1. Schematic representation of system for bacteria cultivation and enrichment (A) valve for effluent solution; (B) valve for cultivated sludge; (C) outlet for circulating water; (D) inlet for circulating water; (E) thermostatic circulating waterbath; (F) magnetic stirrers; (G) double organic-glass cylinder; (H) nitrogen cylinder.

and 0.6 mg H_3BO_3. Unless stated otherwise, acetate ($C_2H_3O_2^-$, 1000 mg/L) and perchlorate (500 mg/L) salts were added as the electron donor and acceptor, respectively.

2.3.2. Analysis of perchlorate reducing bacterial community

The mixed and heterotrophic bacteria were obtained from anaerobic sludge of the wastewater treatment plant. After cultivated in our lab for approximately three months, the mixed bacteria were sent to Human Genome Center in Shanghai for 16S rDNA sequence analysis. Then the sequences were submitted to the GenBank by online BLAST tool for determining the accession number. The GenBank accession numbers of predominant strains obtained from the activated sludge were as follows: isolate EMB 269 (DQ413167), *Methyloversatilis* sp. (KF777434), isolate UKPF6b (AB769215), isolate Chol3 (KC473458), isolate R046 (KC252875), *Ferribacterium* sp. (NR026464), isolate NR80 (KC969642) and *Flavobacterium oncorhynchi* sp. (JX287859). Meantime, the GenBank accession numbers of the known perchlorate reducing bacteria were as follows: strain CKB^T (AF047462), strain CL24+ (AF288774), isolate MissR (AF170357), *Rhodocyclus purpureus* (M34132), strain PS^T (AF170348), isolate SDGM (AF170349), isolate Iso1 (AF170350) and *Pseudomonas stutzeri* (U26415). Sequences entry and manipulation were performed with the MEGA 5.0 sequence analysis software program. To represent the relationship between the perchlorate reducing bacteria obtained in this study and the known perchlorate reducing bacteria in the environment, 16S rDNA sequences of the above were manually added to the alignment using secondary structure information. Thus, the neighbor-joining phylogenetic tree was generated by inserting eight sequences of the predominant strains obtained from acclimated activated sludge and eight sequences of the known perchlorate degrading strains.

2.3.3. Biological regeneration by mixed bacteria

The aim of biological regeneration of amine-crosslinked biopolymer based resin was to reduce the concentrated the perchlorate (on surface of amine-crosslinked biopolymer based resin) to chloride by the cultivated bacteria. The saturated amine-crosslinked biopolymer based resin in column was mixed with 125 mL of mixed bacteria and 125 mL of fresh medium (no ClO_4^-) in a 500 mL sealed container. They were shaken in an orbital incubator at a rotation speed of 150 rpm at 30 °C. After 6 days of biological reduction, the regenerated amine-crosslinked biopolymer based resin was sterilized with 1% of sodium hypochlorite. The sterilized amine-crosslinked biopolymer based resin was then collected and reused for column uptake of perchlorate at same conditions. The column adsorption and bio-regeneration was conducted for two times without changing of cultivated bacteria.

2.4. Chemical regeneration by HCl

The brine desorption technique was also conducted in this test as the control experiment. Chemical regeneration of the amine-crosslinked biopolymer based resin as well as recovery of perchlorate was achieved by eluting HCl solution (0.1 mol/L) through the column packed with spent amine-crosslinked biopolymer based resin. After washed with distilled water, the regenerated amine-crosslinked biopolymer based resin was used again in the subsequent experiments.

3. Results and discussions

3.1. Column adsorption of perchlorate by amine-crosslinked biopolymer based resin

3.1.1. Bed depth

The results in Fig. 2 presented the perchlorate adsorption by different bed depths of amine-crosslinked biopolymer based resin. Columns with 1.8, 3.4 and 5.1 cm of bed depths were packed with 1.0, 2.0 and 3.0 g of amine-crosslinked biopolymer based resin, respectively. When the adsorption zone moves up and the upper edge of this zone reaches the top of the column, the effluent concentration starts to rise rapidly. This is called the breakthrough point (Suksabye, Thiravetyan, & Nakbanpote, 2008). The desired

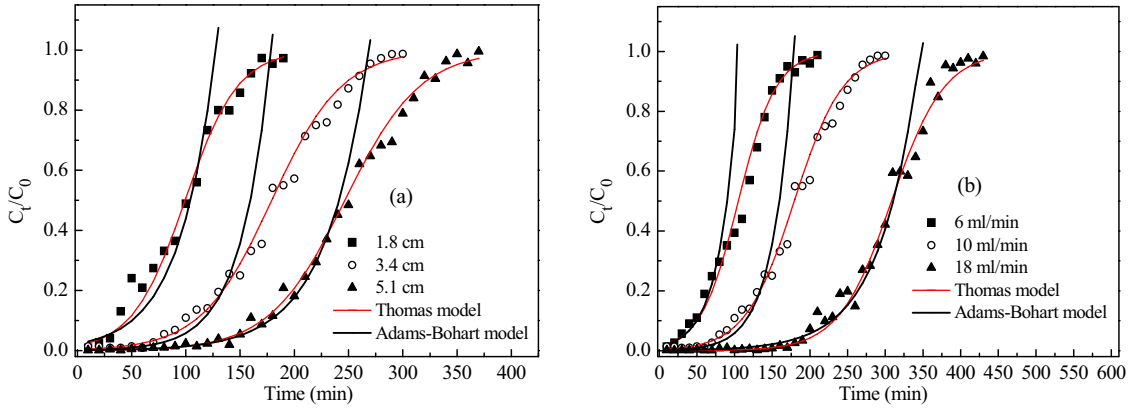

Fig. 2. Column adsorption of perchlorate by amine-crosslinked biopolymer based resin as a function of bed depth (a) and flow rate (b) ((a): flow rate: 10 mL/min, pH: 6.0; (b): bed depth: 3.4 cm, pH: 6.0).

Table 1
Parameters in fixed-bed column for perchlorate.

C_0 (mg/L)	Q (mL/min)	Z (cm)	pH	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg/g)	V_{eff} (L)	Y (%)	EBCT (min)
200	10	1.8	6.0	180	360	185.2	185.2	1.8	51.4	0.46
		3.4		300	600	340.8	170.4	3.0	56.6	0.86
		5.1		370	740	476.8	158.9	3.7	64.1	1.29
	6	3.4	6.0	450	540	353.2	176.6	2.7	65.4	1.44
	10			300	600	340.8	170.4	3.0	56.6	0.86
	18			210	756	342.6	171.3	3.78	45.4	0.48
	10	3.4	*3.0*	220	480	192.8	96.4	2.4	40.2	0.86
			6.0	300	600	340.8	170.4	3.0	56.6	0.86
			12.0	200	400	145.6	72.8	2.0	36.5	0.86

breakthrough point for all bed depths was determined to be 0.05 C_t/C_0. The breakthrough times for 1.8, 3.4 and 5.1 cm of bed depths were found to be 35, 80, and 150 min, respectively. As the stream continued to flow into the column, the point on the S-shaped curve gradually approached its exhaustion value. The exhaustion times (corresponding to $C_t/C_0 = 0.95$) for 1.8, 3.4 and 5.1 cm of bed depths were 170, 265, and 350 min, respectively. The results showed that the breakthrough time and exhaustion time extended with the increase of bed depth. The slope of the plots from breakthrough time to exhaustion time decreased as the bed depth increased from 1.8 to 5.1 cm, indicating the breakthrough curve became steeper as the bed depth decreased. The empty bed contact time (EBCT) increased with the increase in bed depths. It was illustrated that the higher the bed depth the longer the service time at various breakthroughs due to the increase in binding sites on the amine-crosslinked biopolymer based resin.

3.1.2. Stream flow rate

The breakthrough curve, C_t/C_0 versus volume treated with various flow rates at the constant bed depth of 3.4 cm is shown in Fig. 2b. As seen in Fig. 2b, the breakthrough points occurred at 215, 80 and 30 min for flow rates of 6, 10 and 18 mL/min, respectively. The results indicated that an increase in flow rate at this constant bed depth decreased the breakthrough time or breakthrough volume due to a decrease in EBCT, which was 1.44, 0.86 and 0.48 min for flow rates at 6, 10 and 18 mL/min, respectively (Table 1). The removal percentage of perchlorate, *Y*% was also decreased from 65.4% to 45.4% as the increase of flow rates. The lower the EBCT, the less effective the diffusion process becomes, which results in lower adsorption and *Y* %. Thus, the adsorbent needs more time to bond the perchlorate efficiently (Sarin, Singh, & Pant, 2006).

It was observed from Fig. 2 that the shape of the breakthrough curve is saturated earlier at higher flow rates because the front of the adsorption zone quickly reached the top of column (Suksabye et al., 2008). In contrast, lower flow rate provided longer contact time, resulting in a shallow adsorption zone.

3.1.3. The pH of stream

Adsorption medium pH is an important controlling parameter in the adsorption process. The breakthrough curve C_t/C_0 versus breakthrough volume treated with various pHs of stream (3.0, 6.0, and 12.0) was shown in Fig. 3. The breakthrough points occurred at 25, 80 and 15 min for influent pHs of 3.0, 6.0 and 12.0 with perchlorate uptake of 96.4, 170.4 and 72.8 mg/g, respectively. At acidic conditions, the perchlorate was protonated so as the electrostatic interaction between the protonated perchlorate and positively charged amine group was decreased, resulting in the decrease of breakthrough time. The ionic state of functional groups on the amine-crosslinked biopolymer based resin was always affected by the pH at point zero charge (pH_{pzc}: 9.75 for this amine-crosslinked biopolymer based resin). Above this pH value, the surface charge of the amine-crosslinked biopolymer based resin exhibited a negative characteristic and caused the less attractive or more repulsive electrostatic for free perchlorate ions in stream (Chen et al., 2012). As a result, the breakthrough time as well as perchlorate uptake by the amine-crosslinked biopolymer based resin was decreased.

3.1.4. Column adsorption data analysis

The main assumption behind Adams–Bohart model is that the adsorption rate is proportional to the residual capacity of the adsorbent and the concentration of the adsorbate and also equilibrium does not take place instantaneous. As shown in Figs. 2 and 3, the Adams–Bohart model was only applied to describe the initial part of the curve (the concentration $C_t < 0.5\ C_0$). Respective values of N_0 and k_{AB} for all breakthrough curves were calculated and presented in Table 2. The correlation coefficients were between 0.876 and 0.969 for the adsorption processes where relative concentration region was up to 0.5. The value of N_0 decreased with the increasing flow rate, while the value of k_{AB} increased with increasing flow rate. This showed the overall system kinetics is dominated by external mass transfer in the initial part of column adsorption (Aksu & Gönen, 2004; Karimi, Shojaei, Nematollahzadeh, & Abdekhodaie, 2012). Adams–Bohart model may provide a simple and comprehensive approach to evaluating the perchlorate adsorption in column, its validity, however, is limited to the range of conditions used (Kundu & Gupta, 2005).

Thomas model, based on the Langmuir adsorption–desorption and second-order reversible reaction kinetics, is one of the most widely used models (Song et al., 2011). Especially in the absence of internal and external diffusion limitation, this model can be used well (Karimi et al., 2012). It assumes no axial dispersion and adsorption is the rate driving force. The column data for perchlorate were fitted to the linearized form of the Thomas model, and the model parameters (K_{Th} and q_0) for all the experimental breakthrough curves were presented in Table 2. The values of K_{Th} became smaller and the slope of breakthrough curve decreased as the bed depth increased. This was due to the increase in the axial dispersion of the perchlorate over the column with an increase in column

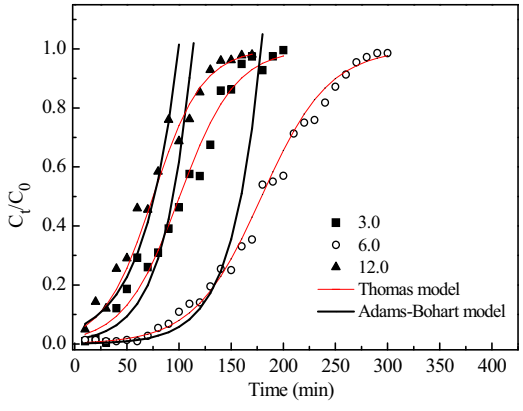

Fig. 3. Column adsorption of perchlorate by amine-crosslinked biopolymer based resin as a function of pH (flow rate: 10 mL/min; bed depth: 3.4 cm).

Table 2
Parameters of Adams–Bohart and Thomas model under different conditions.

C_0 (mg/L)	Q (mL/min)	Z (cm)	pH	q_{ed} (mg/g)	Adams–Bohart model			Thomas model		
					k_{AB} (L/mg min)	N_0 (mg/L)	R^2	K_{TH} (mL/min mg)	q_0 (mg/g)	R^2
200	10	1.8	6.0	185.2	0.00015	35607	0.893	0.212	187.8	0.988
		3.4		170.4	0.00018	26597	0.935	0.156	178.1	0.978
		5.1		158.9	0.00012	29072	0.969	0.145	162.7	0.985
	6	3.4	6.0	176.6	0.00010	48623	0.913	0.146	184.2	0.986
	10			170.4	0.00014	26597	0.935	0.156	178.1	0.978
	18			171.3	0.00016	14811	0.955	0.199	175.6	0.984
	10	3.4	3.0	96.4	0.00019	16732	0.876	0.186	100.5	0.989
			6.0	170.4	0.00018	26597	02.935	0.156	178.1	0.978
			12.0	72.8	0.00015	14811	0.930	0.210	75.23	0.990

height (Song et al., 2011). Analysis of the regression coefficients indicated that the regressed lines provided good fit to the experimental data with R^2 values ranging from 0.978 to 0.990. Values (q_0) calculated from Thomas equations were very close to the experimental values of bed capacity (q_{eq}) obtained at all experimental conditions. Thus, column kinetics could be described more adequately by the Thomas mode than by the Adams–Bohart model. Additionally, Thomas model was suitable for the adsorption process, which indicated that the external and internal diffusions were not the bottle neck of the process.

3.2. Biological regeneration

3.2.1. Analysis of perchlorate reducing bacterial community

After analysis of sequences, the phylogenetic tree was generated by neighbor joining method based on the 16S rDNA gene sequences of our studies and eight other known perchlorate reducing isolates obtained from the GenBank database (Fig. 4). Gene analysis by online BLAST tool indicated that these perchlorate reducing bacteria formed two distinct monophyletic groups. One of these groups was represented by the known perchlorate reducing strain CKB^T and strain PS^T (Achenbach, Michaelidou, Bruce, Fryman, & Coates, 2001). This group, which contained 13 strains within the β-subclass of the Proteobacteria, was relatively diverse with 16S rDNA distances ranging from 0 to 7%. The other group represented by the cultivated perchlorate reducing strain *Flavobacterium* sp. strain R046 contained three strains with distances only ranging from 0 to 1%. Bootstrap using Robust Phylogenetic Analysis represented the relationship between the perchlorate reducing strain obtained in this study and related genera. Therefore, the high Bootstrap and phylogenetic relationship of phylogenetic tree showed that the main predominant strains of the acclimated activated sludge were closely related to the published perchlorate reducing bacteria.

3.2.2. Biological regeneration by mixed bacteria

The column adsorption of perchlorate by bio-regenerated amine-crosslinked biopolymer based resin was shown in Fig. 5a. After the first biological regeneration, perchlorate uptake by bio-regenerated amine-crosslinked biopolymer based resin was about 143.6 mg/g, accounting about 84.1% of the virgin data; it was further decreased to 61.2% (104.5 mg/g) after the second column adsorption and bio-regeneration cycle. It was observed that the bio-regeneration efficiency of the spent amine-crosslinked biopolymer based resin was lower than those of chemical regeneration. The

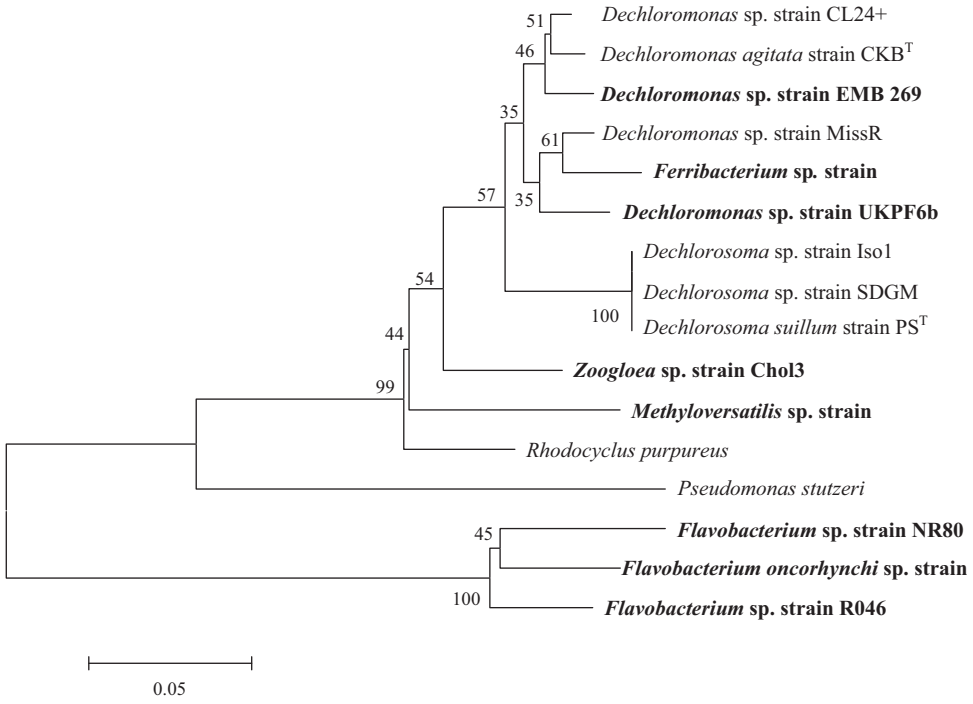

Fig. 4. Phylogenetic relationships between isolated perchlorate reducing bacteria obtained from the activated sludge and the known perchlorate degrading strains based upon the analysis of aligned regions of 16S rDNA gene sequences. (Bootstrap support values from 100 replications are indicated for each node. The scale bar indicates the distance of a 5% sequence divergence.)

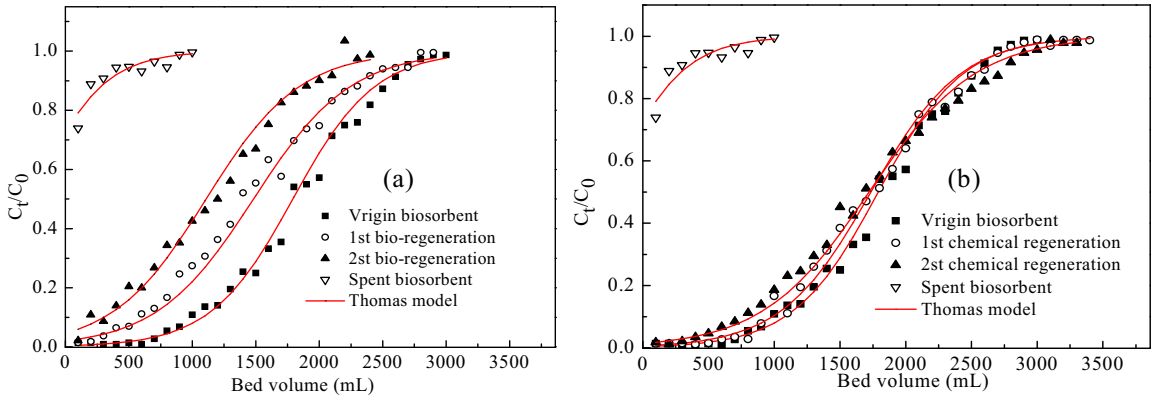

Fig. 5. Column adsorption of perchlorate by spent amine-crosslinked biopolymer based resin after (a) bio-regeneration and (b) chemical regeneration.

concentrated perchlorate was attached on surface of the amine-crosslinked biopolymer based resin by the electrostatic attraction between perchlorate and amine groups. These attached perchlorate ions were reduced to chloride by the mixed bacteria mainly on solid surface of amine-crosslinked biopolymer based resin (Fig. 6a). Basically, reduction ability as well as reduction rate of perchlorate on solid form was significantly lower compared with those on aqueous solutions (Wang et al., 2008a,b). As a result, this may limit the complete bio-regeneration of amine-crosslinked biopolymer based resin.

Another factor affects its regeneration efficiency is the relatively larger weight loss (5–10%) observed after each adsorption and bio-regeneration cycle. One defect of amine-crosslinked biopolymer based resin was its fragility. Physical impact during 6 days of bioregeneration as well as the potential organic dissolution may both contribute the loss.

Based on mentioned above, bio-regeneration of the amine-crosslinked biopolymer based resin with mixed bacteria have shown its merit with regeneration and biological perchlorate destruction simultaneously, although it was less efficient as compared with the that of chemical regeneration. An attempt will be provided in our future research for enhanced bio-regeneration by combining the biological and chemical methods in regeneration process.

3.3. Chemical regeneration of spent amine-crosslinked biopolymer based resin

The chemical regeneration of perchlorate loaded amine-crosslinked biopolymer based resin was conducted by eluting 0.1 mol/L of HCl solution. The amine-crosslinked biopolymer based resin was observed with 2% of weight loss after two cycles of chemical regeneration and column adsorption; this may be partially due to the destruction of cellulose in amine-crosslinked biopolymer based resin at strong acidic conditions. The column adsorption of spent amine-crosslinked biopolymer based resin for perchlorate was also evaluated with uptake of 8.9 mg/g; it could be negligible when comparing with the virgin amine-crosslinked biopolymer based resin of 170.4 mg/g. The perchlorate uptake of spent amine-crosslinked biopolymer based resin after chemical regeneration was about 167.3 mg/g after the first chemical regeneration and 164.5 mg/g after the second chemical regeneration (Fig. 5b).

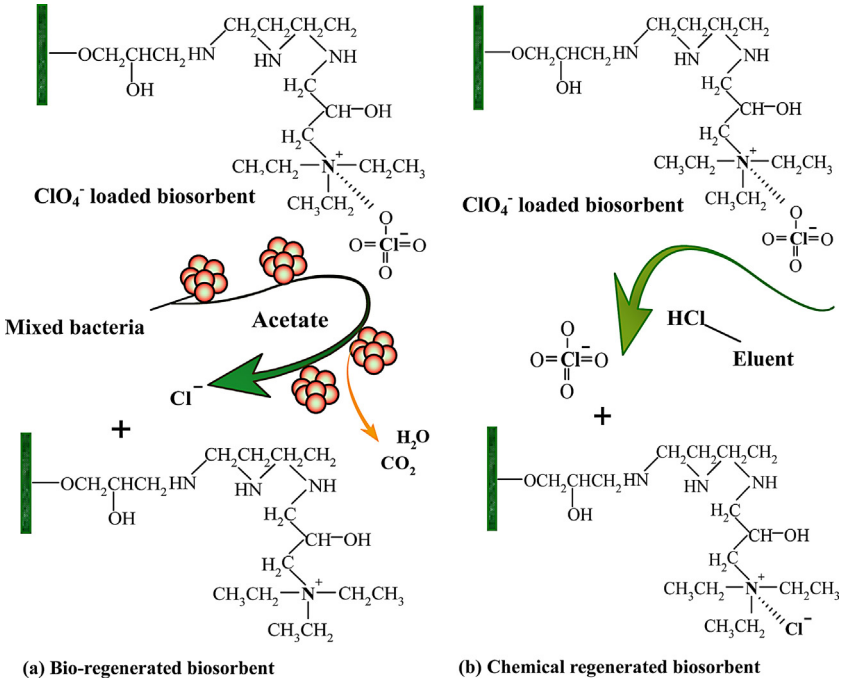

Fig. 6. Scheme of mechanism for bio-regeneration and chemical regeneration of amine-crosslinked biopolymer based resin.

Regeneration efficiency was kept more than 95% after two cycles of column adsorption and regeneration, although a small weight loss of the packed amine-crosslinked biopolymer based resin was observed. The high regeneration efficiency may be primarily due to a reaction of ion-exchange with high Cl^- concentration, which displacing perchlorate ions from the surface of the amine-crosslinked biopolymer based resin (Fig. 6b). As a result, chemical regeneration only transferred the concentrated perchlorate from the amine-crosslinked biopolymer based resin to brine solution.

4. Conclusions

Results showed that columns with bed depths of 1.8, 3.4 and 5.1 cm adsorbed about 185.2, 170.4 and 158.9 mg/g of perchlorate, respectively. Breakthrough time and exhaustion time extended as the increase of bed depth. The breakthrough points occurred at 25, 80 and 15 min for influent pHs of 3.0, 6.0 and 12.0 with perchlorate uptake of 96.4, 170.4 and 72.8 mg/g, respectively. Column kinetics could be described more adequately by the Thomas mode than by the Adams–Bohart model. Bio-regeneration of the amine-crosslinked biopolymer based resin showed its merit with regeneration and biological perchlorate destruction simultaneously with its regeneration efficient of 61.2–84.1%.

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