Removal of tetracycline antibiotics from aqueous solutions using easily regenerable pumice: batch and column study

Jianbo Lu, Kai Xu, Wanlu Li, Dongmei Hao and Lingmin Qiao

ABSTRACT

Mineral pumice as an adsorbent was explored for tetracycline (TC) removal from water. Pumice was characterized by X-ray diffraction, X-ray fluorescence and Fourier transform infrared spectroscopy. Batch and column studies were conducted to investigate the adsorbability of pumice towards TC. Results showed that the TC adsorption amount declined as the pH increased from 3 to 9 and was strongly dependent on ionic strength. Adsorption kinetic data fitted to the pseudo-first-order, pseudo-second-order and Elovich model very well ($R^2 > 0.9$). Intraparticle diffusion was the main rate controlling step during TC adsorption. The Langmuir and Freundlich models were utilized to simulate isotherm data ($10^{-3}$ to $14$). The obtained Langmuir uptake amount ($20$ to $C_14$) was $3.345$ mg/g. Thermodynamic analyses showed that the TC uptake amount increased with the temperature rising, suggesting its endothermic nature. At pH 6 and 8, both Pb$^{2+}$ and Cu$^{2+}$ significantly promoted the TC removal (>25%) via ion bridging action. Adsorption mechanisms mainly involved physisorption (Van der Waals & electrostatic forces) and chemisorption via the formation of inner-sphere complexes. Column tests showed that the exhausted column could be effectively regenerated using alkaline EDTA solution. Current results suggest that pumice is a promising adsorbent for TC removal from aqueous solutions.

Key words | adsorption, fixed bed column, pumice, regeneration, tetracycline

INTRODUCTION

Tetracycline antibiotics (TC) have been one of the most widely used drugs for disease control in humans, livestock and plants for several decades (Gu & Karthikeyan 2005; Rodriguez-Mozaz et al. 2015). Tetracyclines are reportedly the second most common antibiotic drugs in both production and usage in the world (Gu & Karthikeyan 2005). It is known that most tetracyclines are poorly absorbed in vivo and are eventually excreted as unchanged compounds via urine or feces into aquatic environments and soils (Kang et al. 2010). Tetracyclines have been detected in municipal sewage effluents and even drinking water (Li et al. 2015; Wang et al. 2016). Therefore, there is increasing concern about the effective removal of tetracyclines from aquatic systems in order to protect ecosystem functions and human health.

Conventional water treatment methods (biological processes, coagulation, sedimentation, and sand filtration) are generally inefficient for tetracycline removal (Homem & Santos 2011). Therefore, it is of vital importance to develop efficient and low-cost treatment technologies for tetracycline removal from water. Various tetracycline decontamination technologies such as ozonation (Khan et al. 2010), photoelectrocatalytic degradation (Daghrir et al. 2014), photo-Fenton (Yamal-Turbay et al. 2013) and adsorption (Kang et al. 2010) have been reported in recent years. Among these methods, chemical oxidation (ozonation or
photocatalytic oxidation) is seemingly not economical in practice. In addition, more toxic intermediate products may be formed during their oxidation process (Santos et al. 2004). By comparison, adsorption is a promising technology for the treatment of low concentration tetracyclines due to its high efficiency, low cost and recycling of adsorbent. Especially, adsorption does not generate toxic intermediates because it is a process that transfers pollutants from liquid phase to solid phase (i.e. adsorbent materials).

In previous research, a variety of adsorbents have been investigated for tetracyclines removal, which include activated carbon, carbon nanotubes, graphite (Ji et al. 2009), resin, and clay minerals (diatomite, montmorillonite, rectorite, etc.) (Chang et al. 2009; Yang et al. 2011; Zhao et al. 2012; Li et al. 2015). Among the aforementioned adsorbent materials, natural minerals are relatively cheap and are potential adsorbents in water and wastewater treatments. As a porous and light volcanic stone, pumice has a relatively high abundance in nature and can become a potential adsorbent material for practical water and wastewater treatments. Pumice has prominent advantages such as low cost, good hydrophilicity and environmental friendliness when compared to other natural and synthetic adsorbents. The porous structure of pumice can provide more active sites towards pollutants adsorption. In addition, pumice can be easily fabricated into granular adsorbent that is convenient for application in fixed-bed adsorption systems. Compared to powdered adsorbent materials, granular pumice adsorbent can obtain solid–liquid separation easily and has the potential for recycling and reuse via appropriate regeneration methods. So far, however, only very limited information can be found regarding tetracyclines removal using pumice adsorbent from water.

In this study, simply activated pumice as a new adsorbent material was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) analyses. Via batch tests, the effects of aqueous chemistry conditions (pH, ionic strength, temperature and coexisting cations) on tetracyclines adsorption by pumice were investigated. Adsorption isotherms, kinetics, thermodynamics and adsorption mechanisms were also evaluated. Furthermore, tetracyclines adsorption and regeneration tests were performed in the column mode to evaluate the applicability of pumice.

**MATERIALS AND METHODS**

**Experimental materials**

Natural pumice was collected from Changbai Mountain, Jilin Province, China. It was washed with hydrochloric acid and distilled water several times, and dried at 50°C in an oven. The dried pumice was ground to a particle size below 0.180 mm, and was used as adsorption material in batch tests. Tetracycline hydrochloride (TC, USP grade) was purchased from Sangon Biotech Co. Ltd, Shanghai, China. Its chemical structure and species distribution are illustrated in Figure 1. Unless specified otherwise, all chemical reagents were of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd, Beijing, China.

Figure 1 Chemical structure (pK_{a1} = 3.3, pK_{a2} = 7.7, pK_{a3} = 9.7) and species distribution diagram of TC.
The TC stock solution was prepared by dissolving tetracycline hydrochloride in deionized water.

**Characterization of pumice**

The XRD data of original pumice were obtained by an X-ray powder diffractometer (B max-2500, Rigaku, Japan). The specific surface area of pumice was obtained from nitrogen gas adsorption–desorption isotherms using a Nova 6000 analyzer (Quantachrome, USA). The XRF measurement (MagixPW2403, Panalytical, The Netherlands) was also carried out to analyze the compound mass percentage in the pumice sample.

Original pumice samples and the TC-loaded one for FTIR determination were first freeze-dried, and then the dry samples were mixed with spectral grade KBr (about 1% W:W). After the mixtures were ground in an agate mortar, FTIR spectra were obtained on a Tensor 27 FTIR spectrophotometer (Bruker Optics, Germany).

The zeta potentials of the dilute pumice suspensions before and after TC sorption were measured by a Zetasizer analyzer (Malvern Co., NANO ZS, UK). The pumice content of suspensions was 4 g/L. As for the TC-loaded pumice, the TC concentration was 40 mg/L. The background electrolyte was a NaCl solution of 0.01 M.

**Batch experiments**

Batch experiments were carried out to investigate the effects of aqueous chemistry conditions (pH, ionic strength and coexisting cations) on sorption, kinetics, isotherm and thermodynamics. The pH of solutions was kept at a constant pH of 6 by adding HCl or NaOH and the pumice content was 5 g/L. Constant ionic strength (0.01 M NaCl) was maintained. Kinetics experiments were performed at 20 °C in 1 L solutions with a TC concentration of 20 mg/L. The solutions were equilibrated for 1.830 min under moderate magnetic stirring. At specified time intervals, sample aliquots were collected and filtrated immediately through 0.45 μm membrane filters, and then TC concentrations in filtrates were determined using a UV-VIS spectrophotometer (Persee-T6, China).

The above kinetics experiments indicated that a sorption time of 24 h was sufficient to reach equilibrium. Therefore, 24 h of mixing was chosen in subsequent batch experiments. The experiments on the influence of pH and ionic strength were conducted in plastic tubes containing 50 mL of TC solutions and 4 g/L of pumice. The pH of solutions was adjusted to range between 3 and 10 using HCl or NaOH solution. The ionic strength of the solutions varied from 0.001 to 0.1 M by using NaCl. The mixtures were agitated with an oscillator at 20 °C and then the samples were filtrated immediately for TC measurements.

Sorption isotherms experiments were carried out by adding 0.2 g of pumice into 40 mL of TC solutions with varying concentrations (1–60 mg/L). All the solutions were agitated at the desired temperature (10, 20 or 30 °C) for 24 h. During the whole sorption period, solution pH was maintained at 6 and ionic strength was adjusted to 0.01 M by adding NaCl solution.

The effects of commonly coexisting cations (Mg²⁺, Cu²⁺ and Pb²⁺) on TC sorption were investigated at pH 4, 6 and 8. The concentrations of TC and NaCl were separately fixed at 20 mg/L and 0.01 M. The concentrations of coexisting cations were preset at 0 and 0.2 mM, respectively. Pumice of 0.2 g was added into 50 mL mixture solutions containing TC and sole cation.

**Column experiments**

For engineering application of adsorption technology, adsorption column experiments are frequently needed to examine adsorption and regeneration efficiency. Therefore, fixed-bed column studies were conducted using a plexiglass column with a height of 44 cm and internal diameter of 1.5 cm (Figure 2). A certain amount of granular pumice (size: 1–1.25 mm) was packed into the column to achieve the desired bed height (10 cm). The initial TC concentration was held constant at 20 mg/L (C₀) and the solution pH was 6. Column tests were operated with an upflow mode and influent flow rate was controlled at 8 mL/min using a peristaltic pump. Effluent samples were collected at different time intervals for the determination of TC concentration (Cₜ). Whether TC-loaded pumice could be effectively desorbed and reused was quite important and affected its practicability. Via the optimized selection of the regeneration method, EDTA solution was selected as a desorption agent. Desorption experiments were carried out by passing 0.02 M EDTA solution (pH 10) through the bed column.
with upflow mode and flow rate was maintained at 8 mL/min. The TC concentrations in regeneration effluent were collected at preset time intervals and immediately filtrated for measurement. After the exhausted granular pumice was regenerated, it was further rinsed with tap water until the effluent pH of regeneration solutions approached neutral, and then the next adsorption run was conducted. Experiments on the adsorption-regeneration cycle were carried out three times, successively.

RESULTS AND DISCUSSION

Characterization of pumice

Table 1 lists the mass percentage of various compounds in pumice that was obtained by XRF analysis. As can be seen from the table, the pumice mainly contained a variety of metal oxide and silicon oxide. Of those, the mass percentage of SiO$_2$ and Fe$_2$O$_3$ was relatively higher (39.66 and 27.35%, respectively), hinting that they were the two most important components in pumice. Previous studies reported that SiO$_2$ was one of its main components (Ersoy et al. 2010; Asgari et al. 2012). Occurrence of various oxides in pumice may indicate its good adsorbability towards tetracycline.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass percentage (%)</th>
<th>Compound</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>39.66</td>
<td>P$_2$O$_5$</td>
<td>1.66</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>27.35</td>
<td>MgO</td>
<td>0.71</td>
</tr>
<tr>
<td>CaO</td>
<td>14.31</td>
<td>Na$_2$O</td>
<td>0.31</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.44</td>
<td>MnO</td>
<td>0.19</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.98</td>
<td>Loss on ignition</td>
<td>0.44</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.95</td>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The Brunauer-Emmett-Teller (BET) analysis of pumice shows that it had a specific surface area of 6.6 m$^2$/g, average pore volume of 0.012 cm$^3$/g and average pore diameter of 7.6 nm. Further analysis of the XRD pattern was conducted as shown in Figure 3(a). The two peaks at 22 and 27.7° could be attributed to the mineral dachiardite ((Ca, Na, K, Mg)$_4$(Si, Al)$_4$O$_{24}$·13H$_2$O)), which possibly represented some minerals such as zeolite and albite. The strong peak at 35.5° could be associated with SiO$_2$ (Ersoy et al. 2010; Khorzughy et al. 2013).

Figure 3(b) illustrates the FTIR spectra of pumice before and after TC sorption. The broad band around 3,450 cm$^{-1}$ was attributed to the stretching vibration of surface adsorbed H$_2$O molecules in the lattice and the –OH functional group. The band around 1,650 cm$^{-1}$ could be assigned to the deformation of water molecules indicating the presence of physisorbed water on the pumice. The bands at the wavenumber of 650 and 1,010 cm$^{-1}$ were separately due to the symmetric and asymmetric stretching modes of the Si–O–Si group (Mazza et al. 1993). The bands at 1,045 and 1,091 cm$^{-1}$ were mainly attributed to the bending vibration of hydroxyl group (Fe–OH) of iron oxides. After TC sorption, no apparent band shift of FTIR spectra was observed, possibly hinting that the TC adsorption did not remarkably alter the sorbent structure.

Batch studies

Effect of pH and ionic strength

Solution pH and ionic strength are two important parameters in the adsorption process. Solution pH affects the surface charge of adsorbent materials and adsorbate species.
Ionic strength can also affect the electric double layer thickness and accordingly influence the binding of adsorbate. The effects of pH (3–9) and ionic strength (0.001–0.1 M NaCl) on TC sorption are shown in Figure 4. Obviously, TC sorption capacity was pH dependent. At different ionic strengths, TC sorption capacity had an overall tendency to reduce as the pH increased from 3 to 9. In the case of low ionic strength (0.001 M), the TC sorption amount decreased slightly from 2.6 to 2.3 mg/g as the pH increased from 3 to 9. However, for the high ionic strength (0.01 and 0.1 M), the TC sorption amount decreased markedly from 2.8 and 3.0 to 2.1 and 1.4 mg/g, respectively. At low pH, the higher ionic strength resulted in the larger TC adsorption capacity, whereas a converse trend was observed when the solution pH was above 6. Similar results were also reported by other researchers (Parolo et al. 2008). Generally, the pH effect was associated with the TC species and the surface properties of pumice. According to the species distribution diagrams of TC (Figure 1(b)), with the pH rising, the sequence of TC existing forms is as follows: $\text{H}_3\text{L}^+$, $\text{H}_2\text{L}$, $\text{HL}^-$ and $\text{L}^2$. At pH ≤ 5, due to the negatively charged surface of pumice, electrostatic interaction may become the main driving force for the sorption of positively charged TC species (mainly $\text{H}_3\text{L}^+$). Thus, high sorption affinity at low pH could be due to the occurrence of electrostatic attraction.

On the other hand, as Figure 5 indicates, at pH ≤ 5, the zeta potential of original pumice suspensions ranged between −23 and −41 mV, which was in an unstable state and susceptible to foreign electrolyte ions (Franks 2002). High ionic strength caused the increase of Na⁺ concentration, which compressed the thickness of the electric double layer on the negatively charged surface of the adsorbent. This reduced the charge repulsion between adsorbent particles and accordingly the film diffusion distance of adsorbate from bulk solutions to the adsorbent surface, which made TC species access to internal pores easy. This may be another explanation for the large TC sorption amount at high ionic strength when pH was below 5.

However, at pH ≥ 6, high ionic strength reduced the TC sorption capacity on pumice, which may be attributed to the electrostatic competition between TC anions and electrolyte.
anions (Cl\(^{-}\)) for the same adsorption sites on the surface of pumice. Furthermore, it is considered that outer-sphere surface complexes are more sensitive to ionic strength variations than inner-sphere surface complexes since electrolyte ions are placed in the same plane as the outer-sphere surface complexes (Hayes et al. 1988). Therefore, it was presumed that outer-sphere surface complexes were likely formed when TC was adsorbed onto the surface of pumice due to the strong dependence of its sorption capacity on ionic strength.

The zeta potential profiles of pumice suspensions vs. pH were also determined and are given in Figure 5. The zeta potentials of original pumice at different pH were negative, indicating its low pH\(_{zpc}\) (pH of zero point charge), which could be attributed to a relatively high proportion of SiO\(_2\) contained in pumice (Table 1). Previous research also reported that pumice has a negative charge over a wide pH range, which is similar to the current results (Ersoy et al. 2010; Asgari et al. 2012). Thus, in light of the TC speciation distribution diagrams (Figure 1(b)), at pH ≤ 6, positively charged H\(_3\)L\(^{+}\) was one of the main TC species, and its sorption on pumice surface resulted in the shift of zeta potentials to the point near the zero potential because of charge neutralization. Nevertheless, at pH ≥ 6, L\(^{2-}\) and HL\(^{-}\) became the predominant TC species. Charge repulsion occurred between negatively charged TC and pumice, and accordingly the zeta potentials of TC-loaded pumice did not alter markedly compared to original pumice.

**Effect of sorption time and kinetic analysis**

The variation of TC sorption amount \(q_t\) (mg/g) with time \(t\) (min) was further investigated and the data are shown in Figure 6(a). It was seen that TC sorption on pumice was initially fast due to the occurrence of a large number of available sorption sites, and about 80% of TC sorption was accomplished in the first 500 min. After that, the active sites on pumice surface were gradually occupied by adsorbed TC and accordingly its adsorption amount on pumice increased slowly. Eventually, the adsorption reached equilibrium after about 1,500 min.

In order to design an appropriate adsorption system, it is of vital importance to investigate the sorption kinetics. Hence, the time effect data are further utilized to perform the kinetic fitting using common kinetic models, pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models. These kinetic equations can be expressed as follows.

**Pseudo-first-order model:**

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t
\]

**Pseudo-second-order model:**

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

**Elovich model:**

\[
q_t = \frac{\ln t}{\beta} + \frac{\ln(\alpha \beta)}{\beta}
\]

**Intraparticle diffusion model:**

\[
q_t = k_{id} t^{0.5} + C
\]

where \(q_e\) (mg/g) is the equilibrium adsorption amount; \(q_t\) (mg/g) is the adsorbed amount at time \(t\); \(k_1\) (min\(^{-1}\)) and \(k_2\) (g/(mg-min)) is separately the equilibrium rate constant of pseudo-first-order model and pseudo-second-order model; \(\alpha\) is the initial sorption rate (mg/(g-min)); \(\beta\) is the desorption constant (g/mg); \(k_{id}\) is the intraparticle diffusion rate.
The kinetic model parameters were obtained by regression analysis, and are listed in Table 2. It was found that the kinetic data could fit to the pseudo-first-order and pseudo-second-order model very well ($R^2 > 0.98$, Figure 6(a)). Moreover, the experimental data could be simulated very well by the Elovich model ($R^2 = 0.924$, Figure 6(b)). It is generally recognized that the Elovich model was applicable to heterogeneous adsorbent surfaces. This was in agreement with the XRF results, which showed that the pumice contained various oxides (especially iron oxides and aluminum oxides) resulting in its heterogeneous surface. Further, it was demonstrated that iron oxides and aluminum oxides could chemically adsorb TC via the formation of inner-sphere surface complexes (Gu & Karthikeyan 2005).

The intraparticle diffusion model given by Weber & Morris (1965) has been widely applied to analyze adsorption kinetics data and further clarify the rate controlling step (Equation (4)). The parameters obtained from the intraparticle diffusion model are tabulated in Table 2. According to mass transfer mechanisms, the whole adsorption process mainly includes four consecutive steps: (1) transport of adsorbate in the bulk solution; (2) diffusion of adsorbate through the liquid film to the external surface of the adsorbent (film diffusion); (3) diffusion of adsorbate from the adsorbent surface into its interiors (intraparticle diffusion); (4) interaction of adsorbate with the adsorption sites. Usually, for a well-mixing system, steps (1) and (4) are very rapid, thus the total rate of adsorption process may be

\[
\frac{dC}{dt} = -k_1(C - C_0)
\]

\[
\frac{dq}{dt} = \frac{k_2q^2}{1 + q/C_0}
\]

\[
\frac{dq}{dt} = \frac{Aq}{1 + Bq}
\]

\[
\frac{dq}{dt} = \frac{K_{id}q^2}{1 + q/C}
\]

Table 2 | The kinetics model parameters for TC sorption on pumice

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order model</td>
<td>$q_e$ (mg/g)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (L/min)</td>
<td>$k_1$ (L/min)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Pseudo-second-order model</td>
<td>$q_e$ (mg/g)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g/(mg·min))</td>
<td>$k_2$ (g/(mg·min))</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Elovich model</td>
<td>$A$ (mg/(g·min))</td>
<td>$A$ (mg/(g·min))</td>
</tr>
<tr>
<td></td>
<td>$B$ (g/mg)</td>
<td>$B$ (g/mg)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>$K_{id}$ (mg/(g·min$^{0.5}$))</td>
<td>$K_{id}$ (mg/(g·min$^{0.5}$))</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>$C$</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
</tbody>
</table>

Figure 6 | TC sorption kinetics data and fitting curves: (a) pseudo-first-order and pseudo-second-order model; (b) Elovich model; (c) intraparticle diffusion model.

constant (mg/(g·min$^{0.5}$)) and C is a constant associated with the film diffusion effect.
controlled by film and/or intraparticle diffusion (Ho et al. 2000). According to Weber & Morris (1963), if the plot of $q_t$ versus $t^{0.5}$ was a straight line passing through the origin (intercept $C = 0$), the intraparticle diffusion was the sole rate controlling step of the adsorption process. Instead, this straight line did not go through the origin ($C \neq 0$) in the current study (Figure 6(c)), indicating that the diffusion mechanism was complex and might be governed by film and intraparticle diffusion in the adsorption process. Further, the value of intercept $C$ was deemed to provide some information about the importance of the film diffusion effect. The larger the intercept, the greater the film diffusion effect. Obviously, the obtained $C$ value (0.368) in the current study was much lower than the reported value, which was in the order of magnitude of tens, likely implying the slight effect of film diffusion (Khezami & Capart 2005). The above results further confirmed that the intraparticle diffusion played a predominant role in the adsorption process.

**Sorption isotherm and thermodynamics**

The isothermal data of TC sorption on pumice at pH 6 are demonstrated in Figure 7(a). It can be seen that as for different temperature, pumice revealed a high sorption capacity toward TC. At low TC equilibrium concentration ($C_e$), the TC sorption capacity ($q_e$) was relatively high. This possibly hinted at favorable sorption of TC on pumice at low concentrations. The isotherms data were further simulated using

![Figure 7](https://iwaponline.com/wqrj/article-pdf/53/3/143/251999/wqrjc0530143.pdf)
the Langmuir and Freundlich models. The two models were presented as follows.

**Langmuir equation:**

\[ q_e = \frac{bq_mC_e}{(1 + bC_e)} \]  

(5)

**Freundlich equation:**

\[ q_e = K_F C_e^{1/n} \]  

(6)

where \( q_m \) is the maximum sorption amount (mg/g); \( q_e \) is the sorption amount at equilibrium (mg/g); \( b \) is the Langmuir sorption constant (L/mg); \( C_e \) is the equilibrium adsorbate concentration (mg/L); \( K_F \) and \( n \) are constants related to the sorption capacity and affinity, respectively.

For the Langmuir models, the plot of \( 1/q_e \) versus \( 1/C_e \) gives a straight line. For the Freundlich models, plotting \( \ln q_e \) against \( \ln C_e \) also yields a straight line. The isotherm constants of TC sorption were calculated by linear regression as listed in Table 3. It was observed that the pumice displayed a satisfactory sorption performance for TC. With the rise in temperature from 10–20 to 30°C, the obtained Langmuir uptake amount (\( q_m \)) separately increased from 2.594, 3.345, to 4.890 mg/g implying endothermic sorption of TC. The values of correlation coefficient (\( R^2 \)) were all above 0.89 under different temperature conditions, which revealed that the TC sorption on pumice obeyed the Langmuir and Freundlich isotherm very well.

Furthermore, the adsorption affinity constant (\( n \) value) calculated from the Freundlich model ranged from 1 to 10, which suggested the favorable sorption of TC on pumice (Worch 2012).

In order to assess the inherent energy changes of the TC sorption process, adsorption thermodynamic parameters such as free energy change (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) were estimated using Equations (7)–(9):

\[ K_c = \frac{C_A}{C_e} \]  

(7)

\[ \Delta G^0 = -RT \ln K_c \]  

(8)

\[ \ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

(9)

where \( K_c \) is the equilibrium constant; \( C_A \) is the amount of adsorbed TC at equilibrium (mol/L); \( C_e \) is the TC equilibrium concentration in the solution (mol/L); \( R \) is the ideal gas constant (8.314 J/(mol·K)); \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) are separately the changes in free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/(mol·K)) under standard states. \( \Delta H^0 \) and \( \Delta S^0 \) were separately calculated from the slope and intercept of the plot of \( \ln K_c \) against \( T^{-1} \) (K⁻¹).

The plot of \( \ln K_c \) versus \( T^{-1} \) is demonstrated in Figure 7(d). The calculated thermodynamics parameter values by regression analysis are presented in Table 4. The obtained \( \Delta S^0 \) value was positive (54.616 J/(mol·K)), implying that the disorder was increased at the solid/liquid during the TC sorption onto pumice. The \( \Delta G^0 \) values in the current research were also positive, which were separately 2.490, 1.484 and 1.419 kJ/mol. It is generally thought that the change in free energy for physisorption (\( \Delta G^0 \)) is often between –20 and 0 kJ/mol, whereas that of chemisorption is much greater and usually ranged from –80 to –400 kJ/mol (Wu 2007). As such, it was difficult to identify the sorption nature (physisorption or chemisorption) only dependent on the \( \Delta G^0 \) values. Therefore, the thermodynamic parameters were considered for the sorption of TC on pumice.

### Table 3 | Langmuir and Freundlich constants of TC on pumice

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( q_m ) (mg/g)</th>
<th>( b ) (L/mg)</th>
<th>( R^2 )</th>
<th>( K_F )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.594</td>
<td>1.487</td>
<td>0.892</td>
<td>1.103</td>
<td>0.280</td>
<td>0.910</td>
</tr>
<tr>
<td>20</td>
<td>3.345</td>
<td>0.775</td>
<td>0.987</td>
<td>1.111</td>
<td>0.378</td>
<td>0.957</td>
</tr>
<tr>
<td>30</td>
<td>4.890</td>
<td>0.258</td>
<td>0.978</td>
<td>0.966</td>
<td>0.471</td>
<td>0.958</td>
</tr>
</tbody>
</table>

### Table 4 | Thermodynamic parameters of TC sorption on pumice at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
<th>( \Delta H^0 ) (kJ/mol)</th>
<th>( \Delta S^0 ) (J/(mol·K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.15</td>
<td>2.490</td>
<td>17.809</td>
<td>54.616</td>
</tr>
<tr>
<td>293.15</td>
<td>1.484</td>
<td>17.809</td>
<td>54.616</td>
</tr>
<tr>
<td>303.15</td>
<td>1.419</td>
<td>17.809</td>
<td>54.616</td>
</tr>
</tbody>
</table>
The positive value of $\Delta G^o$ also indicated that the TC sorption on pumice was not a spontaneous process under the conditions applied and the system gained external energy as further confirmed by the results on enthalpy changes ($\Delta H^o$). The positive $\Delta H^o$ suggested that TC sorption was an endothermic reaction. This also explained the reason why the adsorption capacity increased with increasing temperature. It is also stated that the $\Delta H^o$ value of physisorption is smaller than 40 kJ/mol (Kara et al. 2003). Thus, based on the calculated $\Delta H^o$ value (17.809 kJ/mol) in the current study, the TC adsorption on pumice was likely attributed to physisorption interactions involving Van der Waals and electrostatic forces. This was consistent with the aforementioned results on ionic strength effects (see ‘Effect of pH and ionic strength’ above). Based on the above consideration, it can be inferred that the TC sorption mechanisms on pumice was mainly attributable to the physisorption through the forming of outer-sphere complex (Van der Waals and electrostatic forces).

**Effect of coexisting cations**

Metal cations such as copper, lead and magnesium often co-occur with TC in aquatic environments, which may affect the TC sorption on pumice (Kang et al. 2010; Andreu et al. 2016). As depicted in Figure 8, at pH 4, 6 and 8, the TC removal increased progressively with increasing cationic concentration from 0 to 0.2 mM. Among these three cations, the presence of Mg$^{2+}$ slightly increased the TC removal under current pH conditions. At pH 4, the promotion effects of Cu$^{2+}$ and Pb$^{2+}$ on the TC removal were also small and the increase efficiency was separately 11.4 and 1.3%, while at pH 6 and 8, this promotion effect became distinct. At pH 6, TC removal separately increased 55.3 and 33.2% in the presence of Cu$^{2+}$ and Pb$^{2+}$. At pH 8, the increase of TC removal was 43.8 and 25.6%, respectively. As a whole, the promotion effect of cations followed the order: Cu$^{2+}$ > Pb$^{2+}$ > Mg$^{2+}$. As shown in Figure 1, at pH 4, the predominate TC species are H$_3$L$^+$ and H$_2$L. As such, the inapparent promotion effect of these cations for the TC removal could be related to the presence of cationic H$_3$L$^+$. At pH 6 and pH 8, neutral H$_2$L and anionic HL$^-$ are separately the main TC forms, thereby, coexisting cations enhanced the TC adsorption on pumice. Similar results were also reported by previous studies, which indicated that the existence of some divalent cations could promote the TC adsorption by acting as a bridge ion (Pils & Laird 2007; Zhao et al. 2015). It was thought that cations such as Cu$^{2+}$ and Pb$^{2+}$ could act as bridge ions between the hydroxyl groups (M-OH) on pumice surfaces and tetracycline via forming surface complexes M-O-Cu-TC and M-O-Pb-TC, whereas Mg$^{2+}$ as divalent cations might form weak outer-sphere complexes with the pumice surface so that it cannot act as a bridge ion to increase the TC adsorption like Cu$^{2+}$ and Pb$^{2+}$.

**Column studies**

For the sustainable use of adsorbent in engineered systems, whether loaded adsorbent can be effectively desorbed and regenerated plays a critical role. Therefore, fixed-bed column studies were carried out to observe adsorption and regeneration efficiency. In previous studies, several regeneration methods such as heating, alkaline solution and organic solvent solution were used for the desorption of organic pollutants from adsorbents (Liu et al. 2013; Güzel & Saygılı 2016; Shan et al. 2016). In the current study, these three regeneration methods were attempted to desorb TC from loaded pumice. By comparison, it was found that organic solvent (alkaline EDTA solution) exhibited the best desorption efficiency. Therefore, alkaline EDTA solution (pH 10, 0.02 M) was selected as the desorption solution for
column regeneration. Figure 9(a) presents the breakthrough curves for three cycles by column adsorption, i.e. the variations of $C_t/C_0$ vs. time. It was found that there was a slight difference among the breakthrough curves for three adsorption cycles. For the three cycles, the average TC removal was separately 27.6, 24.9 and 22.4% within 230 min, which was mainly associated with the bed height, feed concentration and flow rate. After three cycles of adsorption and regeneration, the adsorption capacity of regenerated pumice showed a slight decrease and the pumice adsorbent had the potential for recyclable use many times. This result reveals that TC loaded pumice could be effectively regenerated by alkaline EDTA solution and this regeneration method was relatively inexpensive and feasible for fixed-bed systems.

For each cycle, the TC concentration variation of regeneration effluent with time was also measured and the results are shown in Figure 9(b). It was found that the effluent TC concentrations at 10 min ranged between 59.3 and 60.2 mg/L for the three cycles, which was about two times higher than the influent TC concentration (20 mg/L), indicating the excellent desorption efficiency of TC via alkaline EDTA solution. Thereafter, the effluent TC concentrations were found to decline sharply. After 50 min, the variations of TC concentration in regeneration effluent became apparent and the desorption process gradually approached equilibrium at 200 min. Furthermore, there was a similar trend for the three curves during three adsorption-desorption cycles. The desorption of TC can be basically obtained by using about 800 mL of EDTA desorption solution for the three cycles.

**CONCLUSIONS**

In this study, mineral pumice as an adsorbent material was investigated for TC removal from aqueous solutions. XRF analysis showed that SiO$_2$ and Fe$_2$O$_3$ were the two main components in pumice. Zeta potential results indicated the low pH$_{pzc}$ of pumice. FTIR analysis further confirmed the existence of Si–O–Si and Fe–OH groups on the surface of pumice. The TC adsorption amount declined as the pH increased from 3 to 9. The adsorption process was strongly dependent on ionic strength. Adsorption kinetic data could fit to the pseudo-first-order, pseudo-second-order and Elovich models very well ($R^2 > 0.9$). The regression analysis of the intraparticle diffusion model implied that intraparticle diffusion was the main rate controlling step during TC adsorption. Isotherm data could be well fitted utilizing the Langmuir and Freundlich models. The effect of temperature on TC adsorption was investigated and thermodynamic parameters $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ were estimated. Results showed that the TC uptake amount increased with the increasing temperature and the TC adsorption process was endothermic in nature. Combined results based on ionic strength effect, adsorption kinetics and thermodynamic data indicated that TC adsorption mechanisms mainly involved physisorption (Van der Waals and electrostatic forces) and chemisorption via the formation of inner-sphere complexes.
At pH 6 and 8, coexisting Cu\(^{2+}\) and Pb\(^{2+}\) significantly promoted the TC adsorption via ion bridging action. Column tests showed that TC could be efficiently desorbed from an exhausted column using an alkaline EDTA solution (0.02 M) and the regenerated column could be recycled many times. Results from the current study suggest that pumice is a promising adsorbent for TC removal from water and wastewater.

**ACKNOWLEDGMENTS**

This study was funded by the National Natural Science Foundation of China (No. 51108298) and the Natural Science Foundation of Tianjin (No. 12JCYBJC14800).

**REFERENCES**


Franks, G. V. 2002 Zeta potentials and yield stresses of silica suspensions in concentrated monovalent electrolytes: isoelectric point shift and additional attraction. *J. Colloid Interface Sci.* 249 (1), 44–51.


Mazza, D., Lucco-Borlera, M., Busca, G. & Delmastro, A. 1995 High-quartz solid-solution phases from xenorhesis with composition 2\(\text{MgO}·2\text{Al}_2\text{O}_3·5\text{SiO}_2\) (\(\mu\)-cordierite) and \(\text{Li}_2\text{O}·\text{Al}_2\text{O}_3·\text{nSiO}_2\) (\(n = 2\) to \(4\)) (\(\beta\)-eucryptite): characterization by XRD, FTIR and surface measurements. *J. Eur. Ceram. Soc.* 11 (4), 299–308.


Rodriguez-Mozaz, S., Chamorro, S., Marti, E., Huerta, B., Gros, M., Sánchez-Melsió, A., Borrego, C. M., Barceló, D. &


First received 9 March 2018; accepted in revised form 20 April 2018. Available online 10 May 2018