Perchlorate adsorption onto orange peel modified by cross-linking amine groups from aqueous solutions
Lixiang Zhang, Zhiquan Yang, Ting Li, Shaoqi Zhou and Zhenyi Wu

ABSTRACT
Orange peel was made into a highly efficient bio-sorbent by modification with cross-linking amine groups for perchlorate removal. Bench-scale experiments were performed to explore the factors affecting the perchlorate adsorption onto the modified orange peel (MOP). Perchlorate could be removed effectively at a wide range of pH (from 1.5 to 11). The maximum adsorption capacity of MOP for perchlorate was calculated as 154.1 mg/g within 15 min. The Redlich–Peterson model was fitted to the adsorption isotherm very well ($R^2 > 0.99$). The adsorption process was spontaneous and exothermic, which was proved by thermodynamic parameters (Gibbs energy and enthalpy). The pseudo-second-order kinetic model could provide satisfactory fitting of the experimental data ($R^2 > 0.99$). The scanning electron microscopy and energy-dispersive X-ray analysis indicated that the surface of MOP became smooth and the contents of N and Cl in MOP were increased during the modification process. Elemental analysis results showed that the nitrogen content in MOP was increased to 5.5%, while it was 1.06% in orange peel. The adsorption mechanism was also explored using zeta potential and Fourier transform infrared spectroscopy analysis. Ion exchange was the primary mechanism responsible for uptake of perchlorate onto MOP.

Key words | adsorption, amine groups, modified orange peel, perchlorate

INTRODUCTION
Perchlorate (ClO$_4^-$) has been regarded as an alarming contaminant in soil, public groundwater, and surface water systems. In the United States, the release of perchlorate to surface water and groundwater is observed in more than 35 states, impacting drinking water supplies to more than 20 million people (Yang et al. 2013a). Recently, perchlorate has been detected in retail milk, human breast milk samples, fresh greens (such as lettuce), and other agricultural products and beverages, suggesting that food chain transfer of perchlorate may be relatively ordinary (Parker et al. 2008). The National Resource Council suggests that the maximum intake of perchlorate should not exceed 0.7 μg/(kg d), which corresponds to 24.5 μg/L for a 70 kg man with daily water consumption of 2 L (Baidas et al. 2011).

Both natural and anthropogenic sources lead to the widespread presence of perchlorate in the environment (Blount et al. 2010). Naturally occurring perchlorate is found in the Atacama Desert as a microcomponent of natural NO$_3^-$-abundant salt deposits and is detected in Chilean-based fertilizer (Böhlke et al. 2009). Synthetic perchlorate is widely used in solid rocket fuels, explosives, propellants, and some consumer products (Sahu et al. 2009). The improper disposal of these perchlorate-containing wastes is the primary reason for widespread perchlorate contamination of soil and water sources. The public health concerns surrounding perchlorate contamination are based on the fact that perchlorate can interfere with iodide uptake in the thyroid gland, affecting the production of thyroid hormones when it is ingested. For fetuses and infants, the thyroid has a primary role in central nervous system development and skeletal growth. The lack of thyroid hormones possibly causes mental retardation (Hurley & Shapley 2007).
Because perchlorate ions are characterized by high solubility, kinetic inertness, low adsorptive capacity, and non-volatility, perchlorate can be quite persistent in water and is very difficult to be removed from water (Yoon et al. 2009). A variety of treatment technologies have been developed for perchlorate removal from water. These technologies fall into two general categories: (i) physico-chemical technologies, such as activated carbon adsorption, ion exchange, electrochemical reduction, and membrane filtration; and (ii) biological approaches, such as composting, bioreactors, phytotechnology, and in situ bioremediation (Hurley & Shapley 2007). However, the most cost-effective technologies for perchlorate are currently limited to selective ion exchange and bioremediation (Sahu et al. 2009). A major disadvantage of ion exchange is its cost. Post-separation treatment of the contaminated resin or of the concentrated regeneration brines is necessary for complete disposal (Zhang et al. 2011). The biggest problem with bioremediation is public acceptance of its direct application to drinking water, which may introduce pathogenic microorganisms. In addition, biological reduction is relatively slow and is extremely sensitive to salinity changes and pH (Choe et al. 2010).

Adsorption technology in wastewater treatment is still one of the most important techniques due to its simplicity, high capacity, and treatment efficiency. Many fresh adsorption materials are researched for perchlorate removal from the aqueous solution (Kumar et al. 2010). Activated carbon is widely used to remove contaminants from water. However, it is found to be less effective for adsorbing perchlorate and needs to be modified or tailored (Seliem et al. 2011). In recent years, biomaterials, such as wheat straw and giant reed, have been successfully applied in removal of perchlorate (Tan et al. 2012). However, it is relatively difficult to collect these biomaterials especially in urban areas. Orange peel (OP), as a kind of fruit waste material, is common in our daily life, but has received little attention for adsorption of anion contaminants, especially for perchlorate. It is an environmental way for waste OP to be reused to remove contaminants in water.

In this research, batch experiments are conducted to explore ClO₄⁻ and modified orange peel (MOP) interactions at the interface. The effects of dosages of adsorbent, pH, and initial perchlorate concentration are studied to determine optimal adsorption conditions. Adsorption isotherms and kinetic models are constructed to understand the underlying mechanism of perchlorate adsorption onto MOP. And physicochemical properties of MOP are further illustrated by the zeta potential analysis, Fourier transform infrared spectroscopy (FTIR), elemental analysis, and scanning electron microscopy and energy-dispersive X-ray (SEM–EDX) analysis.

**MATERIAL AND METHODS**

**Preparation**

The OP was obtained from Guangzhou, Guangdong, China. The peel was washed with distilled water to remove the adhering dirt and dried at 333 K for 24 h. The dried peel was crushed and sieved into fragments with diameter from 0.1 to 0.45 mm. These fragments were stored in a drying oven for further OP modification. Four grams of virgin OP was mixed with 60 mL of epichlorohydrin and 80 mL of N, N-dimethylformamide in a 1 L three-necked, round-bottomed flask at 373 K for 1 h. A total of 15 mL of pyridine as catalyst was added dropwise and the solution was stirred for 1 h at 373 K. Thereafter, 30 mL of 33% dimethylamine water solution (w/w) was added and the mixture was stirred for 3 h at 373 K. The final product was washed with four kinds of solution (NaOH (0.1 mol/L), HCl (0.1 mol/L), 50% C₂H₅OH (w/w), NaCl (0.1 mol/L)). Then, it was filtered, dried at 333 K for 12 h and sieved to get particles with lengths of 0.15–0.3 mm. The modified adsorbent (i.e. MOP) was used in all the adsorption experiments.

**Reagents**

All the chemicals purchased from Guangzhou Chemical Reagent Factory were of analytical grade, except where noted otherwise. Agents for modification were epichlorohydrin, N,N-dimethylformamide, pyridine, dimethylamine (chemical pure), NaOH, HCl, C₂H₅OH, and NaCl. Chemicals for adsorption tests were NaClO₄·H₂O, HCl, and NaOH. All stock solutions were prepared using chemicals and ultrapure water. Perchlorate stock solution containing 1,000 mg/L ClO₄⁻ was prepared by dissolving 1.41 g sodium perchlorate monohydrate (NaClO₄·H₂O) in 1,000 mL of ultrapure water.

**Perchlorate analysis**

Perchlorate was measured using the ion chromatography (IC) system ( Dionex ICS-1000). The IC instrument was equipped with an EG40 eluent generator, a suite of 4 × 250 mm AS20 and AG 20 columns, a 1,000 μL sample loop, a DS53 detection stabilizer, and a 4-mm ASRS Ultra II suppressor. The suppressor current was 50 mA. The
mobile phase was set to 2.5 mM NaOH. The injection volume was 1 mL. The sample running time was 17 min.

**Physicochemical measurements**

The physicochemical properties of MOP, virgin OP, and perchlorate-loaded MOP were measured by zeta potential analysis, surface area analysis, FTIR, SEM–EDX, and elemental analysis.

The zeta potentials of OP, MOP, and perchlorate-loaded MOP samples were measured using a Nano ZS90 Zetasizer (Malvern Instruments Limited, Malvern, UK). The three samples were prepared in 100 mL of ultrapure water containing 0.2 g of samples and were shaken for 10 min.

Specific surface area of MOP and virgin OP was measured with an automatic BET (Brunauer–Emmett–Teller) surface area analyzer (Micromeritics ASAP 2020 M apparatus, USA). Prior to analysis, the samples were degassed overnight (12 h) under nitrogen at 373 K.

The surface functional groups of OP, MOP, and perchlorate-loaded MOP were characterized by FTIR spectrometry (Vector 33 Bruker, Germany). The spectrum was scanned from 400 to 4,000 cm$^{-1}$.

Morphological analysis of the three samples was performed by SEM using a Carl Zeiss EVO LS 10 microscope (applied voltage: 10 kV) and EDX. The samples were coated with platinum before the SEM images were obtained. The nitrogen content of MOP was evaluated by an element analyzer (Elementar Vario EL, Germany).

**Adsorption tests**

Isotherm tests were performed to determine the maximum adsorption of MOP for ClO$_4^-$ . MOP (0.2 g) was mixed with 100 mL of solutions in 250 mL beaker flasks containing 100, 150, 200, 250, 300, 400, and 500 mg/L of ClO$_4^-$ respectively. The suspensions were shaken at the speed of 150 rpm in a thermostat shaker for 24 h (303 K). The pH of each solution was controlled at 7.0 ± 0.5 by adjustment with 0.1 M HCl and 0.1 M NaOH. After equilibrium, 10 mL samples with different perchlorate concentrations were collected and filtered using 0.45 μm membrane filter (nylon 66, Jin Teng, Tianjin, China). Then the perchlorate concentration was measured by IC.

Kinetic studies were examined with 0.2 g MOP in a 100 mL suspension containing 100 mg/L ClO$_4^-$ in 250 mL beaker flasks. The suspensions were stirred at 283, 303, and 323 K and the samples were taken at 0, 1, 2, 3, 5, 8, 10, 15, 20, 30, 45, and 60 min, respectively, then analyzed by IC.

The effects of different adsorbent dosage on perchlorate adsorption were investigated by adding MOP of 0.02, 0.05, 0.1, 0.2, 0.4 g in 100 mL solutions containing 100 mg/L of ClO$_4^-$ . The pH effect experiments were studied by adjusting the initial pH of the solution from 1 to 13 using 0.1 M HCl and 0.1 M NaOH, while the initial perchlorate concentration was kept at 100 mg/L.

**RESULTS AND DISCUSSION**

**Effect of adsorbent dose**

The dependence of perchlorate adsorption on adsorbent dose was investigated. As shown in Figure 1, the percentage removal of perchlorate is increased from 32.82 to 93.32% with the adsorbent dose increasing from 200 to 2,000 mg/L, because the number of exchangeable sites is increased with the increase of the adsorbent dose (Jalali & Aboulghazi 2016). However, the removal percentage and adsorption capacity are not increased significantly when the adsorbent dose is increased from 2,000 to 4,000 mg/L. It shows that the adsorption of perchlorate had reached equilibrium when the adsorbent dose exceeded 2,000 mg/L. The reason may be that the adsorptive active sites remain vacant for perchlorate adsorption on further adding adsorbent dose (Murugesan et al. 2013). A total of 2,000 mg/L dosage was selected as optimum dose for further adsorption experiments.

**pH and zeta potential analysis**

The effect of pH on ClO$_4^-$ adsorption onto MOP is illustrated in Figure 2(a). The maximum adsorption capacity of
45.8 mg/g is obtained in the pH range between 1.5 and 11, and the amount of perchlorate removal keeps steady in this pH range. However, the percentage removal of perchlorate is decreased by 87% when the pH is increased from 11 to 13. This accelerating decrease can be interpreted by the presence of excess hydroxide ions competing with perchlorate ions for exchangeable sites at high pH values. Meanwhile, when the pH is lower than 1.5, the perchlorate sorption capacity drops a little. The reason may be that part of the perchlorate ions exist in the form of HClO4 and perchloric acid will interfere with the sorption of perchlorate (Xu et al. 2011). Based on the data of Figure 2(a), optimum efficiency of perchlorate removal was achieved at wide pH range (1.5–11.0).

The change of the zeta potential of OP before and after modification is studied as a function of pH (Figure 2(b)). The zeta potential of virgin OP presents negative charges in the pH range of 3–11, and is decreased from −12.4 to −32.7 mV as the pH increased from 3 to 11, whereas the zeta potential of clean MOP remains positively charged over the entire pH range. The result indicates that the cross-linked quaternary amine functional groups in OP enhanced the surface potential of OP (Yoon et al. 2009). As shown in Figure 2(b), the zeta potential of clean MOP keeps at around 20 mV. Therefore, it was in agreement with the result that perchlorate adsorption onto MOP remained constant in the pH range of 3–11 (Figure 2(a)). When ClO4 was adsorbed to clean MOP, the zeta potential was improved. The reason may be that the chloride on the surface of the adsorbent is replaced by perchlorate. Since the anion volume of chloride (0.047 nm³) is less than that of perchlorate (0.083 nm³) (Jenkins et al. 1999), steric effects results in the adsorbed perchlorate anion occupying more space on the MOP than chloride. This will increase the zeta potential.

**Adsorption isotherms**

The adsorption isotherm is used to describe equilibrium relationships between sorbent and sorbate. In this study, Langmuir, Freundlich, and Redlich–Peterson models were used to determine the adsorption equilibrium between the adsorbent and ClO4. The Langmuir adsorption isotherm assumes monomolecular adsorption onto homogeneous active sites on adsorbents. The equilibrium data for the adsorption of perchlorate are represented using the Langmuir equation, which is expressed as (Jiang et al. 2014):

\[
q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e}
\]  

where \(q_e\) and \(C_e\) are the adsorption capacity (mg/g) and equilibrium concentration of perchlorate (mg/L), respectively. \(K_L\) is the Langmuir constant (L/mg), and \(q_{max}\) is the maximum adsorption capacity (mg/g).

The Freundlich isotherm is based on the assumption that the binding sites on the surface of adsorbent are heterogeneous, and multilayer adsorption can occur during the adsorption process, which can be shown in the following form (Jiang et al. 2013a):

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

where \(K_F\) and \(n\) are the Freundlich constants. \(K_F\) is related to the adsorption capacity [(mg/g)/(mg/L)] and \(n\) is a dimensionless exponent relating to the adsorption intensity.
Incorporating features of both Langmuir and Freundlich isotherms, the Redlich–Peterson model is in line with the Langmuir model at low concentrations and approaches the Freundlich model at high concentrations. The Redlich–Peterson isotherm (Ho et al. 2002) can be described as follows:

\[ q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \]  

(3)

where \( K_R \) and \( a_R \) are the Redlich–Peterson constants. \( b_R \) is an exponent having a value between 0 and 1: when \( b_R = 0 \), the model becomes a form analogous to the Freundlich isotherm; when \( b_R = 1 \), the equation reduces to the Langmuir model.

The parameters of Langmuir, Freundlich, and Redlich–Peterson for the adsorption of perchlorate onto MOP are shown in Table 1. It is found that the adsorption conformed better to the Redlich–Peterson model with correlation coefficient \( R^2 \) of 0.9979, higher than those of the Langmuir model (\( R^2 = 0.9824 \)) and Freundlich model (\( R^2 = 0.9632 \)), indicating that the Redlich–Peterson model better described the adsorption mechanism of the MOP. The results strongly suggested that the perchlorate adsorption onto MOP was not an ideal monolayer adsorption.

At the beginning of the adsorption process with high concentration of perchlorate in aqueous solution, the adsorption conformed to the multiple adsorption. When the adsorption reaction was about to achieve equilibrium, the adsorption would accord with the mono-adsorption. All in all, the value of \( b_R \) (\( b_R = 0.868 \)) showed that the monolayer adsorption had a dominant status in the adsorption process (Yang et al. 2013b).

**Temperature effect**

To analyze the thermodynamic parameters, the temperature dependence of perchlorate adsorption onto MOP was studied at 283, 303, and 323 K. The results are shown in Figure 3(a); it is noticed that the perchlorate adsorption capacities decrease with increase of temperature, indicating the exothermic nature of adsorption. The thermodynamic spontaneity and feasibility of the sorption process were determined by calculating the three basic thermodynamic parameters: free energy change (\( \Delta G \)), enthalpy change (\( \Delta H \)), and entropy change (\( \Delta S \)). These parameters can be determined by using the following equations:

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

(4)

### Table 1 | isotherm parameters for the adsorption of perchlorate onto MOP

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>( K_L ) (L/mg)</th>
<th>( R^2 )</th>
<th>( q_e ) (mg/g)</th>
<th>( K_F ) ((mg/g)/(mg/L))</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( K_R ) (L/g)</th>
<th>( a_R ) (L/mg)</th>
<th>( b_R )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>154.1</td>
<td>0.049</td>
<td>0.9824</td>
<td>31.24</td>
<td>3.376</td>
<td>0.9632</td>
<td></td>
<td>11.86</td>
<td>0.154</td>
<td>0.868</td>
<td>0.9979</td>
</tr>
<tr>
<td>Freundlich</td>
<td>31.24</td>
<td>3.376</td>
<td>0.9632</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td></td>
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</table>

**Figure 3** | (a) Effect of temperature on the adsorption capacity; (b) plots of \( \ln K_c \) versus 1/T for perchlorate sorption on MOP (pH – 8; contact time, 24 h).
\begin{equation}
\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}
\end{equation}

where \( R \) is the ideal gas constant (8.314 J/(mol K)) and \( T \) is the Kelvin temperature. The distribution constant \( K_c = q_e/C_e \), where \( q_e \) and \( C_e \) are equilibrium solute concentration on solid surface and in liquid phases, respectively. The thermodynamic parameters are listed in Table 2. The negative value of \( \Delta G \) suggests the perchlorate adsorption onto the MOP surface was spontaneous, and the results show that the values of \( \Delta G \) become less negative with increasing temperature, indicating that sorption was unfavorable at high temperatures. In addition, it is evidence of an exothermic adsorption reaction that the values of \( \Delta G \) decrease with rising in temperature (Wagle et al. 2013). The \( \Delta H \) values for the adsorption of perchlorate are negative due to the exothermic nature of the adsorption. \( \Delta S \) is calculated as \(-0.036\) kJ/(mol K), indicating that the degree of freedom of adsorbate ion was decreased during the perchlorate adsorption onto MOP (Nibou et al. 2010).

### Adsorption kinetics

Figure 3(a) shows the effect of adsorption time on perchlorate removal by MOP at different temperatures. The amount of adsorbed perchlorate was increased with an increase in contact time. The system attained equilibrium within 15 min in all cases, showing that the adsorption occurred quickly. This can be attributed to two facts: one is that all exchange sites of the fresh adsorbent are available for anion exchange, the other is that initial concentration of perchlorate is high. After 15 min, the curves tend to be horizontal with increasing time, which suggests that the system reached equilibrium. Once the saturation of exchange sites was achieved, the adsorption capacity of perchlorate remained almost constant due to decrease in the number of available sites.

According to the experimental data obtained from the studies of contact time, two different adsorption kinetic models, the pseudo-first-order and the pseudo-second-order, were used to elucidate the mechanisms of adsorption and potential rate-controlling steps (Swain et al. 2013). The linear form of the pseudo-first-order kinetic model can be written as:

\begin{equation}
\ln (q_e - q_t) = \ln q_e - k_1 t
\end{equation}

where \( q_e \) and \( q_t \) are the adsorption capacity of perchlorate (mg/g) at equilibrium and any time \( t \) (min), respectively; \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)).

Another adsorption model is the pseudo-second-order kinetic. Its equation is expressed by:

\begin{equation}
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\end{equation}

where \( k_2 \) is the equilibrium rate constant of the pseudo-second-order adsorption (g/(mg min)); \( q_t \) and \( q_e \) (mg/g) are the amount of perchlorate adsorbed at any time \( t \) (min) and equilibrium, respectively.

The corresponding kinetic parameters from both models are summarized in Table 3. It can be seen from Table 3 that the correlation coefficient \( (R^2) \) from the pseudo-second-order kinetic is larger than that from the pseudo-first-order kinetic at three different temperatures, and the experimental \( q_e \text{exp} \) values match well with the calculated \( q_e \text{cal} \) values obtained from the pseudo-second-order plot. This result indicated that the adsorption of perchlorate onto MOP was better described by the pseudo-second-order kinetic model.

### Table 2 | Thermodynamic parameters for adsorption of perchlorate on MOP

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (kJ/(mol K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>-6.617</td>
<td>-16.805</td>
<td>-0.036</td>
</tr>
<tr>
<td>303</td>
<td>-5.714</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-5.186</td>
<td></td>
<td></td>
</tr>
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</table>

### Table 3 | The pseudo-first-order and pseudo-second-order kinetic parameters of perchlorate adsorption onto MOP

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>Measured ( q_e \text{exp} ) (mg/g)</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 ) (min(^{-1}))</td>
<td>( q_e \text{cal} ) (mg/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>283</td>
<td>48.6</td>
<td>0.0826</td>
<td>4.128</td>
</tr>
<tr>
<td>303</td>
<td>47.7</td>
<td>0.0244</td>
<td>1.272</td>
</tr>
<tr>
<td>323</td>
<td>46.7</td>
<td>0.0337</td>
<td>1.448</td>
</tr>
</tbody>
</table>
than the pseudo-first-order kinetic model. The pseudo-second-order kinetic model assumes that the rate-limiting step might be chemisorption (Wu et al. 2011). The values of the pseudo-second-order rate constant \( k_2 \) are observed to increase from 0.06 to 0.23 g/(mg min) with an increase in temperature from 283 to 323 K, which indicates that the adsorption rate was increased with the increase of temperature.

**Elemental analysis**

The elemental compositions of virgin OP and MOP are listed in Table 4. The virgin OP contains large amounts of C (42.14%), H (6.986%) element, and little N (1.06%) element. After modification, the content of N element is raised to 5.5%, which is caused by the amine cross-linking reaction.

**FTIR analysis**

The FTIR spectra are employed to identify the functional groups of samples (Jiang et al. 2013b). FTIR spectra of virgin OP, clean MOP, and ClO\(_4\)-loaded MOP are characterized and shown in Figure S1 (Supplementary Material, available online at http://www.iwaponline.com/wst/071/130.pdf). In the FTIR spectra of virgin OP and clean MOP, some peaks disappear after modification. It demonstrates that some functional groups in OP were lost during the modification of OP. However, two new peaks at 602 and 1,445 cm\(^{-1}\) are observed in the spectrum of clean MOP. The appearance of the band at 602 cm\(^{-1}\) corresponds to the stretching vibration of the C-Cl bond, which was obtained from the grafted chemical reagent of epichlorohydrin. This peak at 602 cm\(^{-1}\) in the spectrum of clean MOP was observed to shift to 625.52 cm\(^{-1}\) once perchlorate was adsorbed onto MOP. This may be ascribed to the exchange of adsorbed perchlorate with the chloride on the surface of MOP. The broad peaks at 1,445 cm\(^{-1}\) are related to the stretching vibration of \(-\text{NH}_2\) groups (Bayramoglu et al. 2013). Two peaks at 3,441 and 3,460 cm\(^{-1}\) are assigned to hydroxyl groups (–OH) of macromolecular association in cellulose, hemicellulose, pectin, etc. After adsorption of perchlorate onto MOP, the special vibration at 1,445 cm\(^{-1}\) disappeared. This indicates that \(-\text{NH}_2\) groups were involved in the perchlorate adsorption process.

**SEM–EDX analysis**

The SEM micrographs of samples are presented in Figure S2 (Supplementary Material, online at http://www.iwaponline.com/wst/071/130.pdf). The image of virgin OP (Figure S2(a)) illustrates that the biomass had a partly fibrous structure and that there were highly heterogeneous pores in OP particles. After the modification, the SEM micrograph of MOP (Figure S2(b)) indicates that the surface of MOP becomes smooth, which suggests that almost all ash and extractives in OP were removed during the process of modification. The SEM photograph of perchlorate-loaded MOP (Figure S2(c)) indicates that no remarkable difference was observed. Moreover, few porous structures are observed on the surfaces of virgin OP and clean MOP. This phenomenon was consistent with the result obtained by BET surface area tests, which showed that the specific surface area and micropore volume could not be detected. The results showed that the chemical adsorption played a dominant role during the adsorption process, which was in accord with the results of pseudo-second-kinetic.

The EDX analysis spectrums of virgin OP, clean MOP, and perchlorate-loaded MOP are shown in Figure S3 (Supplementary Material, online at http://www.iwaponline.com/wst/071/130.pdf). Comparing the EDX spectrum before and after modification, there is an obvious increase in contents of N and Cl elements (Figure S3(a) and S3(b)). The increase in content of N element is attributed to an increase of amino groups after the dimethylamine is grafted into the structure of MOP. Chlorine element appears at 2.62 KeV (Figure S3(b)) after modification due to the grafted chemical reagent of epichlorohydrin.

**CONCLUSIONS**

1. OP was modified by cross-linking amine groups for perchlorate removal. Optimum efficiency of perchlorate removal was achieved at wide pH range (1.5–11.0).
2. The highest adsorption capacity of MOP for perchlorate was 154.1 mg/g. The adsorption isotherm fitted well with the Redlich–Peterson model. The thermodynamic data indicated that the adsorption process was spontaneous and exothermic.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Elemental compositions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin OP</td>
<td>C 42.14</td>
</tr>
<tr>
<td>MOP</td>
<td>C 49.5</td>
</tr>
</tbody>
</table>

Table 4 | Elemental compositions of virgin OP and MOP
3. Perchlorate adsorption onto MOP occurred rapidly and reached equilibrium within 15 min. Kinetic results were well described by the pseudo-second-order kinetic model.

4. Elemental analysis and SEM-EDX micrographs indicated that large amounts of amine groups were grafted on to the surface of MOP. The analysis from zeta potential and FTIR suggested that the interaction between MOP and ClO₄⁻ was ion exchange.

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