Perchlorate Adsorption by Granular Activated Carbon Modified with Cetyltrimethyl Ammonium Chloride

PENG YIN-XIAN*, 1ZHENG LU, 1CAI CUI-YUN, 1ZHU MING-LONG, 1ZHOU YANG AND 2WU CHUN-DU
1School of Biology and Chemistry Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China.
2School of Environment, Jiangsu University, Zhenjiang 212003, China.
pengyinxian@yahoo.com.cn*
(Received on 4th November 2011, accepted in revised form 30th March 2012)

Summary: To improve the adsorption of perchlorate (ClO\textsubscript{4}\textsuperscript{-}) in contaminated water, granular activated carbon (GAC) was modified with cetyltrimethyl ammonium chloride (CTAC). To investigate the adsorption mechanism of perchlorate the structure of GAC-CTAC was characterized by scanning electron microscopy (SEM) and FTIR spectroscopy. Then the GAC-CTAC was used for the adsorption of perchlorate in water. The effects of the adsorption time, pH, initial ClO\textsubscript{4}\textsuperscript{-} concentration, and co-existed anions on perchlorate adsorbed by GAC-CTAC were studied. The results show that the GAC-CTAC could absorb perchlorate better in water. The adsorption capacity of perchlorate on GAC-CTAC decreases in the alkaline solution, and increases with increasing the initial concentration. The competitive adsorption exists between co-existed anions and ClO\textsubscript{4}\textsuperscript{-} on GAC-CTAC. In addition, adsorption of ClO\textsubscript{4}\textsuperscript{-} on GAC-CTAC fits the Langmuir, Freundlich and Tempkin isothermal models in the range of the experimental concentration. The adsorption process follows pseudo-second order kinetics.

Introduction

Perchlorate (ClO\textsubscript{4}\textsuperscript{-}) is regarded as a new emerging persistent inorganic contaminant because of its specific properties, such as high water solubility, mobility and considerable stability [1]. It is used as a solid rocket oxidant and ignitable combustion source in munitions and fireworks, or in roadside flares and air bag inflation systems [2]. The improper use of perchlorate led to perchlorate contamination in groundwater [3]. Widespread contamination of perchlorate in sewage sludge, rice, bottled drinking water and milk collected from different areas in China has been confirmed. The concentration of perchlorate in sewage sludge, rice, bottled drinking water and milk is in the range of 0.56-379.9 µg/kg, 0.16-4.88 µg/kg, 0.037-2.013 µg/L and 0.30-9.1 µg/l, respectively [4]. The results show that perchlorate pollution is widespread in China.

Different approaches have been made to remove ClO\textsubscript{4}\textsuperscript{-} from wastewater, including chemical reduction, ion exchange, osmosis, biodegradation and adsorption, have been reported [5]. Among them adsorption method is simple and cost-effective, and thus has been widely used. However, we have found that GAC is ineffective for removing ClO\textsubscript{4}\textsuperscript{-} because perchlorate exists in anion species [6, 7], though it is generally considered cost-effective for water treatment in situations where the contaminant can be removed from water solubility [8, 9]. It has been studied that GAC coated with a cationic surfactant is an effective adsorbent for removal of perchlorate [10, 11]. In this study, GAC was modified with cetyltrimethyl ammonium chloride (CTAC). The cationic surfactant utilized in this work contained a quaternary ammonium function group, which is comprised of a positively charged central nitrogen atom with 4 bonds to carbon atoms. GAC could be preloaded with CTAC to adsorb for perchlorate. The influencing factors in the adsorption, kinetic and thermodynamic of perchlorate on GAC-CTAC were studied, to show the adsorption efficiency of GAC-CTAC and therefore to determine its potential applications.

Results and Discussion

Effects on the Adsorption of Perchlorate onto GAC and GAC-CTAC

Effects on the adsorption of perchlorate onto GAC and GAC-CTAC are shown in Fig. 1. Typically, GAC-CTAC exhibited a higher adsorption capacity than GAC, which highlighted the key role of CTAC. The maximum perchlorate adsorbed on GAC-CTAC was about twenty-six times as much as that adsorbed on GAC.

Effects of Reaction Conditions Affecting Adsorption of Perchlorate on GAC-CTAC

Effect of pH

The effect of solution pH (3, 6, 9 and 12) on perchlorate adsorption by GAC-CTAC is shown in
Fig. 2. Solution pH significantly affected perchlorate adsorption. When solution pH increased from 3 to 12, the perchlorate removal percentage decreased from 95% to 35%. Activated carbon has more positive charge with the decrease of pH [14]. This increased the adsorption of perchlorate onto GAC-CTAC. Likewise, with the increase of pH (become more alkalinous), the GAC-CTAC surface became more negatively charged and subsequently less perchlorate was adsorbed.

![Graph showing solution pH significantly affected perchlorate adsorption.](image)

**Fig. 1:** Effects on the adsorption of perchlorate onto GAC and GAC-CTAC (C₀=1.0 mg/L, T=33 °C, pH 3, adsorbent dosage was 0.02g).

**Effect of Initial Perchlorate Concentration**

Fig. 3 shows the adsorption of perchlorate on GAC-CTAC at different perchlorate initial concentrations (0.1, 1.0, 2.0 and 5.0 mg/l). It is shown that the perchlorate removal efficiency decreased with the increase initial perchlorate concentration. When the initial perchlorate concentration increased from 0.1 to 5.0 mg/l, the perchlorate removal percentages change from 100% to 48%. Within the concentration range of the experiments, a lower-concentration of perchlorate could be better bonded with the active adsorption sites on GAC-CTAC. When the concentrations of perchlorate became higher, an amount of perchlorate remained, which was due to the all-occupied active adsorption sites, and therefore, the perchlorate removal percentage was reduced.

![Graph showing effect of initial concentration on perchlorate adsorption on GAC-CTAC](image)

**Effects of Co-existing Anions**

The perchlorate contaminating water always contains several other common anions, such as Cl⁻, NO₃⁻, H₂PO₄⁻, ClO₃⁻, SO₄²⁻ and S₂O₃²⁻, which may compete with perchlorate to occupy the adsorption sites during the adsorption process. Effects of co-existing anions are shown in Fig. 4, where line a was 1.0 mg/L ClO₄⁻ solution with no other ions, while lines b, c, d, e, f and g were 1.0 mg/L ClO₄⁻ solutions with 5.0 mg/L Cl⁻, NO₃⁻, H₂PO₄⁻, ClO₃⁻, SO₄²⁻ and S₂O₃²⁻, respectively. Results demonstrated that the competitive adsorption existed between co-existing anions and ClO₄⁻ on GAC-CTAC and the order of competitive effect was S₂O₃²⁻ > SO₄²⁻ > Cl⁻ > H₂PO₄⁻ ≈ NO₃⁻ ≈ ClO₃⁻. In the tests where there were bivalent anions, such as S₂O₃²⁻ and SO₄²⁻, the removal rate was reduced to 61% and 64% of the original, respectively. For the univalent anions, such as Cl⁻, H₂PO₄⁻, NO₃⁻ and ClO₃⁻, the removal rate was reduced to 67%, 87%, 88% and 85% of the original, respectively. These co-existing anions competitively bonded to the surface of GAC-CTAC, leading to the reduction of the removal rate of ClO₄⁻.

**Adsorption Kinetic**

The pseudo-first-order rate equation and the pseudo-second-order rate equation are defined as follows [15]:

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

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

\[q_e \text{ and } q_t\] are the adsorption capacity at equilibrium and time \(t\), respectively (mg·g\(^{-1}\)),

\(k_1\) (ℓ·min\(^{-1}\)) and \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) stand for the rate constant of pseudo-first-order adsorption, the rate constant of pseudo-second-order, respectively.

\[t\] = \(1/(q_e^2 k_2)+t/q_e\) \hspace{1cm} (2)

\[q_t=kt^{1/2}+ L\] \hspace{1cm} (3)

Fig. 4: Effects of co-existing anions on perchlorate adsorption on GAC-CTAC. (\(C_0=1.0 \text{ mg/L}, \ T=30 \degree \text{C}, \ pH \ 3, \ GAC-CTAC:0.02 \text{ g})\).

The Bangham equation is used to simulate the experimental data, from which it can be ascertained whether pore diffusion is the only rate control step in adsorption or not [15].

\[\log_{10} \left[ \log_{10} \left( \frac{c_0}{c_0 - q_t m} \right) \right] = \log_{10} \left( k_0 \frac{m}{2.303V} \right) + \alpha \log_{10}(t)\] \hspace{1cm} (4)

where:

\(c_0\) is the initial perchlorate concentration (mg/l),

\(m\) is the amount of GAC-CTAC added in per liter solution (g/ℓ),

\(V\) is the solution volume (ml),

\(\alpha\) (<1) and \(k_0\) are constants.

To calculate the kinetic parameters of ClO\(_4^-\) adsorbed on GAC-CTAC at different pH and initial concentrations, equations (1) to (4) were evaluated based on the experimental data. As shown in Table-1, adsorption data were fitted well with the four kinetic models, which indicated that perchlorate adsorption on GAC-CTAC was a complex heterogeneous solid-liquid reaction, and there were several reaction stages corresponding to different reaction kinetic models. The kinetic adsorption process could be best described by the pseudo-second-order rate model (\(r^2 > 0.9840\)), demonstrating that it was the main mechanism for the adsorption of ClO\(_4^-\) on GAC-CTAC [16]. In addition, the initial adsorption rate (h) in neutral or acid condition was larger than that that in alkalinous condition. The pseudo-second-order rate constant \(k_2\) decreased from 0.0546 g/(mg·min) to 0.0038 g/(mg·min) and the initial adsorption rate \(h\) increased dramatically from 0.1298 mg/(g·min) to 1.6866 mg/(g·min), corresponding to the initial perchlorate concentrations increased from 0.1 mg/L to 5.0 mg/L, respectively. This might be due to that the higher initial concentration accelerated the distribution in both liquid and solid phases in the early adsorption, and occupied the limited active adsorption area on the GAC-CTACs, which in turn affected the reaction kinetic. The intra-particle diffusion model and the Bangham equation were well fitted, suggesting that there is a process of big pore diffusion, and the pore diffusion might be the major rate control step.

**Adsorption Isotherm Models**

According to Section 2.2.4, the adsorption isotherms under the different temperature conditions, are shown in Fig. 5. As can be seen in Fig. 5, isotherms of adsorption of perchlorate onto GAC-CTAC are shaped like the letter L. Normally, it can be fitted with the Langmuir, Freundlich and Tempkin isothermal models.

<table>
<thead>
<tr>
<th>Initial condition</th>
<th>Pseudo-first-order rate model</th>
<th>Pseudo-second-order rate model</th>
<th>Intra-particle diffusion model</th>
<th>Bangham equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_0) (mg/L)</td>
<td>pH</td>
<td>(k_1) (h(^{-1}))</td>
<td>(k_2) (g/(mg·h))</td>
<td>(h) (mg/(g·min(^0.5)))</td>
</tr>
<tr>
<td>0.1</td>
<td>3.0</td>
<td>0.1812</td>
<td>0.9854</td>
<td>0.0546</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.0965</td>
<td>0.9579</td>
<td>0.0005</td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>0.0191</td>
<td>0.9557</td>
<td>0.0038</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>0.0104</td>
<td>0.7596</td>
<td>0.0042</td>
</tr>
<tr>
<td>1.0</td>
<td>6.0</td>
<td>0.0357</td>
<td>0.9658</td>
<td>0.0077</td>
</tr>
<tr>
<td>1.0</td>
<td>9.0</td>
<td>0.0256</td>
<td>0.9624</td>
<td>0.0088</td>
</tr>
<tr>
<td>1.0</td>
<td>12.0</td>
<td>0.0228</td>
<td>0.9778</td>
<td>0.0186</td>
</tr>
</tbody>
</table>
Langmuir Isotherm Model

It is assumed by the Langmuir isotherm model that the surface of adsorbent is the same everywhere, as well as the adsorption energy. It is a single-layer adsorption. The adsorption capacity reaches the maximum when the surface of the adsorbent is saturated with adsorbate.

The Langmuir isotherm equation is as follow:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$  \hspace{2cm} (5)

where $C_e$ is the equilibrium concentration of ClO$_4^-$ in solution (mg/L), $Q_0$ is the saturation adsorption capacity of Langmuir adsorption isotherm (mg/g); $b$ is the reciprocal of the half of saturation adsorption capacity in the equilibrium concentration (l/mg); $q_e$ is the equilibrium concentration of solid phase (mg/g). $Q_0$ and $b$ can be obtained by plotting $\frac{C_e}{q_e}$ vs. $C_e$, and are defined by the slopes and intercepts of the line, respectively. The data are summarized in Table-2.

Langmuir isotherm properties can be expressed by the dimensionless coefficient of equilibrium constant $R_L$ which is defined as follow:

$$R_L = 1/(1 + b c_{\text{max}})$$  \hspace{2cm} (6)

where $c_{\text{max}}$ is the largest of initial ClO$_4^-$ concentration, 2 mg/L.

Freundlich Isotherm Model

The Freundlich equation is applicable to highly heterogeneous surfaces, and an adsorption isotherm lacking a plateau indicates a multi-layer adsorption [17].

$$\log_{10} q_e = \log_{10} K + \left(\frac{1}{n}\right) \log_{10} C_e$$  \hspace{2cm} (7)

where $K$ and $n$ are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Based on Eq. (7), a straight line was obtained when plotting $\log_{10} q_e$ vs. $\log_{10} C_e$. The constants, $K$ and $n$, were then defined by intercepts and slopes of the line, respectively.

Tempkin Isotherm Model

Tempkin defined the isotherm adsorption equilibrium equation as follow [18]:

$$q_e = a n k_T + a n c_e$$  \hspace{2cm} (8)

where $a$ is physical quantity related to the heat of adsorption. $k_T$ is equilibrium constant.

Based on Eq. (8), a straight line was obtained when plotting $q_e$ vs. $\log_{10} C_e$. The constants $a$ and $k_T$ were then defined by slopes and intercepts of the lines, respectively, as shown in Table-2.

As shown in Table-2, $1/n$ was less than 0.5 and $R_L$ was between 0 and 1, suggesting that the adsorption of ClO$_4^-$ on GAC-CTAC occurred easily.

In addition, it appears that all of the three kinds of models agreed well with the experimental results, with the correlation coefficient values being closed to 1 at different temperatures. Among the three models, the Langmuir adsorption isotherm model was the best one ($r^2 > 0.98$) depicting the adsorption of perchlorate on GAC-CTAC. As it can be seen from the results of Langmuir adsorption isotherm model, when the temperature rose from 288 K to 308 K, the saturated adsorption capacity decreased from 16.16 mg/g to 12.61 mg/g. In other words, the ClO$_4^-$ adsorption capacity increased with the increased temperature, indicating it was an exothermic reaction.

Table-2: Adsorption isotherm parameters of ClO$_4^-$ on GAC-CTAC under different temperatures.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$Q_0$(mg/g)</th>
<th>$b$(L/mg)</th>
<th>$R_L$</th>
<th>$R^2$</th>
<th>$K$</th>
<th>$1/n$</th>
<th>$R^2$</th>
<th>$k_T$</th>
<th>$a$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>16.16</td>
<td>0.05</td>
<td>0.010</td>
<td>0.9879</td>
<td>1.340</td>
<td>0.49</td>
<td>0.9004</td>
<td>1.57</td>
<td>2.31</td>
<td>0.9569</td>
</tr>
<tr>
<td>298</td>
<td>14.27</td>
<td>0.04</td>
<td>0.012</td>
<td>0.9877</td>
<td>1.0560</td>
<td>0.45</td>
<td>0.9128</td>
<td>1.55</td>
<td>1.98</td>
<td>0.9692</td>
</tr>
<tr>
<td>308</td>
<td>12.61</td>
<td>0.03</td>
<td>0.016</td>
<td>0.9920</td>
<td>1.0280</td>
<td>0.41</td>
<td>0.9813</td>
<td>2.06</td>
<td>1.58</td>
<td>0.9502</td>
</tr>
</tbody>
</table>
Micrography and Chemistry on Improved Adsorption

SEM Micrograph

The SEM images of the GAC and GAC-CTAC are shown in Fig. 6. Numerous small cavities were present over the virgin GAC surface, forming a complicated pore network. The surface of GAC-CTAC was rougher, increasing the contact area. It had larger specific surface area and higher adsorption capacity than GAC.

Chemistry of Perchlorate Adsorption by FTIR Spectra

The differences of GAC, GAC-CTAC, ClO$_4^-$ and perchlorate-loaded GAC-CTAC were further investigated by using FTIR spectroscopy and the results are shown in Fig. 7.

The two peaks at 2925 and 2850 cm$^{-1}$ are likely associated with vibration modes of methylene groups [19-20]. The band at 1627 cm$^{-1}$ suggests that double bond (C=C) vibration bands overlap the C=O stretching vibration and OH binding vibration bands [19, 21]. The band in the range of 1300–1500 cm$^{-1}$ can be attributed to the deformation vibrations of aromatic ring absorption and the OH bending vibration of carboxyl and hydroxyl groups [22, 23]. The bands observed in the range of 1000–1200 cm$^{-1}$ are in accord with C–O single-bond stretching vibrations from phenols and epoxide structures, aromatic ethers, and γ and δ lactone groups [21-24]. The bands in the range of 700–900 cm$^{-1}$, where just one peak is detectable, are assigned to C–H vibrations in aromatic rings [19].

Fig.7: FTIR spectra of activated carbon before and after modification and ClO$_4^-$ adsorption. a: GAC; b: GAC-CTAC; c: NH$_4$ClO$_4$; d: perchlorate-loaded GAC-CTAC

Curve b represented GAC-CTAC, compared with curve a, a absorption at 1469 cm$^{-1}$ is ascribed to ν(CH) of the CTAC [25]. This indicates that CTAC molecules had been efficiently bonded to GAC surface. In curve c, two absorption at 1090.68 and 628.08 cm$^{-1}$ which can be assigned to stretching vibration of the ClO$_4^-$. ν(NH) show the weak absorption at around 3168.62 cm$^{-1}$ due to Hydrogen bond [26]. In addition, a adsorption at 1393.44 cm$^{-1}$ is relegated to NH$_4^+$. Perchlorate-loaded GAC-CTAC is shown in curve d. There are obvious absorption peaks at 1090.68 and 628.08 cm$^{-1}$, it shows that GAC-CTAC had been effectively adsorbing ClO$_4^-$.  

Experimental

Materials

GAC with a size of 0.5–1.5 mm was purchased from Sinopharm Chemical Reagent Co., Ltd. It was soaked in deionized (DI) water for 24 h, then washed with DI water, and dried at 110 °C for 12h.
CTAC(C\textsubscript{19}H\textsubscript{42}NCl) was obtained from Shanghai Feixiang Chemical Plant and was used as received without further purification. Solutions of perchlorate were prepared by dissolving solid NH\textsubscript{4}ClO\textsubscript{4} in DI water.

**GAC Tailoring**

1.60 g GAC was added into 0.4% CTAC solution. The mixture was installed in a rotary shaker at 25 °C for 24h and then put aside for settlement until the aqueous layer was formed. Then the GAC-CTAC solids were collected, rinsed with a large amount of DI water, and finally dried in an oven at 110 °C for 12 h.

**Material Characterization**

The field emission of scanning electron microscope (FESEM, JSM-6701F) was used to determine the surface morphology of GAC and GAC-CTAC.

**Batch Reactions**

The tests were carried out in 250 mL glass flasks with 200 mL of 1.0 mg/L perchlorate. The flasks were installed in a rotary shaker at 120 rpm and at 25 °C. Reaction was initiated by addition of 0.02 g GAC-CTAC [12, 13]. At each designated sampling time, 5mL sample was collected from each designated and filtered through a 0.22 µm membrane filter for sample analysis. In a typical equilibrium test, a 250 mL conical flask containing 200 mL 0.1-5.0 mg/L perchlorate solution was installed in a rotary shaker at 120 rpm and at 25 °C. In the tests to evaluate the pH effect, 0.02 g of GAC-CTAC was introduced to the 250ml conical flasks containing 200ml 0.1-5.0 mg/L perchlorate solution. Solution pH was pre-adjusted to the desired values in a range of 3-12 with 0.1M HCl and 0.1M NaOH. All the glass bottles were installed in a rotary shaker at 120 rpm and at 25 °C, for 72h to ensure that the adsorption process reached equilibrium. Finally, 5ml sample was collected from reactors, and then filtered through a 0.22 µm membrane filter for sample analysis.

**Adsorption Isotherms**

200 mL of 50-2000 µg/L perchlorate solution was transferred into 250 mL volumetric flasks respectively, and then 0.02 g GAC-CTAC was added into each solution. The samples were installed in a rotary shaker at 120 rpm and at 25 °C for 72h. At each designated sampling time, 5mL sample was collected and filtered through a 0.22 µm membrane filter for sample analysis. The process was repeated at 15°C and 35 °C.

**Perchlorate Analysis**

Perchlorate concentration was analyzed using a Metrohm-861 Advanced Compact ion chromatography equipped with a Metrosep A Supp 5 (250×4 mm) analytical separation column, a Metrosep RP Guard column, and a detection stabilizer (providing a temperature of 35 °C). A 5 mmol/L Na\textsubscript{2}CO\textsubscript{3} + 20% acetonitrile solution was used as the eluent. The eluent flow rate was set at 0.70 ml/min.

**Conclusion**

ClO\textsubscript{4}\textsuperscript{-} could be more easily adsorbed by GAC-CTAC, and the kinetic adsorption reaction could be well described by the pseudo-second-order rate model. The perchlorate removal percentage could reach 95% under the following conditions: pH 3, initial ClO\textsubscript{4}\textsuperscript{-} concentration 1.0 mg/l, temperature 33 °C. The co-existing anions in water decreased the removal percentage of ClO\textsubscript{4}\textsuperscript{-}. The order of competitive effect is S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} > SO\textsubscript{4}\textsuperscript{2-} > Cl\textsuperscript{-} > H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} ≈ NO\textsubscript{3}\textsuperscript{-} ≈ ClO\textsubscript{2}\textsuperscript{-}.

Adsorption of ClO\textsubscript{4}\textsuperscript{-} on GAC-CTAC fitted the Langmuir, Freundlich and Tempkin adsorption isotherm models. The interaction of ClO\textsubscript{4}\textsuperscript{-} adsorbed by GAC-CTAC was exothermic. The increased temperature decreased the adsorption capacity. Quaternary ammonium function groups on GAC-CTAC played an important role in adsorption of ClO\textsubscript{4}\textsuperscript{-}.

**Acknowledgements**

This research was supported by Startup Foundation for Docotors of Jiangsu University of Science and Technology (635211202), and the National Natural Science Fund of Jiangsu Province (BK2009721), all in China.

**References**