Using a novel adsorbent macrocyclic compound cucurbit[8]uril for Pb$^{2+}$ removal from aqueous solution

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In this study, cucurbit[8]uril (CB[8]) was utilized as a kind of new adsorbent to remove Pb$^{2+}$ ions from aqueous solution. With the solution pH increased from 2 to 6, the removal efficiency of adsorption increased from 55.6% to 74.5% correspondingly. The uptake of Pb$^{2+}$ increased rapidly in the initial 30 min, and then the adsorption rate became slower. The Pseudo-second order model could be used to interpret the adsorption kinetics satisfactorily; and the rate determining step in Pb$^{2+}$ adsorption onto CB[8] was the external mass transfer step. Equilibrium isotherm study reveals that the Langmuir model gave a better fitting result than Freundlich model. The maximum adsorption capacity calculated by the Langmuir model was 152.67 mg/g for 298 K, 149.70 mg/g for 313 K and 136.42 mg/g for 323 K, respectively. The adsorption is a spontaneous process of exothermic nature. The effect of the adsorbent dosage and the influences of solution pH and co-existing cations were also investigated. The CB[8] was synthesized and characterized by $^1$H NMR, IR, ESI-MS spectra, SEM-EDAX, Zeta-potential and BET-analysis. The adsorption mechanism was due to the coordination between CB[8] molecule and Pb$^{2+}$ ions.

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Introduc
clogging, inefficiency for low metal concentrations, thermal instability, low endurability in acid and alkali, or toxic to organism, which limit their utilization in some extreme situations. New adsorbents with high adsorption capability, good chemical stability and high selectivity, are still the research aim for scientists (Ali, 2012).

Cucurbit[n]uril (CB[n]), as a macrocyclic compound comprising several glycoluril units and methylene groups, has a rigid structure with a hydrophobic carbonyl hollow cavity and polar carbonyl groups (Freeman and Mock, 1981). Because of its unique structure, especially, polar carbonyl groups with electronegativity, CB[n] family is found to be an effective receptor for guest molecules, including neural molecules, anions, metal complex and metal ions (Kim et al., 2007; Gerasko et al., 2003; Whang et al., 1998; Lorenzo et al., 2001; Liu et al., 2004).

Among these guests, CB[n]-based coordination chemistry has been an important research. CB[n]-based complex with alkali and alkaline earth metal ions, transition metal ions, lanthanide metal ions, uranyl metal ions and their clusters have been researched focused on their structures, characters and chemical properties (Heo et al., 2000; Fedin et al., 2001, 2002). But few of these studies are directly related to the coordination of CB[8] with metal ions and the applications of such coordination system were seldom reported either. Since CB[8] has the poorest solubility in CB[n] family and every CB[8] molecule has a large portal size and rich carbonyl oxygen atoms in the structure, it could serve as an acceptor and coordinate with several metal ions at the same time from solution. For example, every CB[8] molecule could be bound to four strontium cations or two [Bi(NO₃)(H₂O)₅]²⁺ fragments (Gerasko et al., 2003; Sokolova et al., 2003).

Cucurbit[8]uril (molecular formula: C₄₈H₄₈N₃₂O₁₆) is stable at high temperature (over 300°C), durable in the medium of acid or alkali, nontoxic to organism and could not be decomposed by enzymes. Furthermore, the macrocyclic structure of cucurbit[8]uril could combine many kinds of organic molecules, such as antibiotics, dyes or pesticides through host-guest supramolecular interactions, which makes CB[8] has the potential to simultaneously remove both classes of contaminants. Above all, we consider that CB[8] might have a high adsorption capability to metal ions and have potential applications in the removal of metal ions from aqueous solutions and act as a new type of adsorbent.

In this report, we synthesized, purified, characterized CB[8] and utilized CB[8] as a kind of new adsorbent to remove Pb²⁺ ions from aqueous solution. The effect of pH, adsorbent dosage and co-existing cations was studied. The absorption kinetics and absorption isotherms are determined. The adsorption mechanism is also discussed.

1. Materials and method


All starting materials were purchased commercially and used without further purification. CB[8] was synthesized and purified according to literatures (Kim et al., 2000). As shown in Fig. 1, glycoluril (28.4 g, 2.0 mol) was solved in 150 mL hydrochloric acid (12 mol/L) and stirred at room temperature. After being dissolved, 12 g paraformaldehyde powder was added and stirred, then the solution was heated to 100°C and kept for 12 hr. After being reacted, brown solution was cooled to room temperature and distilled under vacuum to remove hydrochloric acid, then acetone was added to get cucurbit[n]uril mixture (n = 5, 6, 7, 8). The mixture was washed by plenty of distilled water to remove CB[5] and CB[7]. The residue (CB[8] and CB[6]) was filtered and washed by 4 mol/L HCl to remove CB[6]. The precipitation was washed by distilled water and dried to get pure CB[8].

1.2. Adsorption experiments

The experiments of the effect of pH on the adsorption process were carried out by a batch method at controlled temperature (25°C), 0.02 5 g CB[8] was added into Pb²⁺ solution (50 mL, 100 mg/L) in a pH range from 2 to 6 and shake for 2 hr. pH was adjusted using 0.05 mol/L HCl or NaOH.

The adsorption kinetics experiments were carried out in a 250 mL flask at a controlled temperature 298 K with vigorous stirring. The initial concentration of Pb²⁺ was 100 mg/L, the pH was adjusted to 6.0 ± 0.1, the dosage of adsorbent was 0.5 g/L. The adsorption capacity of CB[8] at time t (qₜ) was

![Fig. 1](https://example.com/fig1.png) – (a) Synthesis of cucurbit[8]uril; (b) molecule structure of cucurbit[8] (hydrogen atoms were omitted for clarity).
calculated by the following equation:
\[ q_e = (C_0 - C_f)/(m/V) \]  
(1)
where \( C_0 \) and \( C_f \) (mg N/L) are the initial concentration of Pb\(^{2+}\) and that at time \( t \), \( V \) (L) is the volume of solution, and \( m \) (g) is the mass of adsorbent.

The equilibrium isotherms were obtained by contacting a constant mass 0.025 g CB[8] with a range of different Pb\(^{2+}\) concentration solutions. The pH of the solutions was adjusted to 6.0 ± 0.1. The solutions were agitated in a series of 50 mL conical flasks placed in a temperature controlled orbital shaker at 298 K, 313 K and 323 K for 2 hr, respectively. The adsorptive capacity of CB[8] toward Pb\(^{2+}\) at equilibrium was denoted as \( q_e \) (mg/g).

To study the effect of the adsorbent dosage, CB[8] in a range from 0.005 to 0.050 g was added into Pb\(^{2+}\) solution (50 mL, 100 mg/L) at pH = 6.0 ± 0.1 and 298 K and shocked for 2 hr. To study the effect of co-existing cations, 0.020 g CB[8] was added into Pb\(^{2+}\) solution contains M\(^{n+}\) cations (50 mL, Pb\(^{2+}\) = 3 \times 10^{-4} \text{ mol/L}, M\(^{n+}\) = K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\) = 3 \times 10^{-4} \text{ mol/L}) with pH = 6.0 ± 0.1 at 298 K and shocked for 2 hr. After each experiment, solutions were analyzed for the concentration of Pb\(^{2+}\) ions.

1.3. Analysis method

The solution sample was filtered by 0.20 \( \mu \text{m} \) membrane before analysis. Pb\(^{2+}\) concentrations of aqueous solution were measured using a TAS-986 flame atomic absorption spectrometry (Persee, China).

\(^1\)H NMR spectra were recorded on a Varian Mercury VX-300 spectrometer. The IR spectra (in KBr pellets) are recorded on a Fourier Transform infrared spectroscopy (FT-IR) 157 spectrophotometer (Shimadzu, Japan). Electrospray Ionization Mass Spectrometry (ESI-MS) spectra were recorded on a ZAB-3F-HF mass spectrometer (FAB-MS, VG Co., England). Zeta-potential under different pH value was measured using Zetasizer Nano ZSP (Malvern, England). Surface area, porosity and pore volume were tested by surface area analyzer (V-Sorb 4800P, GAPP, China). Scanning Electron Microscope - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) had been taken using EDAX TEAM (AMETEK, USA).

2. Results and discussion

2.1. Characterization of adsorbent

2.1.1. \(^1\)H NMR, IR and ESI-MS analyses

The \(^1\)H NMR spectra of CB[8] (300 MHz, 0.2 mol/L NaCl/D\(_2\)O) show that there are three groups of chemical shifts: 6 4.157 (Hx, d, 16H, J = 14.7 Hz), 5.467 (Hx, s, 16H), 5.673 (Hy, d, 16H, J = 16.2 Hz) (Fig. 2a). The up-shift and down-shift of Hx and Hy corresponding to the shielding and deshielding effect of CB[8], which determined that Hx and Hy are near the entrance of macrocyclic structure of CB[8]. The IR spectra of CB[8] (KBr) \( \nu/\text{cm}^{-1} \): 3434 (the O-H stretching frequency of water in the cavity of CB[8]), 3002 and 2935 (C=O of CB[8]), 1736 (C=O of CB[8]) (Fig. 2b). After adsorption, no major changes were observed in the IR spectra, indicating that the CB[8] maintained the basic structure during adsorption process. ESI-MS: m/z (calcld./found) 1328/1329.3 (Fig. 2c). On the basis of \(^1\)H NMR, IR and ESI-MS analyses, it could be concluded that the CB[8] was successfully synthesized with high purity and could be utilized for the adsorptive test.

2.1.2. SEM-EDAX analysis

Fig. 3 is the high vacuum SEM images of gold-coated CB[8] before and after adsorption. Before adsorption, the CB[8] precipitate exhibits irregular morphology with the particle diameter of 2–10 \( \mu \text{m} \). After adsorption, the material morphology became looser, which may attribute to the coordination of CB[8] with metal ions during the adsorption procedure in aqueous solution. Although CB[8] molecule has a rigid structure with a hydrophobic carbonyl hollow cavity and polar carbonyl groups, the SEM image could not reflect its structure at molecular level. Since the CB[8] molecules interact with each other through Van Der Waals forces, the precipitate of CB[8] is unconsolidated with a wide range of diameter and the surface roughness was variable in SEM images. EDAX analyses showed that, the CB[8] was mainly composed of C, N and O elements. After adsorption, Pb element appeared with the atom ratio of 1.38% after adsorption, which indicates that, during adsorption, the coordination of carbonyl oxygen atoms with Pb\(^{2+}\) results in the escape of Pb\(^{2+}\) from aqueous solution during the adsorption for the poor solubility of CB[8].

2.1.3. Physical characterization and BET-analysis

Since electrical characteristic of adsorbent was an important factor influencing adsorption, we tested Zeta-potential under different pH value. From theoretical viewpoint, the Zeta-potential is the electric potential at the location of the slipping plane. As shown in Fig. 4, the Zeta-potential of CB[8] exhibited positive value across in the tested pH range (2–9). Unfortunately, the pH of zero charge was not discovered in this study. Even under higher pH, the decrease of Zeta-potential was not obvious. The results indicated that the carbonyl groups of CB[8] could be coordinated with positive cation and formed a new layer closely attached to the dispersed particle.

Physical characteristics and BET analysis results of CB[8] are listed in Table 1. BET surface area of CB[8] was 0.087 m\(^2\)/g, pore volume was 0.0131 cm\(^3\)/g. The adsorbent could be classified as non-porous material. As reported (Jason Lagona et al., 2005), Cucurbit[8]uril is stable at high temperature (over 300°C), durable in the medium of acid or alkali, nontoxic to organism and could not be decomposed by enzymes. According to single crystal X-ray data (Jason Lagona et al., 2005), the portal diameter of CB[8] is 6.9 Å, the cavity diameter is 8.8 Å, and the cavity volume is 479 Å\(^3\) by calculated from the crystal data. The solubility of CB[8] is less than 0.01 mM, which essentially insoluble in water and any organic solvents.

2.2. Effect of solution pH

The pH of the solution was an important factor for adsorption process. In this study, the effect of pH was explored at controlled temperature (25°C), the initial concentration of Pb\(^{2+}\) was 100 mg/L, and the dosage of CB[8] was 0.5 g/L. In order to avoid precipitation of Pb\(^{2+}\), the pH of the solution varied from 2
The removal efficiency under different pH values were as follows: 55.6% at pH 2; 61.0% at pH 3; 61.2% at pH 4; 62.6 at pH 5; 74.5 at pH 6. With the solution pH increased from 2 to 6, the removal efficiency of adsorption increased from 55.6% to 74.5% correspondingly. The mechanism of pH effect could be speculated as: the coordination of carbonyl oxygen atoms to Pb²⁺ to form Pb²⁺−O=C and escape from aqueous solution for its poor solubility. Carbonyl oxygen will take one proton and get positive charge at low pH, which might prevent the coordination to Pb²⁺ and decrease the removal efficiency of adsorption.

2.3. Adsorption kinetics

The adsorption kinetics of Pb²⁺ onto CB[8] at 25°C is shown in Fig. 5. The uptake of Pb²⁺ increased rapidly in the initial 30 min, and then the curve became flatten due to a much slower adsorption rate. In condition of low adsorbent dosage (0.2 g/L), the removal efficiency achieved 28.2% for 9 min and 30.5% for 120 min adsorption. In condition of high adsorbent dosage, the removal efficiency achieved 55.3% at 4 min while 74.5% for 120 min adsorption, which indicated that the CB[8] exhibited high adsorption rate and the equilibrium could be achieved in 2 hr.

Additionally, First-order kinetics model (Lagergren, 1898) and Pseudo-second-order kinetics model (Ho and McKay, 2000) were utilized to fit the experimental data to get further understanding of the kinetics characteristics:

\[
\ln \left( q_e - q_t \right) = \ln \left( q_e \right) - k_1 t \quad \text{First-order kinetics model} \tag{2}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Pseudo-second-order kinetics model} \tag{3}
\]

where \( t \) is the contact time of adsorption experiment (min); \( k_1 \) (min⁻¹) and \( k_2 \) (g·mg⁻¹·min⁻¹) is the rate constant of each kinetics model.

The mean square error (MSE) was calculated by the following equation during modeling (Alipanahpour et al., 2016; Ghaedi et al., 2016):

\[
\text{MSE} = \frac{1}{N} \sum_{i=1}^{N} \left( q_{\text{cal}} - q_{\text{exp}} \right) \tag{4}
\]

where \( q_{\text{cal}} \) and \( q_{\text{exp}} \) represent the measured adsorptive capacity and predicted by kinetic models value of solid phase Pb²⁺ concentration at equilibrium (mg/g).

As can be seen in Table 2, Pseudo-second order model could be used to interpret the adsorption kinetics more satisfactorily than the First-order kinetics model on the basis of higher correlation constant \( R^2 \) and lower MSE value. The adsorption capacity calculated by Pseudo-second order model \( q_e \) was close to the experimental data. The better application of
the Pseudo-second-order model to the kinetics data indicated that the adsorption attributed to chemisorption reaction and more than one-step adsorption process dominated in the rate controlling step (Ho and McKay, 2000). It could be speculated that the adsorption occurred via chemisorption between Pb²⁺ ions and carbonyl oxygen atoms of CB[8].

The adsorption of Pb²⁺ onto CB[8] mainly involved external mass transfer (film diffusion) and internal mass transfer (intraparticle diffusion). Adapted Weber-Morris model (Weber and Morris, 1963), as known as intraparticle diffusion model (Eq. (5)) was also employed to fitting the experimental data.

\[
q_t = k_3 t^{0.5} + C
\]

where, \(k_3 (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})\) is the rate constant and \(C\) is the constant for intraparticle diffusion model.

If the intraparticle diffusion is the sole mechanism to control the adsorption rate, the fitting plot passes through the origin, the intercept was zero. If more independent adsorption steps take place, multilinearity with different slope could be observed (Mahir et al., 2007). Since the CB[8] BET surface area was 0.87 m²/g, the pore volume was 0.0131 cm³/g, the absorbent could be classified as non-porous material. Therefore, the intraparticle diffusion is less likely to occur and negligible. Same phenomenon was also reported in the adsorption of Hg(II) onto thio-functionalized polymer-coated magnetic particles (Kunawoot et al., 2015). As can be seen in Fig. 5c, the fitting plot consisted of two steps of line. The starting line with sharp slop was attributed to the external mass transfer. The ending line is the final adsorption equilibrium. Consequently, the rate determining step in Pb²⁺ adsorption onto CB[8] was the external mass transfer.
mass transfer step. Compared to high adsorbent dosage 0.5 g/L, the external mass transfer resistance of low dosage (0.2 g/L) was much lower, therefore the slope of starting line of 0.2 g/L was lower than that of 0.5 g/L.

2.4. Adsorption isotherms

Fig. 6a represents the adsorption isotherms for Pb\(^{2+}\) onto CB[8] under 298 K, 313 K and 323 K, respectively. From the isotherm curves, adsorption of Pb\(^{2+}\) decreased with the increase of temperature. The adsorbent exhibited high adsorptive capacity over the tested equilibrium concentration range. The adsorptive capacity exceeded 100 mg/L at low equilibrium concentration at 298 K, indicating the excellent adsorptive property of the adsorbent.

Langmuir and Freundlich isotherm models are the most commonly used model to interpret the adsorptive behavior. The two isotherms are given by Eqs. (6) and (7):

\[
q_e = \frac{Q_0C_eK_L}{1 + C_eK_L} \quad \text{Langmuir isotherm} \tag{6}
\]

\[
q_e = K_F C_e^n \quad \text{Freundlich isotherm} \tag{7}
\]

where \(C_e\) (mg/L) is the concentration of Pb\(^{2+}\) solution at equilibrium, \(Q_0\) (mg/g) is the monolayer capacity of the adsorbent, \(K_L\) is related to the energy of adsorption (L/mg), \(K_F\) (mg/g) (L/mg)\(^n\) and \(n\) are the Freundlich temperature dependent constants.

In this study, the two models were employed to fitting the experimental data; the fitting results are listed in Table 3. The Langmuir model gave a better fitting result on the basis of \(R^2\). The \(K_L\) parameter value reflected a much greater affinity of Pb\(^{2+}\) under lower temperature 298 K than 313 K and 323 K. The maximum adsorption capacity calculated by the Langmuir model was 152.67 mg/g for 298 K, 149.70 mg/g for 313 K and 136.42 mg/g for 323 K. The adsorption reaction was prohibited under higher temperature. Besides, the parameter \(n\) calculated by Freundlich model was in the range of 0.1–0.5 indicates a favorable adsorption process.

Separation factor \((R_L)\) was another essential characteristic of the Langmuir isotherm, represented in Eq. (8) (Langmuir,

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>Molecular weight</td>
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</tr>
<tr>
<td>Port diameter</td>
<td>6.9 Å</td>
</tr>
<tr>
<td>Cavity diameter</td>
<td>8.8 Å</td>
</tr>
<tr>
<td>Cavity volume</td>
<td>479Å(^3)</td>
</tr>
<tr>
<td>Cavity height</td>
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</tr>
<tr>
<td>Solubility in H(_2)O</td>
<td>&lt;0.01 mmol/L</td>
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<tr>
<td>Stability</td>
<td>&gt;420°C</td>
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<table>
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<tr>
<th>Surface area</th>
<th>Value</th>
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<tbody>
<tr>
<td>BET surface area</td>
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</tr>
<tr>
<td>Langmuir surface area</td>
<td>1.11 m(^2)/g</td>
</tr>
<tr>
<td>BJH adsorption cumulative surface area</td>
<td>1.74 m(^2)/g</td>
</tr>
<tr>
<td>BJH desorption cumulative surface area</td>
<td>5.24 m(^2)/g</td>
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<table>
<thead>
<tr>
<th>Pore volume</th>
<th>Value</th>
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<tbody>
<tr>
<td>Single point adsorption total pore volume less than 220.54 nm width at (P/P_0 = 0.9912)</td>
<td>0.0131 cm(^3)/g</td>
</tr>
<tr>
<td>BJH adsorption cumulative volume of pores between 2.078 and 220.54 nm</td>
<td>0.0145 cm(^3)/g</td>
</tr>
<tr>
<td>BJH desorption cumulative volume of pores between 2.057 and 220.543 nm</td>
<td>0.0142 cm(^3)/g</td>
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</tbody>
</table>

<table>
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<tr>
<th>Pore size</th>
<th>Value</th>
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</thead>
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<tr>
<td>Adsorption average pore width (4 V/A by BET)</td>
<td>60.55 nm</td>
</tr>
<tr>
<td>BJH adsorption average pore width (4 V/A)</td>
<td>33.21 nm</td>
</tr>
<tr>
<td>BJH desorption average pore width (4 V/A)</td>
<td>11.03 nm</td>
</tr>
</tbody>
</table>

Fig. 5 – The adsorption kinetic of Pb\(^{2+}\) onto CB[8] at 298 K. (a) Pb\(^{2+}\) concentration at different time; (b) adsorption capacity \(q_t\) at different time (kinetics model non-linear fitting); (c) Weber–Morris plot for Pb\(^{2+}\) adsorption. (\(C_0 = 100\) mg/L, the pH 6.0 ± 0.1).
Where, the $R_L$ value indicates the type of isotherm: favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Langmuir, 1918). In this study, $R_L$ as a function of initial Pb$^{2+}$ concentration under different temperature are represented in Fig. 6b. It was indicated that the adsorption process was favorable for $R_L$ value was lower than 0.3.

The standard free energy ($\Delta G^0$) was calculated by the following equation:

$$\Delta G^0 = -RT \ln K_L$$

(9)

where $R$ (8.314 J/mol·K) is the ideal gas constant, $T$ (K) is Kelvin temperature and $K_L$ (L/mol) is the Langmuir constant. The values of standard enthalpy change ($\Delta H^0$) and the standard entropy change ($\Delta S^0$) were calculated from the slope and intercept of the Van’t Hoff plot by regression:

$$\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

(10)

The calculative results are listed in Table 4. It can be concluded that the adsorption of Pb$^{2+}$ by CB[8] is a spontaneous process ($\Delta G^0 < 0$). And the value of $\Delta H^0$ is negative, indicates that the adsorption process is exothermic in nature, and the negative values of $\Delta S^0$ reveals the decreasing randomness at the solid solution interface of the adsorption process.

The removal of Pb$^{2+}$ has been studied in recent years and some of these reports provided adsorption capacity for Pb$^{2+}$. Although the adsorption capacity was obtained under different experimental conditions, they could be useful as a criterion for comparing the adsorption capacity. It could be seen from Table 5 that the adsorption capacity by CB[8] obtained in this study is larger than that of previous report.

2.5. Effect of adsorbent dosage

The effect of adsorbent dosage was explored in this study. As can be seen in Fig. 7, when adsorbent dosage increased from 0.1 to 1.0 g/L, the removal efficiency increased from 15.0% to 97.5%. And the adsorption capacity decreased from 152.60 mg/g to 97.48 mg/g correspondingly. The increase in adsorbent dosage increased the removal efficiency of Pb$^{2+}$, which was consistent with the expectation that higher adsorbent dosages will result in lower adsorption capacity values.

2.6. Effect of co-existing cations

Various ions that exist in drinking water or wastewater have a relatively binding ability on carbonyl oxygen atoms. Therefore their effects on the adsorption of Pb$^{2+}$ should be considered. In this study, the effect of other competitive ions (such as K$^+$, Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$) was explored, the experimental results are present in Fig. 8. The competitive ion and Pb$^{2+}$ were of equal substance concentration ($3 \times 10^{-4}$ mol/L), compared with the blank experiment, the Pb$^{2+}$ adsorption removal efficiency decreased significantly when other ions exist, especially when Ba$^{2+}$ exists. The detrimental effect of co-existing ion increased as: Mg$^{2+} < K^+ = Ca^{2+} < Ba^{2+}$.
2.7. Mechanism

The adsorption mechanism of CB[8] to Pb²⁺ is due to the unique structures of CB[8] molecules. There are eight carbonyl groups on each side of one CB[8] molecule, in which the oxygen atoms are well situated to coordinate with metal ions at the entrance of CB[8]. Fig. 2b shows that the IR spectra of the CB[8] has no obvious change before and after adsorption. The IR spectra of CB[8] before and after adsorption both have strong peaks at 1736 cm⁻¹ attribute to the stretching vibration of C=O, indicating that most of the C=O groups in CB[8] molecules uncoordinated with metal ions. There are 16 carboxyl groups in each cucurbit[8]uril molecule and the coordination number of carbonyl oxygen atoms with Pb²⁺ are much less than free carbonyl oxygen atoms of CB[8], which makes the peaks of C=O stretching vibration still strong in the spectrum. The diameter of the cavity at the entrance of CB[8] molecule is approximately 0.69 nm, which is much larger than the ionic radius of Pb²⁺ (0.119 nm), it could be speculated that one CB[8] molecule might coordinate with more than one Pb²⁺ ions, which is similar to the coordination of CB[8] with strontium ions (Gerasko et al., 2003).

The adsorption kinetics experiments showed that CB[8] exhibited high adsorption rate in the removal of lead ions in aqueous; the rate determining step in Pb²⁺ adsorption onto CB[8] was the external mass transfer step. Since CB[8] molecules assemble with each other through Van Der Waals forces in solid, the precipitate of CB[8] is unconsolidated, which is conductive to the diffusion and adsorption of Pb²⁺.

The max adsorption capability of CB[8] is up to 152.67 mg/g at 298 K. It could be calculated that the ratio of CB[8]:Pb²⁺ is nearly 1:1, which demonstrates that each CB[8] molecule will averagely adsorb one Pb²⁺ ion. Considering that one CB[8] molecule has 16 carbonyl oxygen atoms to coordinate with metal ions, the possible mode of CB[8] adsorbing Pb²⁺ might be disordered netlike structure in solid (Fig. 9). At low pH, the carbonyl groups of CB[8] will take protons and get positive charge, which will repel Pb²⁺ cations and lead to the decrease of removal efficiency of adsorption.

### Table 3 – Fitting results of adsorption isotherm model under different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Q&lt;sub&gt;max&lt;/sub&gt; (mg/g)</th>
<th>K&lt;sub&gt;L&lt;/sub&gt; (L/mg)</th>
<th>R²</th>
<th>K&lt;sub&gt;F&lt;/sub&gt; (L/mg)</th>
<th>R²</th>
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<tr>
<td>298 K</td>
<td>152.67</td>
<td>0.833</td>
<td>0.9994</td>
<td>0.138</td>
<td>0.9460</td>
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<tr>
<td>313 K</td>
<td>149.70</td>
<td>0.088</td>
<td>0.9851</td>
<td>0.152</td>
<td>0.8144</td>
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<tr>
<td>323 K</td>
<td>136.42</td>
<td>0.060</td>
<td>0.9874</td>
<td>0.141</td>
<td>0.7763</td>
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</table>

![Removal efficiency and Adsorption capacity](image)

### Table 5 – Comparison of maximum Pb²⁺ adsorption capacity (Q<sub>max</sub>⁰).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Q&lt;sub&gt;max&lt;/sub&gt; (mg/g)</th>
<th>pH</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB[8]</td>
<td>152.67</td>
<td>6</td>
<td>298</td>
<td>This study</td>
</tr>
<tr>
<td>Al(OH)₃/ (PAA-CO-PAM)</td>
<td>106.2</td>
<td>5</td>
<td>297</td>
<td>Zhao et al. (2014)</td>
</tr>
<tr>
<td>Sawdust activated carbon</td>
<td>97.35</td>
<td>5</td>
<td>303</td>
<td>Sreejalekshmi et al. (2009)</td>
</tr>
<tr>
<td>Coffee residue</td>
<td>63.29</td>
<td>5.8</td>
<td>298</td>
<td>Boudrahem et al. (2009)</td>
</tr>
<tr>
<td>Polygonum orientale linn activated carbon</td>
<td>98.39</td>
<td>5</td>
<td>298</td>
<td>Wang et al. (2010)</td>
</tr>
</tbody>
</table>

![Effect of adsorbent dosage on removal efficiency and adsorption capacity](image)

### Table 4 – Thermodynamic parameters for fluoride ions adsorbed by CHT4.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>lnK&lt;sub&gt;L&lt;/sub&gt; (kJ/mol)</th>
<th>ΔG&lt;sup&gt;0&lt;/sup&gt; (kJ/mol)</th>
<th>ΔH&lt;sup&gt;0&lt;/sup&gt; (kJ/mol)</th>
<th>ΔS&lt;sup&gt;0&lt;/sup&gt; (J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>12.06</td>
<td>-59.76</td>
<td>-87.29</td>
<td>-193.94</td>
</tr>
<tr>
<td>313 K</td>
<td>9.81</td>
<td>-25.12</td>
<td>-25.32</td>
<td></td>
</tr>
<tr>
<td>323 K</td>
<td>9.43</td>
<td>-25.32</td>
<td>-25.32</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7 – Effect of adsorbent dosage on removal efficiency and adsorption capacity. Conditions: C<sub>0</sub>: 100 mg/L, the dosage of adsorbent 0.5 g/L, pH = 6.0 ± 0.1, 298 K.

3. Conclusions

As a novel adsorbent, CB[8] exhibited high adsorption rate and the equilibrium could be achieved in 2 hr. The Pseudo-second order model could be used to interpret the adsorption kinetics well. The rate determining step in Pb²⁺ adsorption onto CB[8]
was the external mass transfer step. The maximum adsorption capacity calculated by the Langmuir model was 152.67 mg/g for 298 K, 149.70 mg/g for 313 K and 136.42 mg/g for 323 K, respectively. At low pH, the carbonyl groups of CB[8] will take protons and get positive charge, which will repel Pb²⁺ cations and lead to the decrease of removal efficiency of adsorption. The adsorption reaction was prohibited under higher temperature. It was speculated that CB[8] could be coordinated with Pb²⁺, the netlike structure in solid was founded during adsorption process.

Acknowledgements

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