Efficient removal of lead ions from aqueous solution using C-TiO₂ adsorbent

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Abstract. Carbon-doped TiO₂ (C-TiO₂) was fabricated using a facile hydrothermal treatment. It was applied as an adsorbent to remove Pb(II) from the aqueous solution. The morphology and properties of the adsorbent were characterized with TEM, XRD, SAED and XPS. Furthermore, the applicability of Langmuir isothermal model for Pb(II) onto C-TiO₂ was examined. The adsorption capacity of the adsorbent and the determination of Pb(II) were evaluated with ICP-MS. The maximum adsorption capacity is 28.7 mg g⁻¹, and this method has broad application prospects in areas of environmental purification.

1. Introduction
The presence of heavy metal ions in the environment is of serious concerns due to their toxicity. Pb, in particular, is a natural element predominantly used in industrial applications, and wastewater contains a wide range of Pb(II) concentrations [1,2]. It may affect children’s intelligence or cause negative effects on the metabolic process even at low dosages [3]. Unlike organic pollutants that are usually susceptible to biological degradation, Pb(II) does not degrade into harmless end products [4]. Adsorbents with good adsorption capacities are applied to interact with metal ions to reduce metal contamination [5-7]. Therefore, an effective adsorbent for removing Pb(II) is suitable for water treatment.

The use of nano-adsorbent in environmental remediation has attracted considerable interest owing to their activity [8-10]. Remarkably, TiO₂ which has properties such as non-toxicity, relative cheapness, and high specific surface area, is becoming a new functional material [11-13]. Carbon-doped TiO₂ (C-TiO₂) has attracted much interest owing to their potential in the removal of organic pollutants. But the adsorption capacity of modifications of TiO₂ using carbon for heavy metal ions has received less attention. The aim of this paper is to assess the ability of C-TiO₂ to adsorb Pb(II) from an aqueous solution.

Here, C-TiO₂ were fabricated using a hydrothermal process and post-calcination. The morphology and chemical composition of products were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS). An approach for the effective removal of Pb(II) via C-TiO₂ at room temperature was reported.
2. Experimental section

2.1. Instruments and reagents
The main instruments included a Talos F200X high-resolution transmission electron microscope (Thermo Scientific, USA), an EscaLab 250Xi X-ray photoelectron spectrometer (Thermo Scientific), a Grant LMC-3000 centrifuge (Cambridge, UK), a NexION 350 inductively coupled plasma mass spectrometer (PerkinElmer, USA), a SevenExcellence pH meter (Mettler Toledo, USA).

Titanium butoxide (TBT), low-density polyethylene (LDPE), nitric acid and ethanol were of at least analytical grade, and purchased from Macklin (China). The 1000 mg L\(^{-1}\) Pb(II) standard solution was purchased from the Nonferrous Metals and Electronic Materials Analysis Center (China). 18.2 M\(\Omega\) cm water was prepared with a Dura pro 12 water purifier (China).

2.2. Preparation of C-TiO\(_2\) and characterizations
200 mL 98% ethanol (as solvent), 8.0 g LDPE (as carbon source) and 13.6 mL TBT (as a titanium source) were successively added to a beaker under stirring. The resulting liquid was transferred to a PPL-lined hydrothermal reactor when stirring at 170\(^\circ\)C for 5 h. After cooling to room temperature, the precursors were washed with ethanol and water, and then dried in an oven at 80\(^\circ\)C for 30 min; they were calcined in a muffle furnace at 490\(^\circ\)C for 3 h to obtain C-TiO\(_2\) powder.

C-TiO\(_2\) particles were scattered in ethanol by ultrasonic dispersion for 5 min, and then made of 3 mm diameter wafers into TEM. The microstructure of the adsorbent was observed under an accelerating voltage of 200 kV. XRD analysis was performed using Cu-K\(_\alpha\) radiation (\(\lambda = 1.541\) Å) with a Cu X-ray tube at 30 kV. XPS spectra were collected at a power of 150 W using monochromatized Al-K\(_\alpha\) radiation, and the binding energy was scanned from 100 to 700 eV. The SAED analysis of the adsorbent was also performed.

2.3. Adsorption test
Similar amounts of C-TiO\(_2\) were added to colorimetric tubes, and the pH value of the solution was adjusted to 6.5 using diluted nitric acid. The standard solutions of Pb(II) were transferred to microcentrifuge tubes after 2 min of shaking. Followed by centrifugation at 1500 rpm for 10 min and filtration, the Pb(II) concentrations were determined in 5 mL supernatant.

In kinetic energy discrimination mode, the mass spectrometer was attuned by 1.0 \(\mu\)g L\(^{-1}\) mass spectrometric fluid, and Pb(II) was then determined by inductively coupled plasma mass spectrometry (ICP-MS) using high purity helium as the collision gas and high purity argon as the carrier gas.

3. Results and discussion

3.1. Morphology and properties of C-TiO\(_2\)
Nanosized adsorbents were three-dimensional crystallines with partly aggregation (Figure 1A). The average grain size of C-TiO\(_2\) was counted as 27 nm (Figure 1B). The lattice spacings were 0.36 and 0.18 nm corresponding to (101) and (200) crystal planes of high-resolution TEM observation (Figure 1C), which were regarded as the crystal plane of the anatase phase. In general, both XRD and high-resolution TEM analysis can measure the phase of TiO\(_2\) (including anatase, rutile and brookite). For XRD analysis (Figure 1D), the diffraction peaks at 25.3\(^\circ\), 37.9\(^\circ\) and 48.1\(^\circ\) were assigned to the diffraction from (101), (004) and (200) crystal planes of the anatase phase, respectively.

The phase of adsorbent was further identified using SAED pattern (Figure 1E), and regarded as polycrystalline TiO\(_2\), indicating the crystalline shape of the as-synthesized C-TiO\(_2\). Brunauer-Emmett-Teller (BET) method was used to investigate the specific surface and pore volume of C-TiO\(_2\). The specific surface area was determined to be 371 m\(^2\) g\(^{-1}\), and the pore volume was 0.65 cm\(^3\) g\(^{-1}\).
Figure 1. TEM images (A, B), high-resolution TEM image (C), XRD pattern (D) and SAED pattern (E) of C-TiO₂.

The C 1s, Ti 2p, O 1s and Ti 2s core levels were observed over an XPS survey spectrum (Figure 2A). The high-resolution XPS spectra (Figure 2B–D) had C element confirmed by two peaks at 284.7 and 288.8 eV, which were assigned to C–C and C–O bonds. The Ti 2p spectrum displayed two typical peaks of Ti–O at 464.4 and 458.5 eV. These were assigned to the binding energy of Ti 2p₁/₂ and Ti 2p₃/₂. The O 1s spectrum could be deconvoluted into two individual component peaks located at 529.7 and 531.7 eV. They were attributed to surface O–Ti and O–H groups. As shown in Table 1, the C content was about 9.4% as a result of XPS, revealing the elemental generation of C-TiO₂.
Figure 2. XPS survey spectrum (A) and high-resolution XPS spectra of C 1s (B), Ti 2p (C) and O 1s (D) for C-TiO₂ as a function of binding energy.

Table 1. C, Ti and O contents of as-prepared adsorbent.

| Element | XPS (%) |
|---------|---------|
| C       | 9.37    |
| Ti      | 29.89   |
| O       | 60.74   |

3.2. Removal of Pb(II) from water using C-TiO₂ adsorbent

The metal ion concentrations of the collection supernatant via C-TiO₂ were performed using ICP-MS. The net intensities of Pb-208 were in good linear relation to known concentrations. The instrument detection limit (IDL) of Pb(II) was defined as three standard deviations (SD) of eleven measurements of the blank reagent (IDL = 0.006 μg L⁻¹). Adsorption studies were performed at room temperature starting at different concentrations of Pb(II), and the adsorbent dosage was selected as 0.1 g/25 mL. Each test was repeated in triplicate, and the error bars represent SD. The metal ion retained onto the adsorbent is calculated using the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{m} \tag{1}
\]

where \(C_0\) and \(C_e\) are the initial and final concentrations of Pb(II) (mg L⁻¹), term \(q_e\) is the amount adsorbed per specified mass of adsorbent (mg g⁻¹), \(V\) is the volume of solution (mL), and \(m\) is the mass of adsorbent (mg). The adsorption percentage \(A_p\) (%) of the Pb(II) from solution can be calculated by Equation (2):
The $A_p$ of Pb(II) increased with the contact time, and equilibrium was reached within 100 min (Figure 3). The 95% removal efficiency occurred with small fluctuations when the content of Pb(II)/C-TiO$_2$ was 19.3 mg g$^{-1}$ (Figure 4). The adsorption curves suggested that Pb(II) exhibited affinity to C-TiO$_2$ in weakly acidic solutions. The speciation of the adsorbent was an important factor in the adsorption process.

$$A_p = \frac{C_0 - C_e}{C_0} \times 100\%$$  \hspace{1cm} (2)

Figure 3. Effect of contact time on the adsorption of Pb(II) (initial concentration = 30 mg L$^{-1}$ and pH = 6.5).

Figure 4. Adsorption percentage plot of Pb(II) (contact time = 100 min and pH = 6.5).

Isothermal studies show how metal ion distributes between adsorbent surfaces and metal ion solutions at equilibrium. The Langmuir isotherm is represented by the linear Equation (3), and the maximum adsorption capacity ($K$, mg g$^{-1}$) is determined from a plot of $C_e/q_e$ and $C_e$:

$$\frac{C_e}{q_e} = \frac{C_0}{K} + \frac{1}{K \cdot b}$$  \hspace{1cm} (3)

where $b$ is the Langmuir constant (L mg$^{-1}$). $K$ of C-TiO$_2$ for the removal of Pb(II) were determined to be 28.7 mg g$^{-1}$. The removal ability of bare TiO$_2$ for Pb(II) was 16.4 mg g$^{-1}$.

The proposed adsorption mechanism is as follows: Carbon and O–H groups on the adsorbent surface play a part for Pb(II) adsorption. Lead ions were adsorbed onto active sites, while these sites changed with increasing content of metal/C-TiO$_2$: $A_p$ decreased, and the active sites were filled.
According to the calculation of $K$, the adsorbent amount required is $100/28.7 \text{ mg L}^{-1}$ in the case of Pb(II). 3.4 mg adsorbent can be mixed with 1.0 L water to obtain suspensions at pH = 6.5. The quality of adsorbent consumed is small ($<3.5 \text{ mg L}^{-1}$). This reliable method presents a competitive capacity versus other adsorbents previously reported (Table 2). The adsorption capacity of C-TiO$_2$ is higher than other materials, indicating practical significance for Pb(II) removal and future use of nonmetal-doped TiO$_2$.

### Table 2. Comparison of adsorption capacity of adsorbent materials for Pb(II).

| Adsorbent material       | Pb(II) (mg g$^{-1}$) | Reference |
|--------------------------|----------------------|-----------|
| Cassava stem pith        | 3.7                  | [14]      |
| Activated carbon         | 8.7                  | [15]      |
| Cashew-nut shell         | 19.5                 | [16]      |
| Jackfruit wood sawdust   | 4.4                  | [17]      |
| Oryza sativa husk        | 6.1                  | [18]      |
| C-TiO$_2$                | 28.7                 | This work |

### 4. Conclusion

In summary, C-TiO$_2$ was prepared through hydrothermal method and post-calcination. The adsorption capacity and its application for the removal of Pb(II) were fully evaluated. Pb(II) was adsorbed onto active sites, and the sites were filled with increasing content of metal/C-TiO$_2$. In terms of removing heavy metal ions from contaminated water, the adsorbents can be mixed with water in weakly acidic condition and effectively utilized for 100 min. These integrated features will make the C-TiO$_2$ have attractive applications in areas of environmental purification.

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