Mesoporous TiO$_2$ sphere with high adsorbability: Adsorption behavior study of Pb(II) from water

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Abstract. Mesoporous TiO$_2$ sphere was prepared using a template-free solvothermal treatment. The crystalline size, morphology and property of the adsorbent were characterized with transmission electron microscopy and electron probe microanalysis/wavelength dispersive spectroscopy. Moreover, the applicability of three isothermal models for Pb(II) onto mesostructured TiO$_2$ was investigated. The Pb(II) adsorbability of adsorbent was evaluated using inductively coupled plasma mass spectrometry. The maximum adsorbability of mesoporous TiO$_2$ sphere for Pb(II) is 35.2 mg g$^{-1}$, and this material has bright application prospects for the removal of toxic metal ions.

1. Introduction

Removal of toxic metal ions has become a focus in the field of public health and ecological systems [1,2]. Pb is a natural element predominantly used in industrial applications, and some rivers contain a wide range of Pb(II) concentrations [3,4]. It may affect children's intelligence or cause negative effects on metabolic processes even at low dosages [5]. Hence, an effective adsorbent for removing Pb(II) is suitable for water treatment. Adsorbents with good adsorption capacities are applied to interact with metal ions to reduce the metal contamination [6]. Currently, the widely employed methods for water purification are based on physicochemical processes [7-9].

Mesoporous adsorbent in environmental remediation has attracted considerable interest due to its specific surface area and activity [10]. TiO$_2$ has properties such as high corrosion resistance, relative cheapness and high specific surface area, becoming a new adsorbent material [11,12]. The aim of this paper is to assess the ability of mesoporous TiO$_2$ spheres (MTs) to adsorb Pb(II) from water. In this paper, MTs were prepared using a template-free method. The morphology and composition of products were characterized by transmission electron microscopy (TEM) and electron probe microanalysis/wavelength dispersive spectroscopy (EPMA/WDS). An application in efficient removal of Pb(II) via MTs at room temperature was reported.
2. Experimental section

2.1. Instruments and reagents

The main instruments used included a G2 F30 transmission electron microscope (FEI, USA), a JXA-8530F PLUS electron probe microanalyser (JEOL, Japan), a Grant PCV-2400 centrifuge (Cambridge, UK), a NexION 350X inductively coupled plasma mass spectrometer (PerkinElmer, USA), a S210-K pH meter (Mettler Toledo, USA) and a magnetic hotplate stirrer (Talboys, USA).

99% titanium butoxide, 99% glycol, carbamide, acetone and ethanol were of at least analytical grade, and purchased from Aladdin (China). The 1000 mg L\(^{-1}\) Pb(II) standard stock solution was purchased from Zhongke Quality Inspection Biotechnology (China). Water (resistivity of 18.2 M\(\Omega\) cm) was prepared with a Smart-DUV water purifier (China).

2.2. Synthesis of MTs and characterizations

The synthesis of MTs was conducted by treating the following steps. First, titanium glycolate was prepared as precursor. 0.5 mL titanium butoxide was added to 30 mL glycol with stirring, and then it was added to 110 mL 99.7% acetone by staying for 5 min. After centrifuging, the precipitate was washed with ethanol, and then dried in an oven at 70\(^{\circ}\)C to obtain the precursor powder. Next, 0.9 g titanium glycolate was dispersed into the mixed liquid composed of 150 mL ethanol and 3.8 g carbamide. The well-stirred liquid was transferred to a PTFE-lined reactor when stirred at 160\(^{\circ}\)C for 10 h. After cooling to room temperature, the product was collected by centrifugation. Based on solvothermal reaction, the mesoporous materials were obtained via hydrolysis.

MTs were scattered in ethanol by ultrasonic treatment for 10 min, and then made into wafers of 3 mm in diameter. The TEM image of the adsorbent was observed under an accelerating voltage of 300 kV.

Qualitative analysis of the C/Ti/O composition was carried out using EPMA/WDS operated at 15 kV.

2.3. Adsorption measurement

MTs were added to aliquots of colorimetric tubes, and the pH value of the solution was adjusted by diluted nitric acid. The standard solutions of Pb(II) were pipetted into colorimetric tubes, and brought to volume with water. They were transferred to microcentrifuge tubes after 1 min of shaking, and then centrifuged at 2000 rpm for 5 min to obtain supernatant.

The mass spectrometer was attuned by 1.0 \(\mu\)g L\(^{-1}\) mass spectrometric fluid in KED mode to obtain stable signals and high sensitivities. The Pb(II) concentrations of the collection supernatant via MTs were performed by inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Crystalline size, morphology and properties

TiO\(_2\) fabricated by solvothermal treatment appeared to be mesoporous spheres (Figure 1). MTs were well-shaped, whereas the average grain size was counted as 91 nm, which possessed advantages of uniform particle size distribution and obvious porous structure. High-resolution TEM observation combined with BET method were used to investigate the specific surface area and pore volume of MTs. The specific surface area was determined to be 523 m\(^{2}\) g\(^{-1}\), and the pore volume was 0.86 cm\(^{3}\) g\(^{-1}\). The mesostructured material can interact with the contaminant to adsorb more toxic metal ions.

Due to the fine resolution of the EPMA plane scan (Figure 2), it was possible to visualise the element distribution on the surface of as-prepared material. For micro-area elemental analysis, the contents of Ti, O and C in MTs were revealed by EPMA/WDS results (Table 1), indicating the composition of MTs.
Figure 1. TEM (A,B,C) and high-resolution TEM (D) images of MTs.

Figure 2. EPMA/WDS mapping of as-prepared MTs.
Table 1. Ti, O and C contents of MTs.

| Element | EPMA/WDS (%) |
|---------|--------------|
| Ti      | 31.04        |
| O       | 66.81        |
| C       | 2.15         |

3.2. Removal of Pb(II) from aqueous solution using MTs

The net intensities of Pb-208 were in good linear relation to known concentrations, and the correlation coefficient \((R)\) was 0.9996. Adsorption tests were performed at 23±1 °C starting at different concentrations of Pb(II). Each test was repeated in triplicate, and the error bars represent standard deviation. The metal ion retained onto MTs is calculated:

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

where \(C_0\) and \(C_e\) are the initial and final concentrations of metal ion (mg L\(^{-1}\)), \(q_e\) 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 metal ion from solution is calculated by Equation (2):

\[
A_p = \frac{C_0 - C_e}{C_0} \times 100\%
\]

\(A_p\) increased with contact time, and equilibrium was reached within 90 min (Figure 3). The \(A_p\) increased with rising pH value, and a maximum \(A_p\) was obtained at pH 5.6–7.8 (Figure 4). Since the precipitation of metal hydroxide relies on pH value, its pH-dependence is applied to removal procedures of metal ions. In the adsorption process at pH >6.0 for Pb(II) might exist different behaviors, and the precipitation of Pb(II) contributed to uptake of the metal ions at high pH values of solutions. Therefore, the adsorption behavior of Pb(II) onto MTs was studied at pH = 6.0 for subsequent experiments. Pb(II) exhibited a high affinity onto MTs in faintly acidic solutions. Consequently, the pH value of the solution affected the surface charge and speciation of the adsorbents.

Figure 3. Effect of contact time on Pb(II) adsorption using MTs (initial concentration = 30 mg L\(^{-1}\), pH = 6.0, and adsorbent dosage = 4.0 g L\(^{-1}\)).
Figure 4. Effect of pH value on Pb(II) adsorption using MTs (initial concentration = 30 mg L\(^{-1}\), contact time = 90 min, and adsorbent dosage = 4.0 g L\(^{-1}\)).

3.3. Three isothermal models for Pb(II) adsorbed onto MTs

The model parameters were estimated with \( R \) values. The Langmuir isotherm is presented by the linear Equation (3), and the maximum adsorbability \((K, \text{ mg g}^{-1}\)) is determined:

\[
\frac{c_e}{q_e} = \frac{c_t}{K} + \frac{1}{Kb}
\]  

where \( b \) is the Langmuir constant (L mg\(^{-1}\)). \( K \) and \( b \) for the removal of Pb(II) were determined from the slope and intercept of lines.

The Freundlich isotherm equation is:

\[
\log(q_e) = \log(k_f) + \frac{1}{n} \cdot \log(C_e)
\]

where \( k_f \) and \( n \) are the Freundlich constants.

The Temkin isotherm model is described by Equation (5):

\[
q_e = B \cdot \ln(k_t) + B \cdot \ln(C_e)
\]

where \( k_t \) and \( B \) are the Temkin constants.

Table 2 displays the characteristics of adsorption isotherms expressed by the parameters of plots. The \( R^2 \) value of the Langmuir isotherm for Pb(II) was higher than those of Freundlich and Temkin isotherms. The three models closely followed this order: Langmuir > Temkin > Freundlich.

Proposed mechanism in the adsorption process using mesoporous TiO\(_2\) is as follows: polar groups e.g., hydroxyl can interact with metal ions to form complexation reactions. In fact, the adsorption behavior involves ion exchange as the interaction force between Pb(II) and MTs. Metal ions were adsorbed on specific sites, growing into more porous structure. These indicated that the Pb(II) was adsorbed onto the surface of MTs through binding with polar groups.

Table 2. Estimated isothermal models and their constants for Pb(II) onto MTs.

| Cation | Langmuir isotherm | Freundlich isotherm | Temkin isotherm |
|--------|-------------------|---------------------|-----------------|
|        | \( b \)          | \( K \)             | \( R^2 \)       |
| Pb(II) | 0.011             | 35.2                | 0.971           |
|        | \( 1/n \)        | \( k_f \)           | \( R^2 \)       |
| Pb(II) | 0.280             | 4.26                | 0.959           |
|        | \( B \)          | \( k_t \)           | \( R^2 \)       |
| Pb(II) | 0.176             | 1.79                | 0.963           |

2.5 mg adsorbent was mixed with 1.0 L water to obtain suspensions at pH = 6.0. There was only minor amount of adsorbent consumed, which presented a competitive adsorbability versus other adsorbents previously reported (Table 3). The Pb(II) adsorbability of MTs was higher than other materials, which could be useful in treatment of water containing toxic metal ions. Finally, the results conveyed a potential for removing Pb(II), providing practical application of mesostructured materials.
Table 3. Comparison of adsorbability of adsorbent materials for Pb(II).

| Adsorbent material                      | Pb(II) (mg g⁻¹) | Reference |
|----------------------------------------|-----------------|-----------|
| Torrefied poplar-biomass               | 30.0            | [13]      |
| PVC-acetylacetone composite            | 33.1            | [14]      |
| Chicken egg shell powder               | 33.7            | [15]      |
| Poly-o-toluidine/triethanolamine       | 31.3            | [16]      |
| Chitosan-N-lauroyl                     | 31.5            | [17]      |
| Eggshell powder-sericite               | 33.9            | [18]      |
| Mesoporous TiO₂ sphere                 | 35.2            | This work |

4. Conclusion

MTs were synthesized through a solvothermal method using titanium glycolate as precursor. Series of characterizations suggested that the MTs exhibited high crystallinity, uniform morphology and high specific surface area. The adsorbability of MTs and the mechanism of adsorbent interaction were discussed. This study had evidenced that the contact time and pH value of the solution were important factors for Pb(II) adsorption. For water purification, the adsorbents were mixed with water at pH = 6.0 with high adsorption efficiency, and used to treat for 90 min. This approach with suitable conditions can be utilized to prevent Pb(II) contaminant in wastewater from industries.

References
[1] Mercante L A, Andre R S, Schneider R, Mattoso L H, Correa D S 2020 New Journal of Chemistry 44 13030
[2] Che X H, Yuan R H, Tang L C, Xiong Y D, Wu M F, Zhu M H 2021 Journal of Physics: Conference Series 1978 012099
[3] Wei J, Duan L, Wei J, Hoffmann E, Meng X 2021 Journal of Environmental Sciences 101 135
[4] Akbari-Adergani B, Rahnama S, Shirkhan F 2017 J Mazandaran Univ Med Sci 27 162
[5] Zhang P, Ouyang S, Li P, Sun Z, Ding N, Huang Y 2020 Journal of Cleaner Production 246 118728
[6] Qu J, Li Y, Song T, Huang S, Jin Y 2020 Ecological Engineering 142 105639
[7] Yuan R H, Liu W H, Teng Y J, Nie J, Ma S Z 2015 Spectroscopy and Spectral Analysis 35 1276
[8] Liu W H, Yuan R H, Teng Y J 2014 Chinese Journal of Luminescence 35 1124
[9] Sandouqa A, Al-Shannag M, Al-Hamamre Z 2020 Renewable Energy 151 103
[10] Vu D, Li Z Y, Zhang H N, Wang C 2012 Journal of Colloid & Interface Science 367 429
[11] Yuan R H, Wu T H, Hu T Y, Shi L, Shi J 2020 IOP Conference Series: Materials Science and Engineering 892 012014
[12] Chen D, Tu N, Si C, Yin M, Wang X 2019 Water Science & Technology 80 884
[13] Demey H, Melkior T, Chatroux A, Attar K, Sébastien T, Miller H, Muriel M 2019 Chemical Engineering Journal 361 839
[14] Elzbieta R, Katarzyna W 2019 Polymers 11 513
[15] Kim D, Hwang S, Kim Y, Jeong C, Pyo H, Sang R 2019 Bulletin of the Korean Chemical Society 40 1156
[16] Nafisur R, Fazeel K, Mohd N 2020 Environmental Technology & Innovation 17 100634
[17] Vieira C L, Neto F O S, Carvalho-Silva V H, Signini R 2019 Journal of Environmental Chemical Engineering 7 103070
[18] Choi H 2019 Water Science and Technology 79 1922