Adsorption of Pb$^{2+}$ on a layered alkali titanate from water

D A Sruamsiri and M Ogawa
School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555, Payupnai, Wangchan, Rayong 21210, Thailand

E-mail: makoto.ogawa@vistec.ac.th

Abstract. A layered alkali titanate (Cs$_2$Ti$_5$O$_{11}$) was used to concentrate Pb$^{2+}$ from water. The reaction of the layered alkali titanate with an aqueous solution of lead acetate trihydrate was investigated to find an efficient collection of Pb$^{2+}$ from aqueous solutions at room temperature. The adsorption isotherm was H-type, indicating a strong interaction between the titanate and Pb$^{2+}$. The maximum adsorbed Pb$^{2+}$ amount was 1.27 mmol Pb/g Cs$_2$Ti$_5$O$_{11}$, which corresponded to 86% of the cation exchange capacity (2.94 meq/g) of Cs$_2$Ti$_5$O$_{11}$. The adsorption isotherm was fitted with the Langmuir equation with a high correlation coefficient ($R^2 = 0.9997$), suggesting that a high affinity between the titanate surface and Pb$^{2+}$.

1. Introduction
Pollution of water by metals from industrial wastewater is a serious environmental concern. Lead is used in battery, printing, painting, and dyeing industries[1,2], causing the contamination of environments. Due to the toxicity of lead, the removal of lead from aqueous environments is required. Among possible ways of the removal of lead, including membrane separation and precipitation,[3,4] adsorption (ion exchange) on solids is a useful process for metal ions collection from aqueous environments. Various ion exchangers from nature and synthetic materials) are available for the target metal ions to be examined.

Ion exchangers such as inorganic layered solids were known as useful adsorbents. Their advantages over organic and polymeric ion exchangers are chemical and thermal stability.[5] Such ion-exchangeable layered solids as smectite group of clay minerals,[6] layered alkali silicates[7,8], and layered alkali titanates [9,10] are known as non-toxic and environmentally friendly adsorbents.

In the present study, a layered alkali titanate (Cs$_2$Ti$_5$O$_{11}$) was examined to find an efficient collection of Pb$^{2+}$, a common state of lead in aqueous environments, from water at room temperature. The theoretical cation exchange capacity of Cs$_2$Ti$_5$O$_{11}$ is 2.94 meq/g (derived from the chemical formulae), which is high compared with conventional zeolites and bentonite (~1.0 meq/g).

2. Method

2.1. Materials
Lead acetate trihydrate ((CH$_3$COO)$_2$Pb•3H$_2$O, denotes as Pb(ac)$_2$ >99.5% from Merck), anatase (99.8% from Aldrich) and Cs$_3$CO$_3$ (99% from Alfa Aesar) and Milli-Q water (Type II 15 MΩ•cm) were used without further purification.
2.2. Sample Preparation
A layered alkali titanate (Cs₂Ti₅O₁₁) was prepared by the solid-state reaction. The mixture of Cs₂CO₃ and TiO₂ (anatase) (molar ratio of 1:5) was grinding at room temperature. Then, the mixture was heated at 1000°C for 20 h as reported previously [11].

2.3. Adsorption of Pb²⁺ from aqueous solution
Cs₂Ti₅O₁₁ (100 mg) was added in 25 ml of water for dispersion and the reaction was magnetically stirred for 1 h. Then, 25 ml of Pb(ac)₂ solution was added into the suspension of the Cs₂Ti₅O₁₁. The mixture was magnetically stirred further for 24 h at room temperature. The initial concentration of Pb(ac)₂ solution was 0.07, 0.147, 2.2, 2.9 and 3.7 mM. Centrifugation for the solids collection and they were dried in air at 40°C.

2.4. Langmuir model
The adsorption isotherm was described by the Langmuir model. The Langmuir model is expressed as

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

Where \( C_e \) is the concentration at the equilibrium in a unit mmol/L, \( q_e \) is the adsorption amount in a unit mmol/g, \( q_m \) is the maximum adsorption capacity of the adsorbent in a unit mmol/g, and \( K_L \) is the Langmuir constant in a unit L/mmol that may relate to the free energy (\( \Delta G \)) of the adsorption. From the plot of \( C_e/q_e \) (y-axis) versus \( C_e \) (x-axis), the values of \( 1/q_m \) and \( K_L \) were determined from the slope and intercept of the linear plot, respectively.

2.5. Characterization
X-ray powder diffraction (XRD) patterns were performed on a Bruker (Karlsruhe from Germany) with NEW D8 ADVANCE X-ray diffractometer model by using Ni-filtered Cu-Kα radiation (40 kV and 40 mA). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was done to determine the Pb concentration using an Agilent Technologies 700 Series ICP-OES (California from the United States). Scanning electron microscopy (SEM) was done for the samples coated with Pt by using a JEOL (Tokyo from Japan) JSM-7610F scanning electron microscope, and elemental mapping was obtained attached to the SEM using an energy dispersive X-ray fluorescence spectrometer (X-Max 150 mm², Oxford from the UK).

3. Result and discussion
The Pb²⁺ adsorption isotherm onto Cs₂Ti₅O₁₁ from the water was shown (figure 1). The isotherm was indicated as an H-type adsorption isotherm, following the Giles et al. classification.[12] Type H adsorption suggested that a significant affinity between Pb²⁺ and the Cs₂Ti₅O₁₁. The adsorbed Pb²⁺ amount was 1.26 mmol Pb/g Cs₂Ti₅O₁₁ (initial pH 6.1). The dashed line is an ideal value to confirm the amount of adsorbed Pb²⁺, which is derived from the ideal cation exchange capacity (CEC) of Cs₂Ti₅O₁₁ (2.94 meq/g). The adsorption of Pb²⁺ on Cs₂Ti₅O₁₁ almost reached (86%) the theoretical CEC value at the 2.9 mM initial Pb(ac)₂ solution concentration.

The Langmuir plot fitted Cs₂Ti₅O₁₁ with a high correction coefficient (R² = 0.9997) at the concentration between 2.2 and 3.7 mM in figure 2. The maximum adsorption capacity of the adsorbent (\( q_m \)) was 1.20 mmol Pb/g Cs₂Ti₅O₁₁. The Langmuir constant (\( K_L \)) was high (130 L/mmol), suggesting the high affinity between the Cs₂Ti₅O₁₁ surface and Pb²⁺, which \( K_L \) may correlate with the free energy. The Pb(ac)₂ concentration below 2.2 mM was not clearly explained because the mechanism may contribute to the precipitation. The initial pH of Pb(ac)₂ solution, in the present study, was in the range of 5.8-6.1, and the titanate suspension was in the range of 11.3-11.4. After the mixing between the
titanate suspension and Pb(ac)$_2$ solution, the pH of the mixture was in the range of 6.6-11.0. Then, after 24 h of the reaction, the pH became 5.8-10.6.

Figure 1. Adsorption isotherm of Pb$^{2+}$ on Cs$_2$Ti$_5$O$_{11}$ from aqueous solutions at room temperature. The dashed line indicates the ideal value derived from the chemical formulae.

Figure 2. Langmuir plot of Pb$^{2+}$ adsorption on Cs$_2$Ti$_5$O$_{11}$.

The XRD pattern of Cs$_2$Ti$_5$O$_{11}$ before and after reaction with Pb$^{2+}$ was shown (figure 3). The observed basal spacing value of Cs$_2$Ti$_5$O$_{11}$ (1.02 nm) increased to be 1.05 nm after the ion exchange with Pb$^{2+}$, suggesting the hydration state of Cs$_2$Ti$_5$O$_{11}$. The basal spacing of Cs$_2$Ti$_5$O$_{11}$ varied depending on the interlayer cation (such as alkali ion) and the hydration form (such as Cs$_2$Ti$_5$O$_{11}$•H$_2$O and Cs$_2$Ti$_5$O$_{11}$•3H$_2$O) [13]. The observed basal spacing increased from 1.02 nm to 1.05 nm in the present study is similar to that Cd$^{2+}$ exchanged Cs$_2$Ti$_5$O$_{11}$ reported previously (from 1.02 nm to 1.10 nm) [14]. In addition, the d$_{001}$ reflection intensity became weaker after the adsorption of Pb$^{2+}$.

The SEM images, together with elemental mapping of Cs$_2$Ti$_5$O$_{11}$ (figure 4) before and after reaction with Pb(ac)$_2$ solution of 2.9 mM, revealed that, even though the X-ray diffraction became weaker, the
platy shaped morphology of Cs$_2$Ti$_5$O$_{11}$ was retained after the reaction with Pb$^{2+}$. The elemental mapping showed the homogeneous distribution of Pb$^{2+}$ in and on the titanate particles, confirming the successful ion exchange of Cs$_2$Ti$_5$O$_{11}$ with Pb$^{2+}$.

The previous studies on the collection of Pb$^{2+}$ from aqueous solution by using ion exchangers, such as clays and clay minerals [15,16], carbon nanotube[17], activated carbon[18], and zeolite[19] have been reported. The amounts of the adsorbed Pb$^{2+}$ are summarized in table 1. The adsorbed Pb$^{2+}$ amount on Cs$_2$Ti$_5$O$_{11}$ (1.26 mmol Pb/g Cs$_2$Ti$_5$O$_{11}$) was higher than the reported values, [15-19] confirming the advantageous aspects of Cs$_2$Ti$_5$O$_{11}$ for Pb$^{2+}$ collection from water.

![Figure 3. XRD patterns of Cs$_2$Ti$_5$O$_{11}$ after the reactions with Pb(ac)$_2$ solutions of (b) 0.07, (c) 0.147, (d) 2.2, (e) 2.9 and (f) 3.7 mM, together with (a) original Cs$_2$Ti$_5$O$_{11}$.](image)

![Figure 4. SEM images of Cs$_2$Ti$_5$O$_{11}$ (a) before and (b) after the reaction with a Pb(ac)$_2$ solution at the 2.9 mM concentration, together with the elemental mapping.](image)
Table 1. Example of the Pb$^{2+}$ adsorption amounts on other adsorbents.

| Adsorbents | Amount of adsorbed Pb$^{2+}$ (mmol Pb/g adsorbent) | Reference |
|------------|-------------------------------------------------|-----------|
| Magadiite  | 1.23                                            | [12]      |
| Bentonite  | 0.96                                            | [13]      |
| Carbon nanotubes | 0.0048                                      | [14]      |
| Activated carbon | 0.10                                         | [15]      |
| Zeolite    | 0.012                                           | [16]      |
| Cs$_2$Ti$_5$O$_{11}$ | 1.27                                         | This study |

4. Conclusions

Efficient collection of Pb$^{2+}$ from solutions by the reaction with the layered alkali titanate (Cs$_2$Ti$_5$O$_{11}$) at room temperature. The affinity between Pb$^{2+}$ and the titanate was high, confirmed by type H adsorption isotherm and the high correlation coefficient of the Langmuir equation. The maximum adsorbed Pb$^{2+}$ amount was 1.27 mmol Pb/g Cs$_2$Ti$_5$O$_{11}$. The adsorbed Pb$^{2+}$ amount of Cs$_2$Ti$_5$O$_{11}$ was high compared with those reported for other adsorbents (magadiite, bentonite, carbon nanotube, activated carbon, and zeolite), confirming the advantageous aspects of Cs$_2$Ti$_5$O$_{11}$ for the treatment of water containing Pb$^{2+}$.

Acknowledgment

This work was supported by Research Chair Grant 2017 (Grant FDA-CO-2560-5655) from the National Science and Technology Agency (NSTDA), Thailand, and Research Chair Grant 2020 (grant number B05F630117) from Program Management Unit (PMU) and Office of National Higher Education Science Research and Innovation Policy Council (NXPO), Thailand. D.A.S. acknowledges Vidyasirimedhi Institute of Science and Technology, Thailand for the scholarship for her Ph.D. study.

References

[1] Matlock M, M, Howerton B S and Atwood D A 2002 Ind. Eng. Chem. Res. 41 1579-82
[2] Tong S, Schirmding Y Ev and Prapamontol T 2000 Bull. World Health Organ. 78 1068-77
[3] Chen Q, Luo Z, Hills C, Xue G and Tyer M 2009 Water Res. 43 2605-14
[4] Divrikli U, Kartal A A, Soylak M and Elci L 2007 J. Hazard. Mater. 145 459-64
[5] Clearfield A 1996 Comprehensive Supramolecular Chemistry Solid-State Supramolecular Chemistry: Two-and Three-Dimensional Inorganic Networks vol 7 ed G Alberti and T Bein (New York: Pergamon)
[6] Otunola B O and Ololade O O 2020 Environ. Technol. Innov. p 100692
[7] Sirinakorn T T, Imwiset K, Bureekaew S and Ogawa M 2018 Appl. Clay Sci. 153 187-97
[8] Homhuan N, Imwiset K, Sirinakorn T, Bureekaew S and Ogawa M 2017 Clay Sci. 21 21-8
[9] Ide Y, Sadakane M, Sano T and Ogawa M 2014 J. Nanosci. Nanotechnol. 14 2135-47
[10] Saothayanun T K, Sirinakorn T T and Ogawa M 2021 Front. Energy in press
[11] Grey I, Madsen I, Watts J, Bursill L and Kwiatkowska J 1985 J. Solid State Chem. 58 350-6
[12] Giles C, MacEwan T, Nakhwa S and Smith D 1960 J. Chem. Soc. 111 3973-93
[13] Sasaki T, Komatsu Y and Fujiki Y 1992 Chem. Mater. 4 894-9
[14] Sirinakorn T T, Bureekaew S and Ogawa M 2019 Bull. Chem. Soc. Jpn. 92 1-6
[15] Sruamsiri D A, Sirinakorn T T and Ogawa M 2021 Clays and Clay Miner. in press
[16] Glatstein D A and Franciscia F M 2015 Appl. Clay Sci. 118 61-7
[17] Li Y-H, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D and Wei B 2002 Chem. Phys. Lett. 357 263-6
[18] Goel J, Kadirvelu K, Rajagopal C and Garg VK 2005 J. Hazard. Mater. 125 211-20
[19] Jamil T S, Ibrahim H S, Abd El-Maksoud I H and El-Wakeel ST 2010 Desalination 258 34-40