Removal of Cd^{2+} and Pb^{2+} from water by LaGdO$_3$ perovskite

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Abstract

Nanocrystalline LaGdO$_3$ perovskite was synthesized by the co-precipitation method using metal nitrate and carbonate salts as starting materials. The product was characterized with XRD, EDX, SEM, TEM, and BET. The XRD pattern confirmed the formation of perovskite phase. The SEM micrograph indicated that the LaGdO$_3$ was nanosized particles with morphology containing porosity. The measured pH$_{pzc}$ of synthesized LaGdO$_3$ in this work was 8.00, the surface was negative charge. Application as heavy metal ions adsorption was investigated and found positive with cadmium and lead. Langmuir and Freudlich isotherms were used to describe the adsorption behavior of heavy metal ions. The LaGdO$_3$ perovskite obtained from this work could adsorb heavy metal ions which should be of interest in application such as wastewater treatment.

Keywords: LaGdO$_3$; Perovskite; Chemical co-precipitation process; Heavy metal adsorption; Adsorption isotherms; Wastewater treatment

1. Introduction

Wastewater from industries process contains many toxic heavy metal such as Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, etc. These metal ions causing diseases in living organisms [1-3]. The method for removing the heavy metal are available but the sorption of heavy metal ions onto solid adsorbent are the most common route applied for wastewater treatment and industrial effluents [4, 5]. Many adsorbent such as zeolite, metal oxide, perovskite, activated carbon, are highly effective and can be easily regenerated [6].

Nano-LaGdO$_3$ perovskite has interesting properties such as porous material and electrocatalytic [7, 8]. The properties of this material beneficial for application as heavy metal adsorbent. Many method to prepare nanostructure perovskite such as solid state reaction, hydrothermal, sol-gel method, chemical co-precipitation [9, 10]. All method, however, have some disadvantage with preparation of high purity and high surface area perovskite.

The aim of this work is to study the preparation, characterization and application of nano-LaGdO$_3$ perovskites. In the first stage, to find a simple route to prepare nano-LaGdO$_3$ perovskites through low calcination temperature

that yield high purity perovskite phase. The precursor for $LaGdO_3$ will be synthesized by chemical co-precipitation process. The precursor then will be calcined at 1,200 °C to obtain the desired perovskites $LaGdO_3$. This route should have several advantages such as simplicity, low cost, no waste, and no environmental pollution compared with other routes. The application presented in this work is the possible use as Cd^{2+} and Pb^{2+} remover from aqueous solutions. The factors of contact time and heavy metal concentration shall be investigated. The adsorption capacity the Langmuir and Freundlich isotherms shall be studied and discussed.

2. Materials and methods

Preparation of nano- LaGdO₃ perovskite by chemical co-precipitation method

Nano-$LaGdO_3$ perovskite was prepared by chemical co-precipitation process reported previously [11] with some modifications displayed in Fig. 1. Starting materials for this perovskite were $La(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$. A specific amount of each was dissolved in distilled water to make 1 M solutions. Both solutions with equal volume were mixed together with vigorous stirring. Then 2 M $K_2CO_3 \cdot 1.5H_2O$ solution, same volume as one of the nitrate solutions, was rapidly added. After the precipitation was complete, the precipitate was filtered and washed with distilled water several times until the washed water became neutral (pH =7). The product was then dried at 100 °C for 6 h to yield the "precursor" after which it was calcined at 1,200 °C for 2 h to obtain the $LaGdO_3$ perovskite.

$$1M\ La(NO_3)_3 \cdot 6H_2O \qquad\qquad 1M\ Gd(NO_3)_3 \cdot 6H_2O$$

stirring

$$2M\ K_2CO_3 \cdot 1.5H_2O$$

dried at 100 °C for 6 h

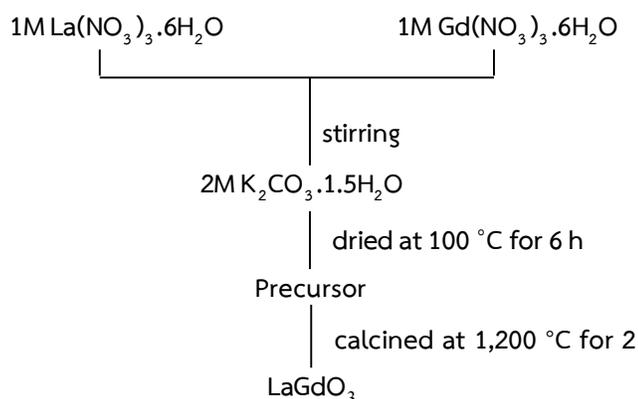Precursor

calcined at 1,200 °C for 2

$$LaGdO_3$$

Fig. 1 Chemical co-precipitation process for preparation of $LaGdO_3$.

Characterization of product

The structure, microstructure, morphology, elements composition, and surface area were investigated by X-ray diffraction (XRD, CuKα radiation, PHILIPS), scanning electron microscope (SEM, SEM-5800 LV, JEOL), transmission electron microscope (TEM, JEM-2100, JEOL), Dispersive X-ray spectrometer (EDAX, ISIS 300, Oxford), and N_2-isotherm BET method (BET, model SA 3100, USA)

Determination of pH at point of zero charge (pHₚᵤ꜀)

The pH_{pzc} of the sample was determined by the pH drift method [12], the detail of which has been described earlier. Briefly, 0.10 M NaCl was prepared. The 50 mL each of 0.10 M NaCl were pipetted into 12 flasks of 250 mL

Erlenmeyer flasks. The pH of these solutions were adjusted to 1 – 12 using diluted HCl or NaOH solution and recorded as initial pH, pH_i.

About 0.05 g of LaGdO$_3$ was added into each flask and sealed for 24 h with constant agitation using a magnetic stirrer. At the end of experiment, the pH was measured as final pH, pH_f. A graph was constructed by plotting pH_i against pH_f and the pH_{pzc} was determined from the crossover point of pH_i and pH_f in the graph.

Adsorption study

The effect of parameters such as initial concentration and contact time for the adsorption of cadmium and lead ions on LaGdO$_3$ perovskite nanoparticles were studied in a 100 mL Erlenmeyer flask containing 0.20 g of adsorbent. The flask was then stirred at 300 rpm until reaching the equilibrium. The resultant solution was centrifuged and the supernatant liquids was analyzed by an inductively couple plasma-optical emission spectrometer (ICP-OES, Optima 4,300 DV, Perkin Elmer, USA). The amount of adsorbed metal ion at equilibrium condition, q_e (mg g^{-1}), was calculated using Eq. (1),

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Where q_e is the mass of adsorbed metal ion at equilibrium condition (mg g^{-1}), C_0 is the starting concentrations (mg L^{-1}), C_e is the equilibrium concentrations (mg L^{-1}), V is the volume of metal solution (L), and W is the weight of adsorbent (g)

Effect of contact time

The solution of 1 mmol L^{-1} for Cd^{2+} and Pb^{2+} volume 100 mL was pipetted into the beaker containing 0.20 g of LaGdO$_3$. Then stirring for 1-40 minutes, filtered and the supernatant was collected. Determination of M^{2+} (M = Cd, Pb) in the supernatant by ICP.

Effect of metal ions concentration

Solution of cadmium and lead with initial concentrations 1, 5, 9, 13, 17, 21 and 25 mmol L^{-1} were used. The weight of LaGdO$_3$ adsorbent was fixed at 0.20 g. The volume of heavy metal ion solution was fixed at 100 mL. The solution of each concentration for Cd^{2+} and Pb^{2+} was pipetted into the beaker. Then stirring 1 and 30 minutes for Cd^{2+} and Pb^{2+}, respectively. Filtered and the supernatant was collected. Determination of M^{2+} (M = Cd, Pb) in the supernatant by ICP.

3. Results and Discussion

Preparation and Characterization of LaGdO$_3$ product

In the chemical co-precipitation process, the precursor obtained in the first stage was white which after calcination at 1,200 °C for 2 h it turned to white LaGdO$_3$ product. The formation of synthesized powder was

investigated by XRD measurement using CuK_α radiation at 2θ between 20° and 80° and calculated the average crystalline size by the Debye-Scherrer equation. From the XRD spectra of $LaGdO_3$ perovskite, the perovskite phase formed at 1,200 °C match with JCPDS file no. 42-1465 of monoclinic $LaGdO_3$ perovskite (Fig. 2(a)). The average crystalline size of synthesized $LaGdO_3$ powder was 71 nm. The purity of the $LaGdO_3$ was also checked with EDX spectrometer (Fig. 2(b)). From the clean spectra of both XRD and EDX, the $LaGdO_3$ product can be considered as high purity perovskite phase.
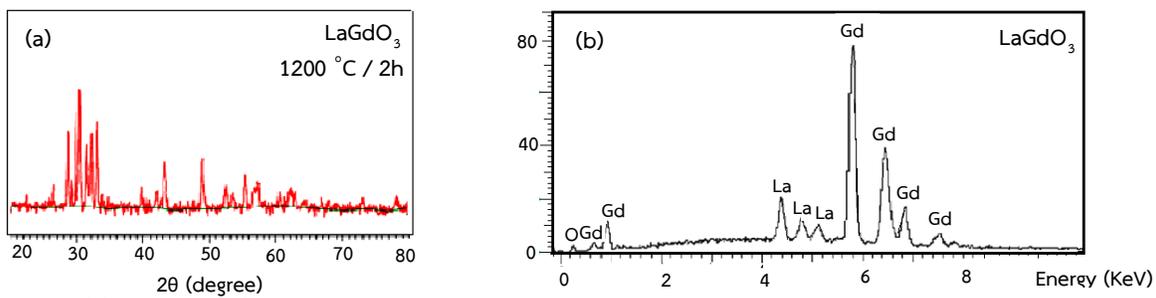

Fig. 2 (a) XRD and (b) EDX pattern of $LaGdO_3$ perovskite obtained from calcinations at 1,200 °C for 2 h

The surface of nano-$LaGdO_3$ perovskite was checked with the SEM microscope (Fig. 3(a)). It can be seen that the surface of $LaGdO_3$ contain long grains shape with nanometer scale**.** This should give an advantage in term of bulk surface and high concentration of inter-particle porosity. The TEM micrograph of sample is shown in Fig. 3(b) which we can see the porosity between the long grains which should give them distinct advantage for heavy metal adsorption.
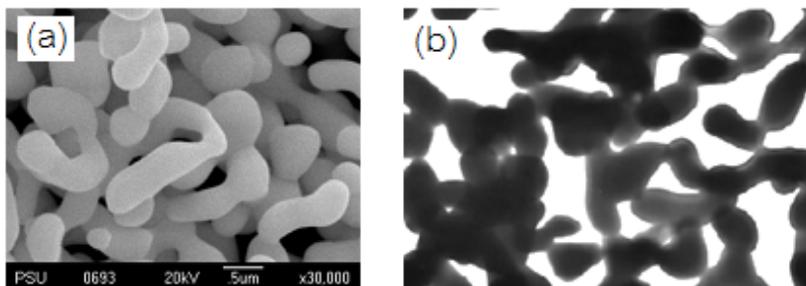

Fig. 3 (a) SEM and (b) TEM photographs of synthesized $LaGdO_3$ perovskite

The BET surface area was determined based on N_2-adsorption isotherm. The $LaGdO_3$ had surface area of 5.43 m^2 g^{-1}, total pore volume of 0.03 cc g^{-1}, and pore size diameter of 206.60 °A. The pH_{pzc} of $LaGdO_3$ was found to be 8.00 from the graph where the curve of pH_f as a function of pH_i crossed the line $pH_i = pH_f$ (Fig. 4). It is indicated that the surface of $LaGdO_3$ was basic.
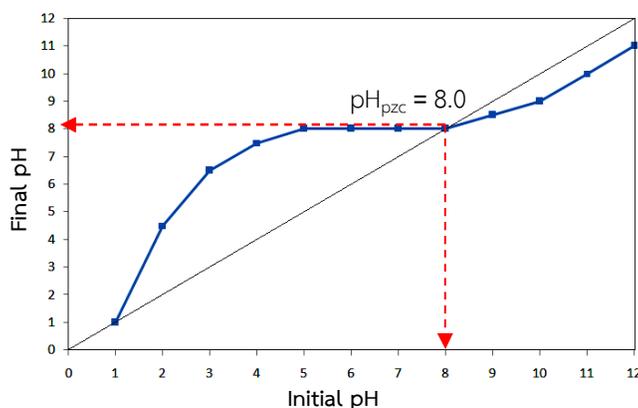
Fig. 4 The plot of final pH (pH$_f$) versus initial pH (pH$_i$) of the LaGdO$_3$ sample to determine the pH$_{pzc}$.

Application to heavy metal adsorption

The effect of contact time and heavy metal ion concentrations

The effect of contact time and metal ion concentration for the removal of cadmium and lead on LaGdO$_3$ perovskite nanoparticles were studied as being explained in Section *Effect of contact time* and *Effect of metal ions concentration*. The adsorption capacities for Cd^{2+} and Pb^{2+} were determined with different stirring times. The experimental data of the adsorption with respect to contact time on surface of LaGdO$_3$ are shown in Fig. 5(a). For Cd^{2+}, the removal of Cd^{2+} very rapid. The equilibrium reached at 1 min, may be due to present of more binding sites for metal ion adsorption [13]. For Pb^{2+}, The results indicated that the amount adsorbed increased with an increase in stirring time and reached equilibrium at 30 min (Fig. 5(a)). After 30 min, the surface pore of adsorbent may be covered and it become difficult for Pb^{2+} into the interior of the pores [13]. The amount of metal adsorbed (q$_e$) was found to be 8.06 mg g^{-1} for cadmium ion 1 mmol L^{-1} (103.90 mg L^{-1}) and 15.31 mg g^{-1} for lead ion 1 mmol L^{-1} (186.60 mg L^{-1}). The adsorption capacities for 1 min and 30 min equilibrium of Cd^{2+} and Pb^2, respectively were determined at different concentrations and are shown in Fig. 5(b). The concentration of heavy metal ions were varied in range 1 – 25 mmol L^{-1} giving the q$_e$ range of cadmium ion 8.06 – 274.35 mg g^{-1} (for Cd^{2+} concentrations 103.90 – 2,629.40 mg L^{-1}). The q$_e$ of Lead ion was in range of 15.31 – 392.40 mg g^{-1} (for Pb^{2+} concentrations 186.60 – 4,745.50 mg L^{-1}). The results indicated that the amount adsorbed increased with an increase in concentration of Cd^{2+} and Pb^{2+} ions. The adsorption of Cd^{2+} and Pb^{2+} onto surface of LaGdO$_3$ perovskite resulted from the electrostatic attraction between positively charged sorbate (Cd^{2+} and Pb^{2+}) and negatively charged sorbent (LaGdO$_3$, pH$_{pzc}$=8.00). From the experiment, the LaGdO$_3$ can application as the heavy metal sorbent with exhibited moderate efficiency of q$_e$ = 274.35 mg g^{-1} for Cd^{2+} 25 mmol L^{-1} (2,629.40 mg L^{-1}) and q$_e$ = 392.40 mg g^{-1} for Pb^{2+} 25 mmol L^{-1} (4,745.50 mg L^{-1}).

The effect of contact time and metal ion concentration are important parameter. For application, the contact time use for determines how long the heavy metal ion adsorbed onto adsorbent completely. The study of effect of metal ion concentration help to know the adsorption capacities, it use for evaluation of adsorbent because it determines how much adsorbent is required for the quantitative enrichment of the analyte from a given solution [14].
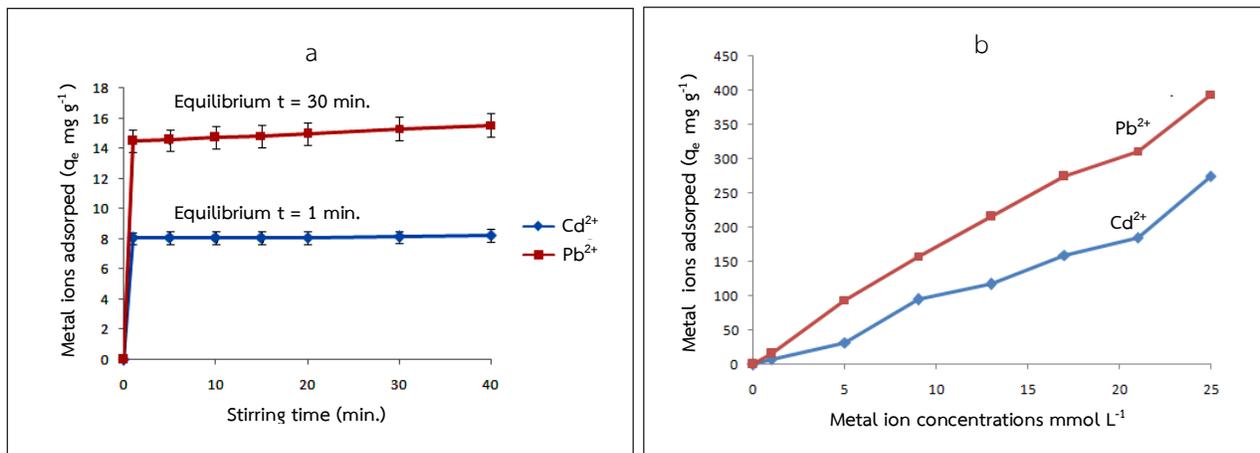
Fig. 5 (a) The effect of contact time to the adsorption of Cd^{2+} and Pb^{2+} and (b) The effect of metal concentration on the adsorption of $LaGdO_3$

Adsorption isotherms

Heavy metal ions (Cd^{2+} and Pb^{2+}) adsorption isotherm data starting at different initial concentration were investigated following the models of Langmuir and Freundlich. The information of isotherms given in Table 1.

Table 1 Adsorption isotherm of heavy metal ions adsorption

Isotherm	Langmuir	Freudlich
Typical of adsorption	Monolayer adsorption	Multilayer adsorption
Equation	$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$$ K_L is Langmuir constant	$$q_e = K_F \cdot C_e^{\frac{1}{n}}$$ K_F is Freudlish constant, and n is an empirical parameter relating to the adsorption intensity

A linear relationship between the amount of $LaGdO_3$ (g) against the concentration of cadmium (and lead) ions in the remaining solution (mmol L^{-1}) was observed. The values of linear correlation coefficients R^2, Langmuir parameters, and Freudlich parameters are given in Table 2. The results fitted well with the Langmuir model. From the R^2 values of Langmuir and Freudlich isotherms with cadmium, the adsorption of cadmium and Lead are better described with the Langmuir model since the R^2 value was close to 1. The typical of adsorption are monolayer adsorption.

The maximum adsorption capacity (q_m) was found to be 0.87 mg g^{-1} for cadmium ion and 1.31 mg g^{-1} for lead ion. The K_L value was found to be 0.17 for cadmium ion and 0.99 for lead ion. The value of q_m obtained above may be on the low side of q_m values of the same metal ions adsorbed on many types of adsorbent

reported by several researchers. Examples are: 0.37 mg g^{-1} for Cd^{2+} and 0.31 mg g^{-1} for Pb^{2+} on biosorbent [15], 2.88 mg g^{-1} for Cd^{2+} and 2.90 mg g^{-1} for Pb^{2+} on activated carbon prepared from plant leaves [16], 12.05 mg g^{-1} for Cd^{2+} and 9.41 mg g^{-1} for Pb^{2+} on oil shale ash [17].

Table 2 Adsorption isotherms parameters for cadmium and lead ions on LaGdO$_3$

Metals	Langmuir isotherm constants			Freundlich isotherm constants		
	q$_m$ (mg g^{-1})	K$_L$	R^2	n	K$_F$	R^2
Cd^{2+}	0.87	0.17	0.985	0.92	3.50	0.981
Pb^{2+}	0.99	0.99	0.996	1.01	2.64	0.991

4. Conclusion

Nanocrystalline of LaGdO$_3$ in powder can prepared using the chemical co-precipitation process followed by calcination at temperature of 1,200 °C. The products were characterized with XRD, EDX, SEM, TEM, and BET which revealed purity perovskite phase. The LaGdO$_3$ perovskite can acted as metal ions adsorber in the toxic heavy metal ions (cadmium and lead) adsorption experiment. Heavy metal ion adsorption isotherm data were studied. The adsorption isotherm of Cd^{2+} and Pb^{2+} ion was better described by the Langmuir isotherm model, it is confirmed that the adsorption of Cd^{2+} and Pb^{2+} onto LaGdO$_3$ perovskite were monolayer adsorption.

5. Acknowledgements

6. References

[1] M.A. Rehab, A.H. Hesham, M.H. Mohamed, F.M. Gihan, Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis, Ecol Eng. 91 (2016) 317 − 332.

[2] B. Sun, X. Li, R. Zhao, M. Yin, Z. Wang, Z. Jiang, C. Wang, Hierarchical aminated PAN/γ–AlOOH electrospun composite nanofibers and their heavy metal ion adsorption performance, J Taiwan Inst Chem E. 62 (2016) 219 − 227.

[3] A.K. Biswas, C. Tortajada, Water quality management : an introductory frame work, Water Resources Management. 27 (2011) 5-11.

[4] M.A. Rauf, S.M. Qadri, S. Ashraf, K.M. Al-Mansoori, Sorption and desorption of Pb^{2+} ions by dead *Sargassum* sp. Biomass, Chem Eng J. 150 (2009) 90-95.

[5] K. Rusevova, R. Koferstein, M. Rosell, H.H. Richnow, F.D. Kopinke, A. Georgi, LaFeO$_3$ and BiFeO$_3$ perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton like reactions, Chem. Eng. J. 239 (2014) 322 − 331.

[6]   D. Zhang, C.L. Zhan, P. Zhou, Preparation of porous nano-calcium titanate microspheres and its adsorption behavior for heavy metal ion in water, J Hazard Mater. 186 (2011) 971 − 977.

[7]   S.P. Pavunny, R. Thomas, A. Kumar, N.M. Murari, R.S. Katiyar, Dielectric properties and electrical conduction of high-k $LaGdO_3$ ceramics, J Appl Phys. 111 (2011) 102811 − 102816.

[8]   S.P. Pavunny, J.F. Scott, R.S. Katiyar, Lanthanum Gadolinium Oxide: A New Electronic Device Material for CMOS Logic and Memory Devices, Materials. 7 (2014) 2669 − 2696.

[9]   M. Popa, J. Frantti, M. Kakihana, Characterization of $LaMeO_3$ (Me: Mn, Co, Fe) perovskite powders obtained by polymerizable complex method, Solid State Ionics. 154 − 155 (2002) 135 − 141.

[10] Z. Junwu, S. Xiaojie, W. Yanping, W. Xin, Y. Xujie, L. Lude, Solution-phase synthesis and characterization of perovskite $LaCoO_3$ nanocrystals via a co precipitation route, J. Rare Earths. 25 (2007) 601 − 604.

[11] J.A. Villoria, M.C. Alvarez-Galvana, SM. Al-Zahranib, P. Palmisanoc, S. Specchiac, V. Specchiac, Oxidative reforming of diesel fuel over $LaCoO_3$ perovskite derived catalysts: Influence of perovskite synthesis method on catalyst properties and performance, App. Cat. B: Environmental. 105 (2011) 276 − 288.

[12] H.K. Liao, L.L. Chi, J.C. Chou, W.Y. Chung, T.P. Sun, S.K. Hsiung, Study on pH_{pzc} and surface potential of tin oxide gate ISFET, Mater Chem Phys. 59 (1999) 6 − 11.

[13] R.M. Ali, H.A. Hamad, M.M Hussein, G.F. Malash, Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis, Eco. Eng. 91 (2016) 317-332.

[14] A.A Gouda, S.M. Al-ghannam, Impregnated carbon nanotubes as efficient sorbent for the solid phase extraction of trace amounts of heavy metal ions in food and water samples, Food Chem. 202 (2016) 409 − 416.

[15] A.H. Sulaymon, S.E. Ebrahim, T.J. Al-Musawi, S.M. Abdullah, Removal of lead, cadmium, and mercury ions using biosorption, Iraqi J Chem Petro Eng. 11 (2010) 1 − 13.

[16] M. Singanan, Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon, ScienceAsia. 37 (2011) 115 − 119.

[17] B.L. Zhu, Z.M. Xiu, N. Liu, H.T. Bi, C.X. Lu, Adsorption of lead and cadmium ions from oil shale ash, Oil Shale. 29 (2012) 268 − 278.