

Study on adsorption of phosphate from aqueous solution by nanomaterial CeO₂

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Abstract

The synthesis of nanosize single phase CeO₂ by gelatine gel combustion method was investigated. The prepared material was characterized by X-ray diffraction, thermogravimetric and differential thermal analysis, scanning electron microscopy and transmission electron microscopy measurements. At optimum conditions, such as pH 3, the molar ratio of Ce⁴⁺/gelatine 1/1, and a calcination temperature of 550 °C for 2 hours, the material with average size < 30 nm was synthesized. From the results of phosphate adsorption, adsorption equilibrium time of the material was determined at 60 minutes. The phosphate adsorption process in aqueous solution followed the Langmuir isothermal model with Q_{max}= 152.66 mg/g.

Keywords. CeO₂, gelatine, combustion method, phosphate (PO₄³⁻) adsorption.

1. INTRODUCTION

Currently, the excessive use of chemicals in agriculture has been the cause of contaminated water with fluoride, phosphate, ammonium... In the aqueous environment, the excess of phosphate cause extensive eutrophication, all kinds of algae, moss. Algae growth leads to massive changes to ecosystems and environmental conditions. Phosphate residues or excess in the body both are dangerous poison to the human body such as osteoporosis (because calcium can react with phosphate) and clogged blood vessels leading to stroke or heart attack leading or heart failure [1]. So, the treatment of phosphate in the water is needed now, in order to reduce environmental pollution, ensure people's living environment. There are methods of treatment of phosphate in the aquatic environment including biological and chemical methods.

Biological methods are the use of some microorganisms to accumulate more phosphorus in the body than we need. Many of the microorganisms involved in the process of absorption - storage - disposal, the microorganisms, in general, is called bio-P microbial groups that microorganisms are primarily Acinetobacter. Biological methods are

environmentally friendly, but besides that these methods depend on environmental conditions and the composition of pollutants in the wastewater. Because each type of microorganisms living in different conditions and the impact of pollution components on them are different. On the other hand, the processing time by this method is relatively long.

To overcome the limitations of biological methods while ensuring the handling of phosphate in water, chemical methods are prospective promise solutions. The chemical method in handling phosphate in particular or pollutant, in general, is not dependent on external conditions and the impact of pollution indices, short processing time, ease to desorption. The most important factor in the chemical method is a synthesis of materials.

The chemical methods are being applied in the manufacture of materials including co-precipitation techniques, sol-gel, hydrothermal technique. These are classics, controllable to synthesized the morphology and the chemical composition of the materials. The advantage of these methods is that improved uniformity and high specific surface area of the material lead to increase their activity [2, 3, 6, 8, 10-12].

On the other hand, oxide CeO₂ is widely applied

in various fields such as cerium catalytic exhaust treatment, solar batteries, fluorescent materials, and UV adsorption [2-5]. In this paper, the adsorption of phosphate anions from the solution will be studied by using CeO₂ nanomaterials synthesized by sol-gel with gelatine.

2. EXPERIMENTAL

2.1. Chemicals

All agents were analytical grade including Ce(NO₃)₄, gelatine, Na₃(PO₄), (NH₄)₂MoO₄, NH₄VO₃, HCl, NaOH were purchased from Sigma-Aldrich and Merck.

2.2. Synthesis

Weight an amount of gelatin and put into 30 ml of distilled water and continuously stirr at 80 °C with a magnetic stirrer until gelatine is completely dissolved, add slowly an amount of Ce⁴⁺ solution to the gel with a molar ratio Ce⁴⁺/gelatine 1/1, pH 3. The mixture was kept stirring to obtain a colorless transparent gel. After 4 hours dried out at 110 °C, a part of the sample was analyzed by the thermal analysis method, the rest products were calcinated at 180, 450, 550 and 650 °C during 2 hours.

2.3. Characterization

The products obtained during different stages were characterized by X-ray diffraction (XRD) using D-8Advance - Bruker diffractometer with CuKα radiation ($\lambda = 0.15406 \text{ \AA}$) in the range of $2\theta = 10^\circ - 95^\circ$, and a scanning rate of 0.02°s^{-1} . The micromorphology of the nanomaterial was evaluated by field emission scanning electron microscopy (FE-SEM) by Hitachi S-4800 microscope (Japan) and transmission electron microscopy (TEM) by JEOL JEM-1010 (Japan). Thermal analysis (TGA-DTA) of the gel precursors was carried out on a Setaram Labsys EVO (France) from room temperature to 850 °C in the air with a heating rate of 10°min^{-1} .

The concentration of PO₄³⁻ was determined by the photometric colorimetric method by the UV-1800 Shimadzu spectrophotometer (Japan) using ammonium molybdate/vanadate according to ISO 5815:2008 [7].

Assessment of PO₄³⁻ adsorption capacity from the solution follows the Langmuir adsorption isotherm model. The maximum adsorption capacity and isothermal constants are determined by regression. The correlation between the experimental data of PO₄³⁻ concentration remaining

in solution (C_f, mg/l) under saturated adsorption capacity (q, mg/g) was treated on Table Curves calculation software.

Langmuir adsorption isotherm was successfully applied in many adsorption processes of pollutants and the most widely used to describe the process of adsorption of solutes from the solution according to the Langmuir equation of the form:

$$q = \frac{Q_{\max} \cdot b \cdot C_f}{1 + b \cdot C_f}$$

Where: Q_{max}: The maximum adsorption capacity on the monolayer surface (mg/g); q: Adsorption capacity (mg/g); b: Isothermal constants (dm³/mg); C_f: The phosphate remaining concentration (mg/l).

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of materials

3.1.1. TG-DTA curves

The thermal analysis results of Ce-gelatine gel samples were recorded in figure 1. As can be seen from the figure 1, there are two discrete weight losses.

+ The first major weight loss (55.90 %) at temperatures below 200 °C which accompanied by a peak at 185 °C on the DTA curve due to dehydration of water in the gel samples.

+ The second effect with 34.45 % of weight loss occurred in the temperature range of 200-475 °C, reduced volume due to the decomposition of gelatin gel. Corresponds to the effects on the DTA curve at 460 °C are the formation of CeO₂ and the burning of some residual precursors or intermediate formed during the formation of CeO₂. When the temperature is higher than 500 °C, it almost does not see any weight loss or peaks on the DTA, it proves the stabilization of the nano CeO₂.

3.1.2. XRD diagrams

From the results of the thermal analysis as the basis for selection of gel calcination temperature, the sample was annealed at different temperatures of 180, 450, 550 and 650 °C for 2 hours. The analytical results of the samples were recorded by XRD method in figure 2.

It can be clearly seen from the XRD diagram, the figure shows that the sample heated at 180 °C have no specific peak of the single phase. This especially agrees with the TG analysis results above.

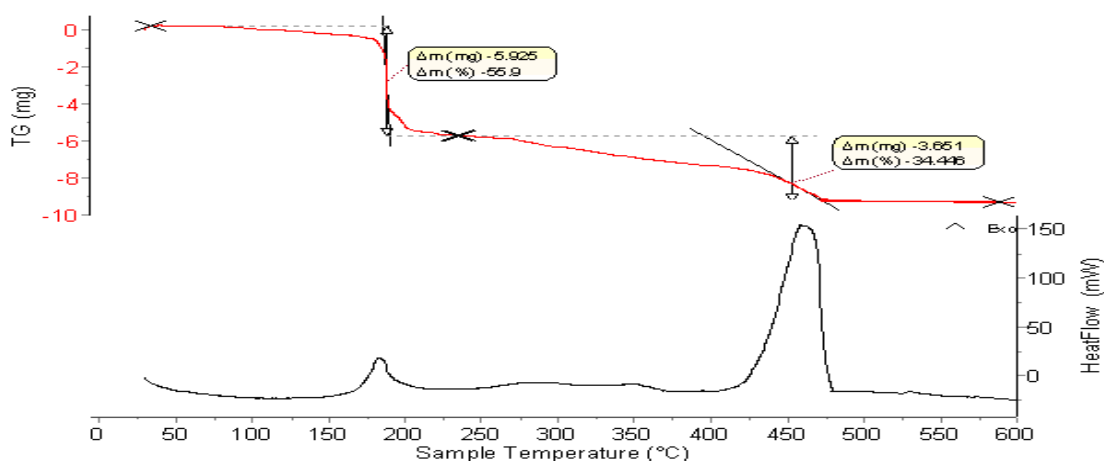


Figure 1: TG-DTA curve of the Ce-gelatin gel sample

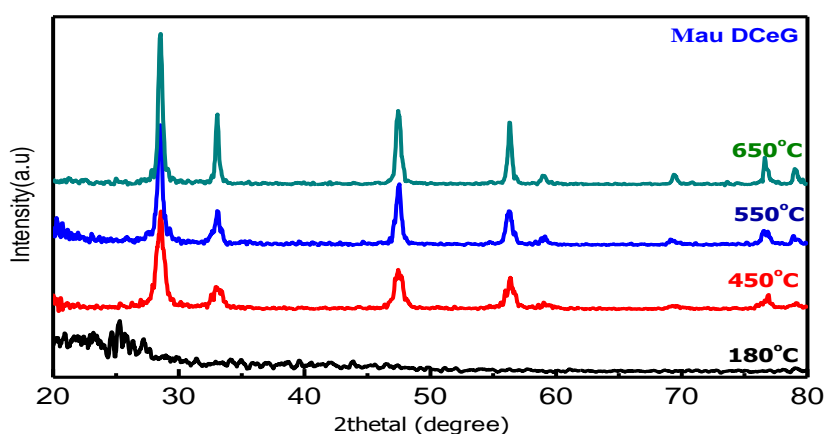


Figure 2: XRD diagrams of samples calcined at 180, 450, 550, and 650 °C

Calcined samples from 200 to 350 °C were almost no mass loss on the TG curve (Fig. 1). So, no phase formation of CeO_2 which similar to the study [3]. When samples are calcined at higher temperatures: 450, 550 and 650 °C, there were the characteristic reflection peaks for the formation of CeO_2 single crystalline phase.

The results showed that increasing of calcination temperature created the crystalline phase of CeO_2 . Calcination temperature has affected the formation of CeO_2 phase. To comparison with gel-PVA combustion method, the forming of CeO_2 single phase occurred at 100 °C lower by gel-gelatin [3]. This is a positive sign for to preparing materials using gel-gelatin combustion method. It can be a scientific basis for further studies on the use of gelatin to other synthetic materials.

3.1.3. SEM and TEM images

Characteristic morphology and size of the nanopowders CeO_2 surface were recorded on SEM and TEM images (figure 3). The FE-SEM and TEM

showed particles of relatively uniform size range < 30 nm. Particles have cavity structure which similar to the study [3].

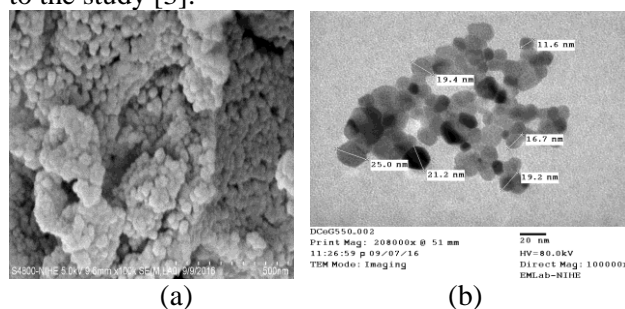


Figure 3: FE-SEM (a) and TEM (b) images of the sample

3.2. PO_4^{3-} adsorption capacity of nano CeO_2

3.2.1. Adsorption equilibrium time

To investigate the adsorption equilibrium time of PO_4^{3-} by CeO_2 nanoparticle, a series of experiments were conducted as follows: add 0.05 g of the material CeO_2 into 100 mL PO_4^{3-} solution with

concentration 10 mg/l, stir constantly by magnetic stirrer for different reaction time, sampling every 30 minutes to analyze the remaining phosphate concentration. The analytical results and calculations are recorded in table 1.

Table 1: Effect of reaction time of the phosphate adsorption by nanomaterial CeO₂

t (min)	C ₀ (mg/l)	C _f (mg/l)	q (mg/g)	Adsorption efficiency H (%)
30	10	5.52	8.96	44.80
60	10	3.72	12.57	62.85
90	10	3.85	12.30	61.50
120	10	4.50	11.00	55.00

Table 1 shows that the adsorption capacity PO₄³⁻ increased over time, PO₄³⁻ adsorption capacity of the material reached the highest value in a period of 60 minutes to 90 minutes, while the adsorption capacity tended to decrease when the time increased to 120 minutes. The adsorption performance decreases at 120 minutes compared to 90 minutes because the process of adsorption is the reversible process. The adsorption capacity is greatest at the adsorption equilibrium time. When prolonged adsorption causes a part adsorbed substance was eluted. Therefore, the adsorption equilibrium time of the materials is 60 minutes, it was chosen as a condition of following studies.

3.2.2. PO₄³⁻ adsorption capacity by nanomaterial CeO₂

PO₄³⁻ adsorption capacity was evaluated in similar experiments to the previous part with a solution PO₄³⁻ concentrations ranging from 5 to 180 mg/l. Results analysis and calculations are shown in figure 4.

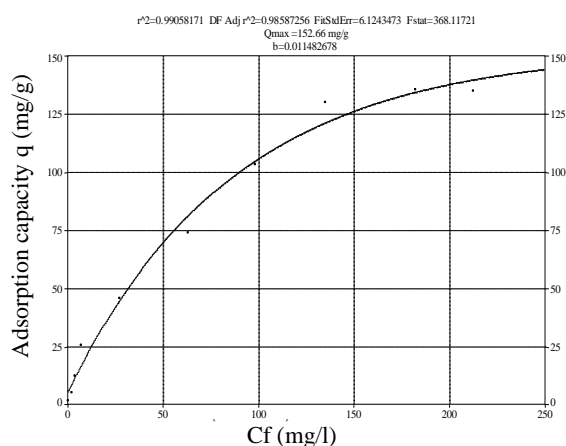


Figure 4: Langmuir adsorption isotherm of phosphate by the nanomaterials CeO₂

From the experimental results, obtained Q_{max} = 152.66 mg/g by using regression calculated software Table - the curve of experimental results. The phosphate adsorption of nanoparticle CeO₂ materials with Q_{max} = 152.66 mg/g and regression coefficient r² = 0.99. The results are well described by the Langmuir isotherm adsorption coefficient with regression r = 0.99.

4. CONCLUSION

Synthesized nanomaterials CeO₂ have average size < 30 nm by gel combustion method using gelatin, under conditions: molar ratio of Ce⁴⁺/gelatin is 1/1, the gelling temperature of 80 °C, pH 3 and calcination temperature at 550 °C for 2 hours. The phosphate adsorption capacity from the solution of nanomaterials CeO₂ also was fully conducted as follows: adsorption equilibrium time of the nanomaterials is 60 minutes and the maximum adsorption capacity of the nanomaterials CeO₂ is 152.66 mg/g with regression r² = 0.99.

REFERENCES

1. Phuong Thao, Do Quang Trung, Dang Thi Thu Huong, Cong Tien Dung. *Research by lanthanum modified laterite material treatment fluoride ion adsorption and phosphate in wastewater*, Vietnam Journal of Chemistry, **54(3)** 356-361(2016)
2. Recillas S., Colón J., Casals E., González E., Puentes V., Sánchez A., Font X. *Chromium VI Adsorption on Cerium Oxide Nanoparticles and Morphology Changes during the Process*. J. Hazard. Mater., **184(1-3)**, 425-431 (2010).
3. Luu Minh Dai, Nguyen Gia Hung, Vo Quang Mai, Dao Ngoc Nhiem. *Low temperature synthesis of nanostructured cerium dioxide by auto combustion process of polyvinyl alcohol-cerium nitrate gel*. Vietnam Journal of Chemistry, **42(4)**, 444-448 (2004).
4. Luu Minh Dai, Dao Ngoc Nhiem, Nguyen Van Phu, Duong Thi Lim. *Synthesis of nanostructured of CeO₂-Al₂O₃ by combustion method*, Vietnam Journal of Chemistry, **49(4)**, 405-408 (2011).
5. Dao Ngoc Nhiem, Luu Minh Dai, Nguyen Duc Van, Duong Thi Lim. *Catalytic oxidation of carbon monoxide over nanostructured CeO₂-Al₂O₃ prepared by combustion method using polyvinyl alcohol*, J. Ceramics International, **39**, 3381-3385 (2013).
6. Bui Van Thang, Le Ba Thuan. *An investigation of phosphorus adsorption capacity by modified bentonite: effect of pH, concomitant anion and adsorption mechanism*. Vietnam Journal of Chemistry, **51(3AB)**, 407-412 (2013).
7. Vietnam Organization for Standardization 5815:2001. NPK fertilizer-Test Method, (2008).

8. Hui Deng, Xili Yu. *Adsorption of fluoride, arsenate and phosphate in aqueous solution by cerium impregnated fibrous protein*, Chemical Engineering Journal, **184**, 205-212 (2012).
9. Liu Chang - jiu, Li Yan-zhong et al. *Adsorption removal of phosphate from aqueous solution by active red mud*, Journal of Environmental Science, **19**, 1166-1170 (2007).
10. Contreras A. R., García A., González E., Casals E., Puentes V., Sánchez A., Font X. *Recillas S. Potential Use of CeO₂, TiO₂ and Fe₃O₄ Nanoparticles for the Removal of Cadmium from Water*, Desalin. Water Treat, **41(1-3)**, 296-300 (2012).
11. Recillas S., García A., González E., Casals E., Puentes V., Sánchez A., Font X. *Use of CeO₂, TiO₂ and Fe₃O₄ Nanoparticles for the Removal of Lead from Water. Toxicity of Nanoparticles and Derived Compounds*. Desalination, **277(1-3)**, 213-220 (2011).
12. Yin S., Minamide Y., Tonouchi S., Goto T., Dong Q., Yamane, Sato T. *Solution synthesis of homogeneous plate-like multifunctional CeO₂ particles*, RSC Advances, **2**, 5976-5982 (2012).

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