

INVESTIGATION OF THE ADSORPTION OF PHOSPHATE IN GROUNDWATER ON MODIFIED LATERITE ORE BY CERIUM

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SUMMARY

Removal of phosphate from surface water and wastewater has been studied well, but there are a few studies in relation to undergroundwater. In order to increase adsorption capacity for phosphate, natural laterite was used to modify with cerium tetrachloride. Modification condition and characterization of the adsorbent material was investigated. Maximum phosphate adsorption capacity of the activated laterite was found to be 3.88 mg/g. Phosphate adsorption process is good at acid, reduce at neutral medium and alkaline medium. Effects of co-ions, including iron calcium, manganese, ammonium and phosphate on the adsorption were also studied. Iron has a great influence on phosphate adsorption capacity while calcium, manganese and ammonium do not interfere.

Keywords: Adsorption, groundwater, laterite, modified, phosphate removal.

I. INTRODUCTION

Groundwater is the main source of water for many countries and residential areas all over the world. According to the General Department of Environment, Ministry of Natural Resources and Environment, in Vietnam, there is about from 35 to 40% of total water supply coming from groundwater (2015). In addition, it is also an important source of water for agriculture and industry. Nowadays, groundwater contamination and degradation are prevalent in urban areas and in major cities around the world, greatly affecting the quality of human habitat.

Groundwater contamination by pesticides and chemical fertilizers in intensive farming areas, significant amounts of fertilizers and fertilizers are not received by plants. They will spread and accumulate in soil, water and agricultural products in excess of fertilizers and pesticides.

Phosphate is a nutrient, often is found in natural water sources, in human activities and productions, which increases the concentration of these ions in groundwater (Jianfeng Ma, Lizhong Zhu, 2006; Kamiyango et al., 2009;

Syed Mustafa et al., 2008). Although they are not toxic to human, but as they are present in water at relatively high concentrations, along with nitrogen, phosphates, they may cause eutrophication.

Recently, some researches with different methods have been implemented to introduce procedures for the removal of phosphate from contaminated water sources, such as precipitation methods, biological methods, adsorption and ion exchange methods, etc. In particular, the method of adsorption is highly valued for its efficiency, simplicity, low cost as well as environmentally friendly process (Abhijit Maiti et al., 2012; Liu Chang-jun et al., 2007; Peter Makie et al., 2012; Yanzhong Li et al., 2006).

Adsorbent materials used to remove phosphate in water were studied extensively. The published phosphate adsorbents include fly ash, red mud, activated alumina and iron oxide (Liu Chang-jun et al., 2007; Peter Makie et al., 2012; Yanzhong Li et al., 2006).

Overview of phosphate adsorbent materials shows that the similarity of materials using this type of adsorber is based on aluminum and iron based materials (Liu Chang-jun et al., 2007; Peter Makie et al., 2012; Yanzhong Li et

al., 2006). In order to achieve high economic efficiency, the adsorbent material studied in this paper is laterite, a mineral rich in iron and aluminum, formed in the tropics of hot and humid, available in Vietnam. To improve the adsorption capacity, natural laterite was studied to activate by impregnating with cerium tetrachloride. Modified materials are studied structural characteristics and investigated the ability of phosphate adsorption as well as investigate factors affecting the adsorption process such as blocking ions and pH.

II. RESEARCH METHODOLOGY

2.1. Modification of laterite ore

The process of modified laterite was performed by impregnating overnight laterite after heat treatment in HCl 3 M, then shaking with a solution of cerium tetrachloride corresponding to the percentage of cerium was carried on with the laterite at 1%, 2%, 3%, 4%, 5% for 4 hours. Neutralizing with NH₃ 1 M to pH medium, incubating for 8 hours was also conducted. Obtained materials, after washing off excess salt and drying at a temperature of about 100⁰C, continued to be heated at different temperatures of 300⁰C, 500⁰C, 700⁰C. With the process of impregnating cerium tetrachloride above, ions Fe³⁺, Al³⁺ were drawn to the surface and precipitated simultaneously with Ce⁴⁺ in the form of hydroxides of iron, aluminum and amorphous cerium, resulting in laterite material becoming more porous with adsorbent centers and larger affinity for phosphate ion. The heating process was done for the purpose of investigating the effect of temperature on the material after impregnating with cerium tetrachloride.

2.2. Adsorption capacity of modified laterite ore

In order to evaluate the adsorption capacity of the modified laterite, study proceeded to determine the adsorption equilibrium time, the

maximum adsorption capacity and the effect of ions are present with phosphate in water. The adsorption process was carried out in batches, with the rate of adsorbed solution/adsorbent is 10 ml/1 g at acid pH and room temperature. The adsorption capacity of the material was calculated by the following formula:

$$q = \frac{C_o - C_e}{m} \times V(\text{mg} / \text{g})$$

Where: q is adsorption capacity (mg/g); C_o is initial phosphate concentration before adsorption (mg/l); C_e is phosphate concentration when reached equilibrium (mg/l), V is volume of adsorption solution (l) and m is mass of adsorbent (g).

To determine the adsorption equilibrium time, the adsorption process was performed at different time intervals from 5 minutes to 150 minutes. The isothermal adsorption model was constructed by varying the phosphate concentration in the solution from 5 mg/l to 100 mg/l. pH, Fe³⁺, Ca²⁺, NH⁴⁺, Mn²⁺ ions were investigated to consider the influence of phosphate adsorption.

2.3. Analytical method

In this research, phosphate was determined according to the 4500 F-D method: SPADNS *Method* (APHA, 1998) and the 4500 P.C method of Vanadomolipdophosphoric acid (APHA, 1998). Each measurement was performed twice and results were taken as an average.

2.4. Effects of cerium contents

As shown in 2.1 section, initial laterite is impregnated in HCl to dissolve and attract Fe³⁺ and Al³⁺ onto the surface to precipitate in the form of hydroxide. In order to find the appropriate cerium content carried on laterite, study has conducted the experiment with varying cerium/laterite content from 1% to 5%. The results are shown in figure 1.

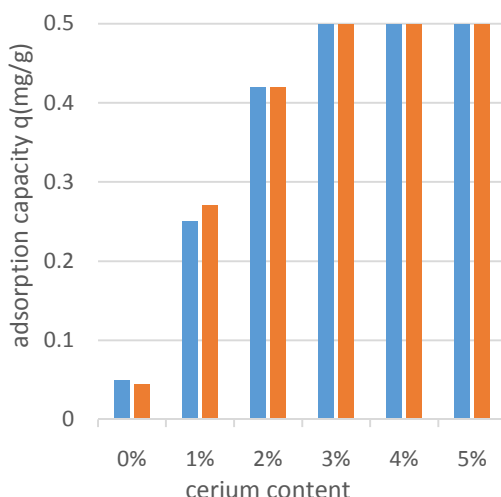


Figure 1. Diagram showing the ability of phosphate adsorption of laterite when carrying different cerium content

As indicated in figure 1, as the cerium was carried on laterite, the adsorption capacity increased significantly compared to the original laterite. The phosphate adsorption capacity increased when the cerium content increased from 1% to 3%, then no change when it continued to increase to 5%. Consequently, the appropriate cerium content carried on laterite at 3% by volume.

In order to find optimal temperature for this process, the laterite impregnated cerium tetrachloride at temperatures ranging from 100⁰C to 700⁰C. Phosphate adsorption capacity was calculated through adsorption capacity after adsorbing with phosphate solution 10 mg/l for 2 hours. Figure 2 shows that the

higher the heating temperature is, the lower the adsorption capacity of the modified laterite decreases. At a drying temperature of around 100⁰C, the result is the best with a phosphate adsorption capacity of 0.5 mg/g. This can be explained as follows: Each material has a certain temperature tolerance, when heating the Ce(OH)₄ components impregnated on the surface of the laterite are decomposed. This leads to loss of OH radicals, generates oxides that lead to loss of adsorption centers, thus reducing their absorption capacity. In conclusion, the appropriate condition of modified laterite is determined to be impregnated laterite with 3% cerium and then dried at 100⁰C.

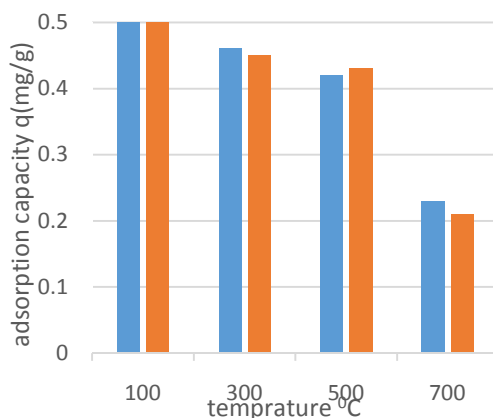
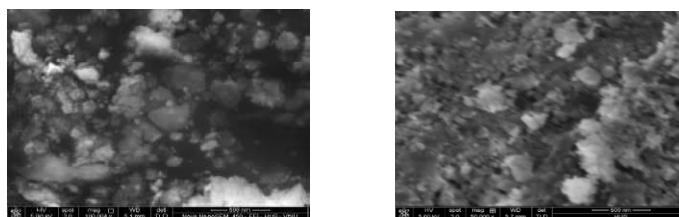


Figure 2. Diagram showing the adsorption capacity of laterite phosphate carrying 3% of cerium when heated at different temperatures

III. RESULTS AND DISCUSSION

3.1.1. SEM image

3.1. Characteristics of modified laterite ore



a) Laterite before modification b) Laterite after modification

Figure 3. Image of the laterite surface before and after modification through scanning electron microscope

SEM image of the laterite surface before and after modification shows that it is quite porous and has holes, which are characteristic for surface material with high surface area. The surface of the material after the modification is more rugged, has more slots, surface area increases compared to the original laterite surface, contributing to raise the adsorption capacity.

3.1.2. Spectrum of diffraction of laterite before and after modification

Results from figure 4 shows the major components of laterite are Fe₂O₃ and FeO(OH), after adsorption of phosphate, peaks of the compound between phosphate and Ce appeared. Therefore, it can be asserted that phosphate is adsorbed on laterite when it was carried on 3% cerium.

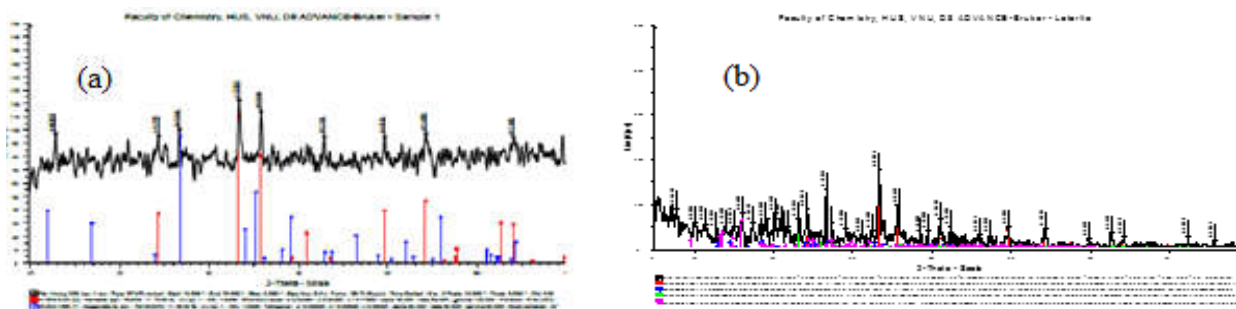


Figure 4. XRD diffraction sample of natural laterite (a) and laterite modified after adsorption (b)

3.1.3. Determination of material composition by ICP - MS

The elemental content of the modified material with 3% cerium was determined by mass spectrometry on the Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Elan 9000. The major metal components of laterite

are iron, aluminum, manganese and cerium with percentage of weight are 58.83%; 12.13%; 4.06% and 2.83%, respectively. Thus, it can be confirmed that cerium is successfully impregnated on laterite, the composition of mass is quite similar to the amount of cerium impregnated during material modification.

Table 1. Table of elements of content

No.	Elements	Content (µg/L)	Mass composition %
1	Fe	45892.65	58.83
2	Al	9641.39	12.13
3	Mn	3164.83	4.06
4	Ce	2211.26	2.83

3.2. Phosphate adsorption on laterite modified laterite ore 3.2.1. Effects of pH

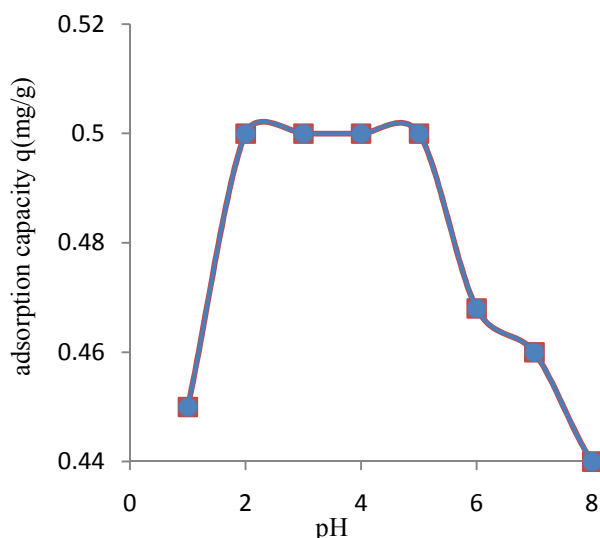
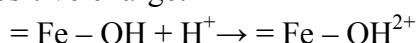


Figure 5. The influence of pH on phosphate adsorption capacity of material

Figure 5 shows the phosphate adsorption capacity of the material was strongly correlated with pH (Figure 5). At pH > 5, the absorption capacity is lower. At pH 2 ÷ 5, the adsorption capacity of the modified material is greatest. This can be explained that: at this pH, the dominant form of phosphate is $H_2PO_4^-$, the surface of material is protonated with positive charge:



(Symbol = Fe - OH: Laterite surface)

As pH of the solution increases, the surface of the material is negatively charged, it will increase the thrust of negative charges in the

solution and therefore the adsorption capacity of the material will decrease. In addition, in the alkaline medium, the competition of OH^- ions is also responsible for the decrease of phosphate absorption capacity.

3.2.2. Effect of time to reach equilibrium absorption

Time absorption equilibrium is the exposure time between adsorbent material and adsorbent so that the adsorption process is balanced. Initiate adsorption of 50 ml of phosphate solution at a concentration of 10 mg/l per gram of material in different time intervals from 5 minutes to 150 minutes.

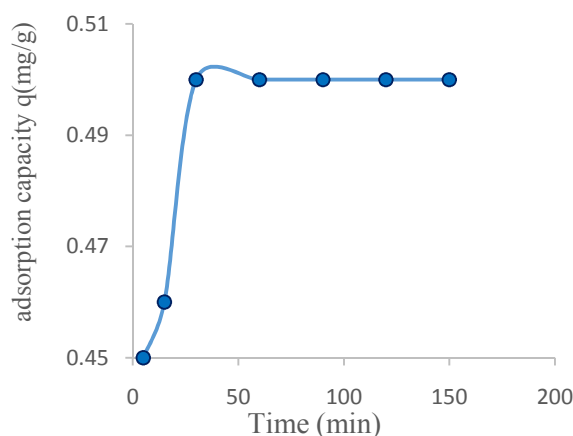


Figure 6. Effect of time on the balance of phosphate adsorption of modified material

When the exposure time increases, adsorption capacity increases and adsorption is balanced after 30 minutes (Figure 6). Thus, time to reach equilibrium absorption with modified laterite is 30 minutes.

3.2.3. Effects of initial phosphate concentration on modified laterite

The linear equation describing the relationship between C_e/q_e and C_e obtained during the adsorption of phosphate is shown in figure 7.

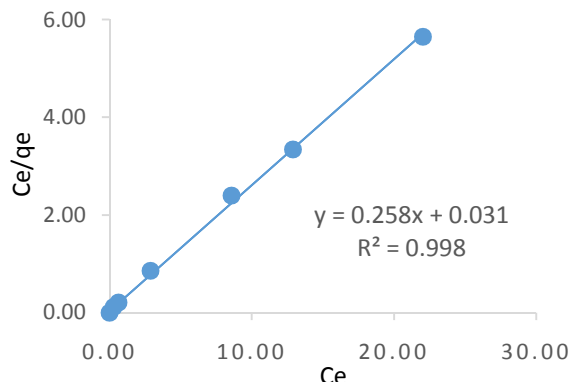


Figure 7. Langmuir linear of material for phosphate

With the coefficient of regression R^2 of the Langmuir linear equation obtained from the phosphate adsorption process is 0.9988 shows that the Langmuir isothermal adsorption model described appropriately phosphate adsorption on modified laterite. Also, from the Langmuir linear equation, the maximum absorbed phosphate capacity is 3.88 mg/g. Compared to previous studies with the original laterite, modification has increased the phosphate adsorption capacity by three times. This result is also quite satisfactory compared to materials commonly used as phosphate adsorption

materials such as modified carbon, modified clay, modified alumina, bone char, red mud and iron hydroxide.

3.2.4. Influence of competitive ions

In fact, apart from the ions that need to be treated, groundwater often contains other ions that can compete in adsorption. Thus, to consider the applicability of the material, the influence of some anions on the ability of phosphate adsorption on modified material. The selected anions are commonly found in groundwater: Fe^{3+} , Ca^{2+} , NH_4^+ , Mn^{2+} .

Table 2. Effect of Ca^{2+} , NH_4^+ , Mn^{2+} on phosphate adsorption capacity of laterite after modification

No.	Ion	Content of ions influence (mg/l)	C _o (mg/l)	C _e (mg/l)	q (mg/g)
1	Mn ²⁺	0	10	< 0.1	0.5
		0.5	10	< 0.1	0.5
		1	10	< 0.1	0.5
		5	10	< 0.1	0.5
		0	10	< 0.1	0.5
2	Ca ²⁺	50	10	< 0.1	0.5
		100	10	< 0.1	0.5
		150	10	< 0.1	0.5
		0	10	< 0.1	0.5
3	NH ₄ ⁺	10	10	< 0.1	0.5
		20	10	< 0.1	0.5
		30	10	< 0.1	0.5

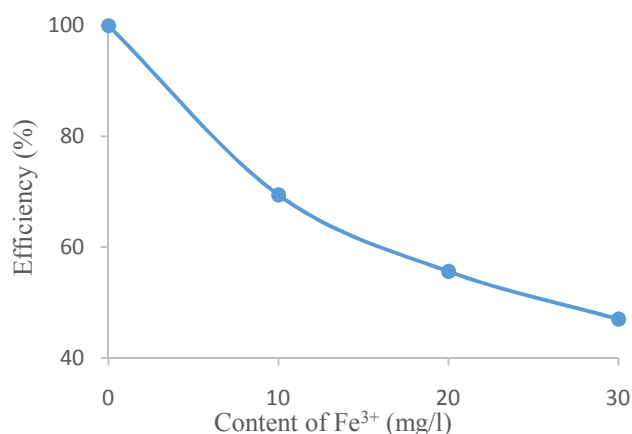


Figure 8. Effect of Fe³⁺ on phosphate adsorption capacity of laterite after modification

The presence of ion Fe³⁺ strongly affects phosphate adsorption capacity when the concentration is changed from 0 mg/l to 30 mg/l. As iron is present at a concentration two times than than the ion concentration of the survey, adsorption capacity of phosphate decreases by about 50%. However, it is almost unaffected by the presence of Ca²⁺, NH⁴⁺, Mn²⁺ even in the presence of Ca²⁺ at concentrations up to 15 times. Thus, in order to study the application of modified laterite materials in practical handling, it is necessary to pay attention to the influence of competing ions.

IV. CONCLUSIONS

Natural lateritic modification by impregnating 3% cerium raises the maximum absorbed phosphate capacity (3 times) than the original material. The absorption equilibrium time is quite fast after 30 minutes for phosphate. The appropriate pH for adsorption of phosphate is the acidic medium (pH at 2 ÷ 5). Iron has a great influence on phosphate adsorption capacity while calcium, manganese and ammonium do not interfere. Initial research has shown that laterite impregnated cerium is high potential for treating phosphate in groundwater when present at high concentration.

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KHẢO SÁT KHẢ NĂNG HẤP PHỤ ION PHOTPHAT TRONG NƯỚC NGẦM TRÊN LATERIT BIẾN TÍNH BẰNG XERI

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TÓM TẮT

Việc loại bỏ photphat khỏi nước mặt, nước thải đã được nghiên cứu, nhưng hàm lượng photphat trong nước ngầm chưa có nhiều nghiên cứu. Để tăng khả năng hấp phụ photphat, quặng laterit tự nhiên đã được nghiên cứu để biến tính bằng cách ngâm tẩm với xericlorua. Điều kiện biến tính và đặc tính của vật liệu hấp phụ đã được xác định. Tải trọng hấp phụ photphat cực đại của vật liệu sau biến tính là 3,88 mg/g. Quá trình hấp phụ photphat rất tốt ở môi trường axit, giảm dần ở môi trường trung tính và môi trường kiềm. Ảnh hưởng của các ion thường có mặt đồng thời cùng photphat trong nước ngầm như sắt, canxi, mangan, amoni cũng đã được nghiên cứu: Các ion Mn^{2+} , Ca^{2+} , NH_4^+ không ảnh hưởng tới quá trình hấp phụ photphat của vật liệu trong khi ion Fe^{3+} làm hiệu suất hấp phụ photphat giảm đi rõ rệt.

Từ khóa: Biến tính, hấp phụ, laterit, nước ngầm, photphat.

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