

Adsorption Control Performance of Phosphorus Removal from Agricultural Non-Point Source Pollution by Nano-Aperture Lanthanum-modified Active Alumina

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Abstract: It is great significance to control the phosphorus pollution from agricultural non-point source pollution. In this study, adsorption control performance of phosphorus removal from agricultural non-point source pollution by manual nano-aperture Lanthanum-modified active alumina was a great inspiring from urban-rural-integration-area. About 10 to 30 nanometers aperture on granule surfaces from the active alumina ($\gamma\text{-Al}_2\text{O}_3$) which average sphere diameters is 3 nm, was formed after modification from Lanthanum (III) chloride. Results show that the adsorption performance of phosphorus removal by using nano-aperture Lanthanum-modified active alumina was much higher percent 50% than active alumina under the optimum condition of pH (pH = 4), adsorption time (12 h) and adsorption dosage of Lanthanum-modified active alumina (0.2 g/50 mL). The adsorption performance of phosphorus removal by nano-aperture Lanthanum-modified active alumina can reach the percentage of 96 from water samples in agricultural non-point source pollution. The adsorption kinetic accorded with the Pseudo-Second-order Kinetic Equations ($R^2 = 0.9955$). The isothermal adsorption property was described by the Langmuir Equation ($R^2 = 0.9982$) which the biggest adsorption capacity was 0.257 mg/g. The average removal efficiency of phosphorus from general farmland, corn field, paddy field, vegetable land was above 92%. It is very evident that the nano-aperture Lanthanum-modified active alumina will be a promising material for phosphorus removal control from agricultural non-point source pollution.

Keywords: Activated alumina, agricultural non-point source pollution, lanthanum-modified, phosphorus adsorption

INTRODUCTION

The agricultural non-point pollution is an important source of pollution affecting the water quality and plays a gradual increase annual contribution to pollution loads. The control of phosphorus pollution has become the bottleneck for agriculture environmental protection and water environment quality development (Sims *et al.*, 1992; Quan and Yan, 2002; Tang *et al.*, 2011; Xie *et al.*, 2010). Experiments show that H_2PO_4^- was the main formation of dissolved phosphorus running off in Taihu Lake (Guodong *et al.*, 2006).

Phosphorus is the key factor impacting the eutrophication. Looking for efficient, low-cost phosphorus removal materials has been the research focus, especially suitable for the removal of hazardous substances in wastewater in the world (Xi *et al.*, 2008). Reducing the loss of phosphorus in Agricultural Non-point Source Pollution also has been a research hotspot (Tang *et al.*, 2011).

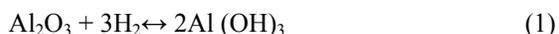
Phosphorus adsorption is a major mechanism for phosphorus co precipitation which involves the adsorption of phosphorus onto the surface of the co precipitant, followed by a slow incorporation of

phosphorus into the crystal structure of the co precipitant to scavenge phosphorus from the water column (Hart *et al.*, 2003). Materials such as limestone, gypsum, fly ash and natural calcite (lake marl) have been tested (Higgins *et al.*, 1976; Drizo *et al.*, 1999; Wadpersdolf *et al.*, 2004). Because either some of them such as sands, limestone; fly ash, gypsum, etc., do not have sufficient adsorption capacities or some like steel slag, zeolite and red mud have potential toxic effects on aquatic species in lakes, conventional adsorbents may not be feasible in practical wastewater treatment and eutrophication control (Xiong and Peng, 2008). A novel phosphorus adsorbent, ferrihydrite-modified diatomite has been developed with high phosphorus removal (Xiong and Peng, 2008).

Nano-materials with high surface activity, high specific surface area and high surface energy, show promising potential in the preparation of high performance adsorption and is widely used as adsorbents (Wang *et al.*, 2004; Wang *et al.*, 2006; Cao *et al.*, 2008). For instance, after using the nano-particulates of Hydrated Ferric Oxide (HFO) within macro porous activated carbon fibers, the phosphate removal behaviors and mechanisms of the new hybrid

phosphate adsorbent named as ACF-NanoHFO was studied within a calculated maximum adsorption capacity of 12.86 mg/g (Zhou *et al.*, 2012).

The γ -Al₂O₃ is a popular adsorbent with wide usage range and strong capacity of adsorption, but the phosphorus removal only by γ -Al₂O₃ cannot meet the discharge standards and steady effluent (Levin and Brandon, 1998; Li *et al.*, 2009a; Ding *et al.*, 2011). Adsorption mechanism of dephosphorization by γ -Al₂O₃ is generally expressed as:



Research results of phosphorus removal show that the rare-earth elements such as the Lanthanum, Cerium, etc., have a strong anionic phosphorus adsorption capacity (Ding and Huang, 2002; Zhang *et al.*, 2010; Ning *et al.*, 2008; Wang *et al.*, 2011).

Thus, in this study, main research objects are as follows:

- To develop a kind of nano-aperture active γ -Al₂O₃ by using the modification method of Lanthanum Lanthanum (III) chloride
- To determine the phosphorus adsorption mechanism from agricultural non-point source pollution by Nano-aperture Lanthanum-modified active alumina
- To discuss the application of phosphorus adsorption by Nano-aperture Lanthanum-modified active alumina in agriculture environmental protection

MATERIALS AND METHODS

Materials:

- **Main materials:** Activated Alumina, Lanthanum (III) chloride
- **Materials manufacturing method:**
 - The γ -Al₂O₃ raw materials were immersed in 5% LaCl₃ solution for 4 h at 25°C
 - After drying at 110°C, the γ -Al₂O₃ was put into the muffle furnace for certain time at 300°C (the Lanthanum-modified nano-aperture activated alumina were shaped and formed)
 - To cool produced nano-aperture materials

Methods:

Surface structure characterization of nano-aperture Lanthanum-modified active alumina: The SEM (Scanning Electron Microscopy) for Lanthanum-modified nano-aperture activated alumina was analyzed by the JSM-5600LV equipment.

Water sampling: To collect the water sample from agricultural non-point pollution from urban-rural-integration-area based on different agricultural activities such as the general farmland planting, corn planting, vegetable planting and paddy planting in Dujiangyan City of Sichuan Province in China. Water sampling came respectively from the Puyang Town, Chongyi town, Yutang Town and Guankou Town.

Experiment process of phosphorus adsorption:

• Basic experiment process:

- To filter water sample by filter membrane (0.45 μm)
- Fifty mL of water sample was taken in 150 mL conical flask, then a certain amount of nano-aperture Lanthanum-modified active alumina were added to this conical flask
- This conical flask was shaken with a certain speed in an oscillator
- A single factor variable method was designed and used to determine the optimization of adsorption condition of pH value, adsorption time, adsorbent dosage of nano-aperture Lanthanum-modified active alumina, etc.,
- The orthogonal experiment method was designed and used with pH value, adsorption time, adsorbent dosage of nano-aperture Lanthanum-modified active alumina, etc.,

Phosphorus removal performance: Determination of total phosphorus is the ammonium molybdate spectrophotometric method (MEP, 1989; Wei, 2002). The phosphorus removal rate was used to evaluate Phosphorus removal performance by nano-aperture Lanthanum-modified active alumina:

$$\eta = \frac{C_o - C_e}{C_e} \times 100 \% \quad (3)$$

where,

- η : The phosphorus removal rate (%)
- $C_o(\text{mg/L})$: The total phosphorus concentration before adsorption
- $C_e(\text{mg/L})$: The total phosphorus concentration after adsorption

Adsorption kinetics model: Kinetic model is usually used to study the changes of the adsorption process, the Pseudo-First and Pseudo-Second order Kinetic Equations commonly used to describe the liquid-solid adsorption process. In this study, these two models were used to probe the process of phosphorus adsorption by Lanthanum-modified nano-aperture γ -Al₂O₃. Relevant equations are as follows (Chang and Juang, 2005; Zeng *et al.*, 2010).

Pseudo-First-order Kinetics model:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

Pseudo-Second-order Kinetics model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where,

t (min) : The adsorption time

Q_e (mg/g): The phosphorus adsorption capacity for the adsorption equilibrium

Q_t (mg/g): The phosphorus adsorption capacity for the adsorption at time t

K_1 (min) & K_2 (min) : A constant of adsorption rate

Adsorption isotherm: The adsorption isotherm can be described by Langmuir equation and Freundlich equation.

Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_1} + \frac{C_e}{Q_m} \quad (6)$$

Freundlich equation:

$$\ln Q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (7)$$

where,

Q_e (mg P/g): The amount of P adsorbed per gram of adsorbent at equilibrium

Q_m (mg P/g): The monolayer saturation adsorption capacity

C_e (mg/L) : The total phosphorus concentration after adsorption

K_1 : The adsorption equilibrium constant

K, n : The Freundlich constant

RESULTS AND DISCUSSION

Scanning electron microscopy: Active alumina was surface modified by the Lanthanum (III) chloride. The SEM was employed to determine the surface structure difference between raw γ - Al_2O_3 and Lanthanum-modified γ - Al_2O_3 . Figure 1 shows an electronic micrograph of raw γ - Al_2O_3 . Figure 2 presents an electronic micrograph of raw diatomite. There are many microporous in the surface. It can be inferred from the SEM micrograph in Fig. 2 that about 10 to 30 nm aperture on the surface of the Lanthanum-modified γ - Al_2O_3 , the appearance of nano-aperture increased the adsorbent surface area.

Porous material with apertures between 2 to 50 nm is mesoporous materials. The formation of crystalline mesoscopic morphology is derived from the directional growth of the crystal surface, which formed through the selective adsorption of the impurity ions or additives epitaxied in the existing structure. A large number of 10 to 30 nm apertures on modified γ - Al_2O_3 surface formed after modification from Lanthanum (III) chloride, namely mesoporous. It can be concluded that the lanthanum chloride solution used in this experiment played the role of the impurity ions, so that the original micropores changed into the nanopores, which can explain the reasons for improved adsorption capacity by modified- γ - Al_2O_3 .

Adsorption time: Main adsorption processes and steps were:

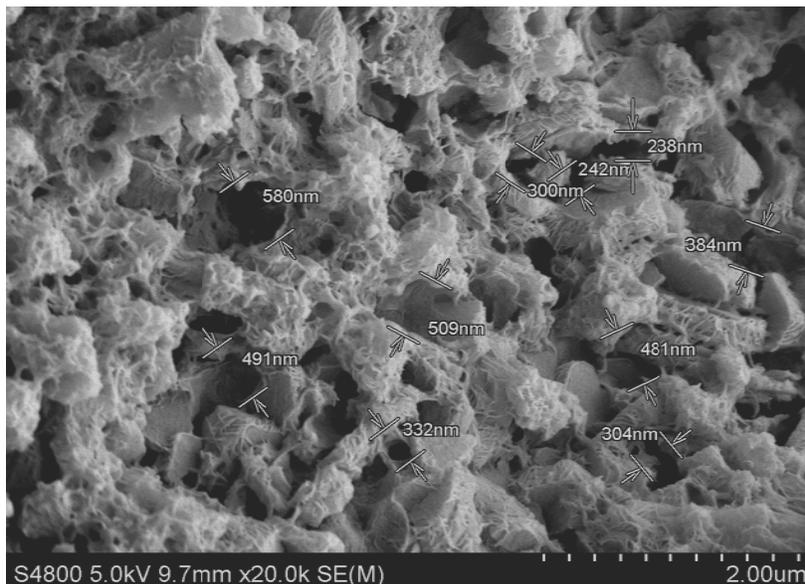


Fig. 1: SEM images of unmodified γ - Al_2O_3 ($\times 20000$)

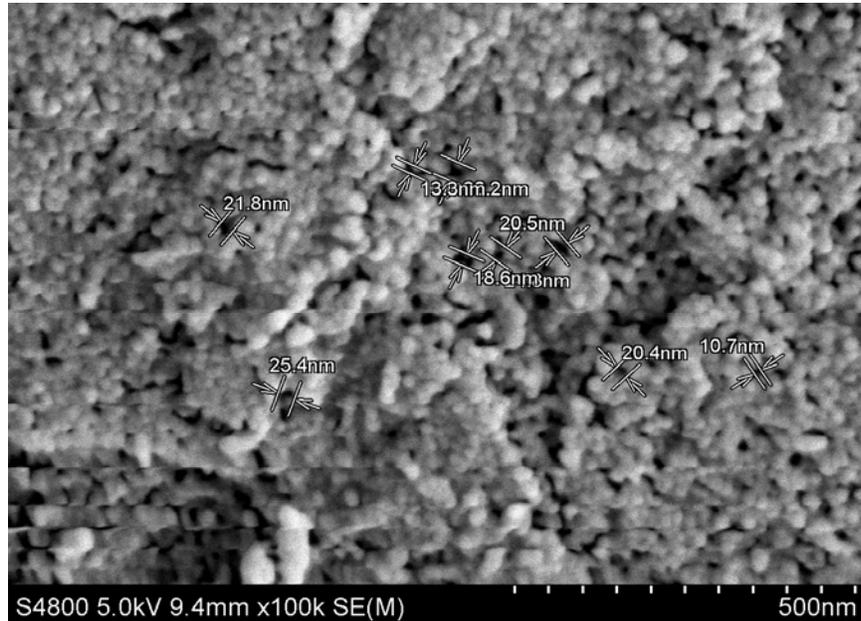


Fig. 2: SEM images of lanthanum-modified $\gamma\text{-Al}_2\text{O}_3$ ($\times 100000$)

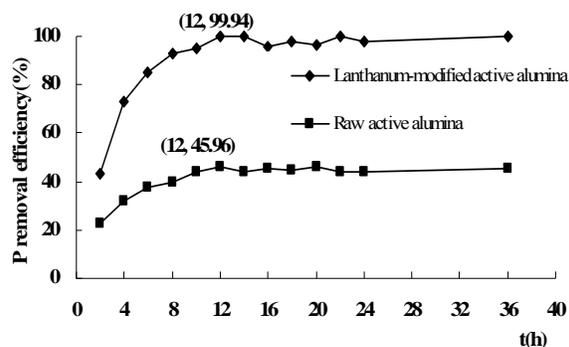


Fig. 3: Effect of adsorption time and the removal of phosphate

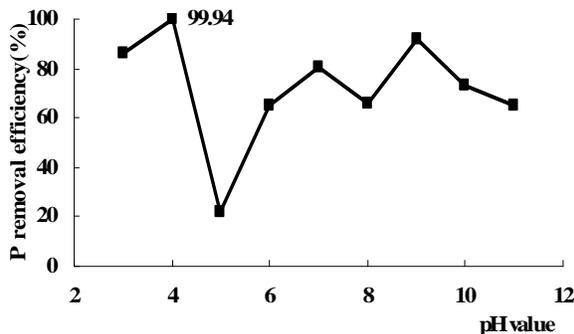


Fig. 4: Effect of pH on the removal of phosphate

- Fifty mL of water sample was taken in 150 mL conical flask, then 0.2 g of nano-aperture Lanthanum-modified $\gamma\text{-Al}_2\text{O}_3$ and Unmodified $\gamma\text{-Al}_2\text{O}_3$ were added to this conical flask
- To adjust the pH of the water sample to 4

- This conical flask was shaken with a certain speed in an oscillator
- Total Phosphorus (TP) concentrations at different times were determined

Figure 3 show that removal rate increases with increasing adsorption time. After 12 h, removal rate was not obviously increase, with a little constant percentage range. As a result, the adsorption performance of phosphorus removal by using nano-aperture Lanthanum-modified $\gamma\text{-Al}_2\text{O}_3$ was much higher 53.98% than by un-modified $\gamma\text{-Al}_2\text{O}_3$. The optimum adsorption time in Fig. 3 can be considered as 12 h where the removal rate of phosphorus was 99.94%.

Adsorption equilibrium time of the $\gamma\text{-Al}_2\text{O}_3$ used in this study is 12 h, which is different from the 1 and 6 h of the $\gamma\text{-Al}_2\text{O}_3$ (Ping *et al.*, 2002; Ning *et al.*, 2008; Li *et al.*, 2009b). The difference may due to the difference origin and production process of the $\gamma\text{-Al}_2\text{O}_3$.

pH value: The pH value range of the water sample was from 3 to 11 with same adsorption processes and steps which 50 mL of water sample was taken in 150 mL conical flask, then 0.2 g of nano-aperture Lanthanum-modified $\gamma\text{-Al}_2\text{O}_3$ were added to this conical flask on the condition of that the absorption time was 12 h. Figure 4 shows the phosphate removal rate with different pH value. The pH value with higher phosphate removal rates in Fig. 4 was 4 and 9 where the phosphate removal rate was 99.9 and 92.2%, respectively.

It is very evident that the pH value has a very important influence on the phosphate adsorption by Lanthanum-modified $\gamma\text{-Al}_2\text{O}_3$. The results of pH

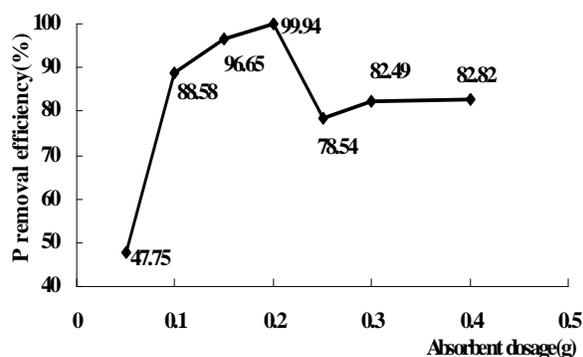


Fig. 5: Adsorbent dosage and phosphorus removal

conditions in this study show that the smallest phosphorus release was at pH = 4 and pH = 9, then phosphorus release will increase when pH value increases or decreases. These results have the same research conclusions with other researcher (Henning and Frede, 1992; Sui and Luo, 2001).

Formula (1) and (2) show that the concentration of $H_2PO_4^-$ will increase under the gradually increasing pH value. Low pH values will cause the acid dissolution of the activated alumina. Therefore, when reducing the pH value, it is beneficial to P adsorption.

Phosphorus removal capacity of $\gamma-Al_2O_3$ has reduced under the $pH < 4$, which is similar to the phosphate adsorption on $\gamma-Al_2O_3$ with the suitable pH value from 3 to 4 (Ping *et al.*, 2002; Ning *et al.*, 2008). But another research results show that the optimum phosphorus adsorption condition of pH value for $\gamma-Al_2O_3$ is from 5 to 6 (Brattebo, 1986), which was different from the result obtained in this experiment. The possible reason is that the difference was caused by the treatment of lanthanum chloride solution.

Absorbent dosage: With same adsorption steps from determined absorption time and pH values, the absorbent dosage of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 g, respectively nano-aperture Lanthanum-modified $\gamma-Al_2O_3$, respectively, were separately added to 150 mL conical flasks on the condition that the pH was 4 and the adsorption time was 12 h. Then Total Phosphorus (TP) concentrations were analyzed. Figure 5 presents adsorbent dosage and phosphorus removal efficiency. The P removal rate by Lanthanum-modified $\gamma-Al_2O_3$ firstly increases with increasing adsorbent dosage until a maximum removal rate is established, then decreases and finally maintains a balance. When adsorbent dosage was 0.2 g/50 mL, the removal rate reached the maximum. Thus, the best absorbent dosage in this study was 0.2 g/50 mL.

Higher or lower absorbent dosage than 0.2 g/50 mL caused the decrease of P removal efficiency, which was different from the absorbent dosage of 0.5 mg/50 mL about Sulfate-modified $\gamma-Al_2O_3$ adsorption removing

trace phosphorus in water bodies and P removal efficiency increased with absorbent dosage increased. The difference may be caused by the changeable modified $\gamma-Al_2O_3$ surface structure when dealing with different phosphorus concentrations of water samples.

Adsorption kinetics equation: The results of the Kinetics model in this study are as follows:

Pseudo-First-order Kinetics Equation:

$$y = -0.0029x - 2.0213 \quad (R^2 = 0.7243) \quad (8)$$

Pseudo-Second-order Kinetics Equation:

$$y = 3.2357x + 363.95 \quad (R^2 = 0.9955) \quad (9)$$

Since the phosphorus absorption with correlation coefficient and R^2 from the Pseudo-Second-order Kinetics model were both larger than the Pseudo-First-order Kinetics model, the equilibrium adsorption capacity ($Q_e = 0.309$ mg/g) has been calculated by the pseudo-two equation was much closer to the experimental measured values (0.288 mg/g). The results suggest that the phosphorus adsorption kinetic by Lanthanum-modified $\gamma-Al_2O_3$ should be expressed below:

$$Q_t = \frac{2.7476 \times 10^{-3} t}{1 + 8.8992 \times 10^{-3} t} \quad (10)$$

Adsorption isotherm: Results of adsorption isotherm were as follows:

• Langmuir Equation:

$$y = 3.888x - 0.0057 \quad (R^2 = 0.9982) \quad (11)$$

• Freundlich Equation:

$$y = -0.0176x - 1.3565 \quad (R^2 = 0.7543) \quad (12)$$

Thus, the isothermal adsorption properties can be better described by the Langmuir Equation, the Langmuir Equation was expressed as:

$$Q_e = \frac{175.30227C_e}{1 + 682.11C_e} \quad (13)$$

The Langmuir Equation from phosphate absorbent also can be better described by $\gamma-Al_2O_3$ (Ping *et al.*, 2002; Ning *et al.*, 2008). It can be speculated that the adsorption isotherms of modified $\gamma-Al_2O_3$ changed most likely because of the impact from lanthanum chloride. P adsorption by Lanthanum-modified $\gamma-Al_2O_3$ increases

with increasing P concentration until a maximum adsorption is established.

Other results from other research found that the isothermal adsorption properties by the silica gel (immersed in lanthanum (III) chloride) also was described by the Freundlich Equation about P removal (Wassay, 1996).

Removal efficiency of the adsorbent on different types of water samples: The removal efficiency of the Lanthanum-modified γ -Al₂O₃ adsorbent on different types of water samples which coming from different types of non-point source pollution including general farmland, corn field, paddy field, vegetable land, had been applied in agricultural land's runoff in this study. The average removal efficiencies of phosphorus were above 92% and the effluent water quality can meet the second standard from environmental quality standards for surface water (MEP, 2002). It concluded that the Lanthanum-modified γ -Al₂O₃ adsorbent with nano-aperture characteristic has a promising application for agricultural non-point source pollution.

CONCLUSION

- The SEM was analyzed to determine the surface structure characterization between raw γ -Al₂O₃ and Lanthanum-modified γ -Al₂O₃. The SEM micrograph of Lanthanum-modified γ -Al₂O₃ shows that the aperture and surface construct of raw γ -Al₂O₃ are modified and formed to nano-aperture with bore diameters of 10-30 nm in Fig. 1 and 2. It reveals the appearance of nano-aperture can greatly enhance the phosphorus adsorption capacity of γ -Al₂O₃
- The adsorption performance of phosphorus removal by nano-aperture Lanthanum-modified active alumina can reach the percentage of 92 from water samples in agricultural non-point source pollution on the optimum condition of pH (pH = 4), adsorption time (12 h) and adsorption dosage of Lanthanum-modified active alumina (0.2 g/50 mL). Results show that the adsorption performance of phosphorus removal by nano-aperture Lanthanum-modified active alumina was much higher percent 53.98% than raw active alumina.
- The adsorption kinetic accorded with the Pseudo-second-order Kinetic Equations ($R^2 = 0.9955$). The isothermal adsorption property was described by the Langmuir Equation ($R^2 = 0.9982$) which the biggest adsorption capacity of phosphorus was 0.257 mg/g.
- The application concentration range of total phosphorus removal is about 0.05 to 5 mg/L from agricultural non-point source pollution. It is very evident that the nano-aperture Lanthanum-modified active alumina will be great promising

materials for phosphorus removal control from agricultural non-point source pollution.

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