Removal of Phosphate from Water by Alumina Prepared from Sodium Aluminate

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ABSTRACT--- A sample of sodium aluminate was prepared from aluminum waste by the reaction with sodium hydroxide. From sodium aluminate, aluminum hydroxide was precipitated by formalin solution. The prepared aluminum hydroxide was characterized using DTA, TGA and XRD. Aluminum oxide was obtained by heating aluminum hydroxide from which adsorbent was obtained and used for removal of phosphate from wastewater. The mechanism of adsorption was discussed.

Keywords--- Sodium aluminate, potassium phosphate, adsorption, isotherms.

1. INTRODUCTION

Pollution of water bodies by phosphorus, an essential macronutrient, is a wide-spread environmental problem, causing eutrophication in lakes and seas and posing a great threat to aquatic environments. In environmental systems, the interaction between phosphate and aluminum hydroxides has attracted considerable attention in two respects. The first concerns the reaction of phosphate with aluminum hydroxide minerals in soils, which controls its availability to plants and leaching into water bodies [1-3]. The second is related to the removal of phosphate with aluminum hydroxides. Through the application of positively-charged aluminum hydroxides as adsorbents, phosphate removal can be enhanced in tertiary wastewater treatment systems [4-6].

Phosphate is nutrients that are natural part of aquatic ecosystems. Phosphorus supports the growth of algae and aquatic plants, which provide food and habitat for fish, shellfish and smaller organisms that lives in water. But when too much phosphorus enters the environment usually from a wide range of human activities the air and water can become polluted.

The removal of phosphate with aluminum hydroxides has been investigated by several researchers [7-9]. These studies have examined the sorption capacity of aluminum hydroxide [Al(OH)₃] for phosphate [10], effect of pH on adsorption of phosphate to bauxite, which has a major mineral of boehmite [γ-AIO(OH)][4] enhancement of phosphate adsorption capacity through acid and heat treatments[11] adsorption isotherms, rate, and selectivity of phosphate to aluminum oxide hydroxide [5], influence of humic substances on phosphate adsorption on aluminum hydroxide [12], competitive adsorption between phosphate and natural organic matter on aluminum hydroxide [13], role of the surface acid-base properties of aluminum hydroxides [pseudo-γ-AIO(OH) and a-Al₂O₃ in phosphate adsorption [14].

The objective of this study was to investigate the removal of phosphate from aqueous solution using alumina prepared by precipitation from sodium aluminate, produced by the reaction of sodium hydroxide and Al-waste. The characterization of the starting and/or the used materials was performed by XRD, DTA, TGA and SEM. The phosphate in solution was determined spectrophotometrically.

2. EXPERIMENTAL

2.1 Materials

Aluminum foil, NaOH, K-phosphate and formalin were used in this investigation.

2.2 Preparation of Sodium Aluminate

Al-foil was cut into small pieces 0.5 x 0.5 cm and was reacted with 30% NaOH solution to produce sodium aluminate solution.
2.3 Preparation of Al(OH)$_3$ and Al$_2$O$_3$

Al(OH)$_3$ was obtained by adding a certain volume of formalin to the same volume of sodium aluminate with constant thorough stirring at room temperature for 50 minutes. Al(OH)$_3$ was precipitated and separated from the mother liquor by filtration and rinsed with distilled water until pH=7. The precipitate obtained was dried by washing with acetone and heating in muffle furnace at 200°C to remove water of hydroxide and 500°C to convert the hydroxide into oxide.

2.3 Characterization of Adsorbents

Differential thermal analysis of aluminum hydroxide was performed using simultaneous thermogravimetry/differential thermal analyzer DTG-G0AH (Shmadzu, Japan).

XRD investigation of the prepared [Al(OH)$_3$] and calcined Al$_2$O$_3$ was carried out using a Philips diffractometer (type PW 1390). The patterns were run with CuK$_\alpha$ irradiation ($\lambda$ = 1542 nm) at 30kv and 10 mA with a scanning speed in 2θ of 2 min$^{-1}$.

2.4 Phosphate Adsorption on Al(OH)$_3$ and Al$_2$O$_3$

The adsorption experiments were carried out by agitating 0.2g adsorbent in 50 ml potassium phosphate solution having concentrations ranging from 10 to 800 mg/L at 30°C in 250ml conical flasks. Shaking was carried out for 24h, in shakes operating at 150 rpm. The measurements of the residual concentration of potassium phosphate solutions were performed using UV-Vis spectroscopy (2401PC Shima model, Germany at $\lambda_{\text{max}}$ = 824nm) by using molybdenum blue method [15].

The amount of phosphate adsorbed at equilibrium was calculated using the formula

$$q_e = \frac{(C_o - C_e)V}{m}$$

where $q$ denotes the amount of phosphate adsorbed per gram mg/g, where $C_o$ and $C_e$ are the initial and equilibrium concentration (mg/L), respectively, $V$ is the volume of adsorption solution (L) and $m$ is the mass of adsorbent (g).

3. RESULTS and DISCUSSION

3.1 Physical Properties of Al(OH)$_3$

The results of DTA of Al(OH)$_3$ are shown in Fig.(1). An endothermic reaction occurred at a calcining temperature of about 100°C. This means that Al(OH)$_3$ is assumed to have undergone dissociation to release the water of crystallization at a temperature near 100°C.

The results of XRD analysis of Al(OH)$_3$ are shown in Fig.(2). These results confirmed that Al(OH)$_3$ has an amorphous structure. The calcining of the Al(OH)$_3$ at 550°C transforms its structure into $\gamma$-type structure. It is known that alumina produced from unstable aluminum compounds been reported to have a $\gamma$–type structure.

![Fig.(1) DTA and TGA of aluminum hydroxide](image_url)
3.2 Phosphate Adsorption on Al(OH)$_3$ and Al$_2$O$_3$

Equilibrium data are the fundamental requirements for the design of adsorption systems. The adsorption isotherm of phosphate from solution on Al$_2$O$_3$ and Al(OH)$_3$ is presented in Fig.(3). Two models sorption isotherm expression have been applied to sorption experimental. These models are Langmuir [16] and Freundlich [17] isotherms.

The linear form of the Langmuir isotherm can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e$$

Where $q_m$ is the maximum adsorption capacity (mg/g), $K_L$ is the Langmuir constant related to adsorption heat. By plotting $C_e/q_e$ against $C_e$, $q_m$ and $K_L$ constants can be calculated from the slope and intercept. Their values along with the regression coefficient ($R^2$) are presented in Table (1).

The Freundlich model is expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where $q_e$ is the amount adsorbed (mg/g), $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $K_F$ is a constant related to the maximum amount adsorbed and $1/n$ is a measure of the binding energy between the adsorbate molecule and the adsorbent surface.

The adsorption of phosphate ions onto Al$_2$O$_3$ and Al(OH)$_3$ were well fitted by the Langmuir isotherm model as shown in Fig.(4), as demonstrated by the high correlation coefficient obtained compared to that for Freundlich isotherm model (not shown).
Figure (3): Adsorption isotherms for phosphate adsorption onto Al₂O₃ and Al(OH)₃ at 30°C.

Figure (4): Linear Langmuir plots of phosphate sorption onto Al₂O₃ and Al(OH)₃ at 30°C.

Table (1): Langmuir parameters for phosphate sorption onto Al₂O₃ and Al(OH)₃ at 30°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qₑₒₑ (mg/g)</th>
<th>Kₑ</th>
<th>Kₑₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃</td>
<td>14.51</td>
<td>0.0014</td>
<td>0.997</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.67</td>
<td>0.0199</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table (1) shows that Al₂O₃ has more capacity for adsorption of phosphate than Al(OH)₃, this can be attributed to the removal of (OH) groups of hydroxide by heating Al(OH)₃ leaving more pores and consequently more adsorption occurred.

3.3 Mechanism of Adsorption of Phosphate on Alumina

The adsorption of phosphate ions (monovalent: H₂PO₄⁻, divalent: HPO₄²⁻) to aluminum hydroxide surfaces can be described by ligand exchange mechanism [18&19]. In the adsorption process, phosphate ions can replace hydroxyl ions (OH⁻) on the surfaces of aluminum hydroxides, forming inner-sphere complexes including monodentate, bidentate, and binuclear complexes [4, 20 &21].

Also, this mechanism can be referred to as Lewis acid-base interaction in which phosphate ions (Lewis base) are adsorbed to the surface sites (Lewis acid) of aluminum hydroxides [21, 22]. This mechanism can be referred to as Lewis
acid-base interaction in which phosphate ions (Lewis base) are adsorbed to the surface sites (Lewis acid) of aluminum hydroxides [21 & 22]. Additionally, electrostatic (Coulombic) interaction can occur between positively-charged surfaces of aluminum hydroxides and negatively-charged phosphate ions, forming outer-sphere complex [2, 21 & 23].

4. CONCLUSIONS

From the above data it can be concluded that aluminum hydroxide or aluminum oxide prepared from sodium aluminate were active for the adsorption of phosphate from wastewater. The phosphate was adsorbed on aluminum oxide more than on aluminum hydroxide. The mechanism of adsorption was explained in the light of Lewis acid and Lewis base, beside the electrostatic interaction hydroxide and phosphate ions forming outer-sphere complex.

5. REFERENCES
