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Phosphate adsorption characteristics of alunite to be used as a cement additive

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Abstract

The adsorption of phosphate from aqueous solution by alunite has been investigated as a function of calcination temperature, particle size, pH, agitation time and initial phosphate concentration. Phosphate adsorption was seen to increase with increasing calcination temperature, decreasing adsorbent particle size and pH. The adsorption isotherm data were fitted to the Langmuir isotherm. The alunite exhibited the highest phosphate uptake capacity at 1073 K calcination temperature, at a particle size of 90–150 μm, at the initial pH of 5.0, at an equilibrium time of 60 min and at the initial phosphate concentration of 20×10^{-4} mol/l. The adsorption capacity, Q, was 4.697×10^{-3} mol/g at initial pH 5.0.

Keywords: Alunite; Calcination; Phosphate ions; Adsorption; Adsorption isotherms

1. Introduction

When phosphogypsum is added to cement as a set retarder, setting times are significantly extended [1]. This phenomenon is ascribed to the action of the phosphate ions present in the gypsum in various forms. It is quite conceivable that the phosphate ions going into solution upon water addition to the phosphogypsum containing cement interferes in some way with the hydration process and this is the basis for the delayed setting times observed. However, it has been found that cement containing fly ash is less sensitive to this phenomenon than ordinary Portland cement [1,2]. Alunite instead of fly ash can be used, since alunite is used as an accelerator in cement production [3]. Alunite, $KAl_3(SO_4)_2(OH)_6$, is a mineral not soluble in water in its original form. It is a basic potassium-alum occurring in rhombohedral crystals and one of the minerals of the jarosite group. It formed when volcanic rocks charged hydrothermally and it occurs with SiO_2 minerals. Therefore, it contains approximately 50% SiO_2 [4]. Alunite additive cements are rapidly hardening and have high-strength properties [3,5]. When alunite is added to Portland cement, hardening time decreases, while expansion increases [6,7]. It is also possible to achieve high early strength in concrete by adding alunite to cement [5].

In addition, constructed wetlands have been used for decades to remove pollutants from wastewater. The performance of such wetlands to remove pollutants from wastewater can be improved by using suitable substrates. The phosphate adsorption capacities of soils, industrial by-products (fly ash and slags) and zeolite were investigated for their potential use as substrates to remove phosphate in constructed wetlands [8–10]. This immediately raises the question whether or not there is, perhaps, some type of interaction between the alunite and the phosphate ions (e.g. adsorption or 'binding'). It is known in case of chloride ions causing corrosion of reinforcement in concrete that cement replacement material such as alunite can 'bind' the chloride ions to their hydration products and therefore limit their mobility and ultimate influence on the rebar in concrete [11].

It was therefore decided to investigate the adsorption of phosphate ions on alunite. Factors such as calcination temperature of adsorbent, particle size, pH, contact time and concentration of phosphate affecting the adsorption of phosphate by the alunite were investigated. The Langmuir and Freundlich adsorption isotherm models were also tested for their applicability.

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2. Materials and methods

A sample of alunite was obtained from Kütahya–Şaphane, Turkey. It was analyzed chemically and surface area determination was conducted using a BET instrument. The composition and some important physical characteristics of the adsorbent are presented in Table 1. Alunite was prepared by grinding it in a laboratory type ball-mill. The alunite samples were calcined in a muffle furnace at the temperature from 773 to 1173 K for 30 min. Then it was sieved to give 90–150, 150–250, 250–315, 315–500 and 500–710 μm size fractions using ASTM standard sieves.

Standard phosphate solutions were prepared by dissolving the anhydrous potassium phosphate (K_2HPO_4) (Merck) in appropriate amounts in distilled water. One hundred milliliters of the chosen desired concentration of K_2HPO_4 solutions were transferred in 250 ml Erlenmeyer flasks together with 1 g adsorbent, and the contents of the flasks were shaken on a horizontal bench shaker (Nüve SL 350) at the desired duration of the tests. All experiments were performed at 298 K, 100 rpm and at the natural pH of phosphate solution except those in which the effect of pH of the solution was investigated. The pH of the solution was adjusted with HCl or NaOH solution by using a pH meter. The flasks were also shaken for sufficiently long periods to attain an equilibrium which was ascertained and ensured through the last two consecutive readings (at 20–30 min intervals) of the residual phosphate concentrations being identical. Such adsorption tests were terminated of the attainment of equilibrium and the bottle contents were filtered through 0.45-μm Milipore filter paper and analyzed for residual phosphate concentrations. Residual phosphate concentration was determined using a UV-spectrophotometer (Shimadzu UV-150-02) by the stannous chloride method described in Ref. [12]. The measurements were done at the wavelength $\lambda = 690$ nm, which corresponds to maximum absorbance. The amounts of phosphate adsorbed were calculated from the concentrations in solutions before and after adsorption. Each experimental point was an average of three independent adsorption tests.

Table 1
The chemical composition and physical characteristics of alunite

Component	Weight percent (%)
SiO_2	43.83
Al_2O_3	22.61
SO_3	19.61
Fe_2O_3	0.10
TiO_2	0.15
CaO	0.17
MgO	0.12
K_2O	5.07
Na_2O	0.05
H_2O	8.29
Total BET surface area (m^2/g)	133.27
Density (g/cm^3)	2.58

3. Results and discussion

3.1. Effect of calcination temperature of alunite

Alunite calcined at 773–1073 K temperatures yields $Al_2(SO_4)_3$ and $KAl(SO_4)_2$ which are soluble in water. If adequate amount of water is added to obtain their crystal forms, they form $Al_2(SO_4)_3 \cdot 18H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$. These salts accelerate cement hardening. $KAl(SO_4)_2 \cdot 12H_2O$, the most effective additive, increases compressive strength of concrete several times. It was therefore decided that alunite calcined at 773–1173 K for 30 min should be used in the adsorption experiments. The adsorption experiments, using a phosphate solution having a concentration of 10×10^{-4} mol/l, were run to determine the effect of thermal treatment on the adsorption of phosphate by alunite. The results obtained are shown in Fig. 1.

It can be seen from Fig. 1 that the adsorption of phosphate on calcined alunite changes with calcination temperature of the alunite and it is highest at a temperature of 1073 K. It is related to a solid-phase reaction, which happens during calcination. The solid-phase reaction during calcination is written as [13,14].

$$2KAl_3(SO_4)_2(OH)_6 \rightarrow 2KAl(SO_4)_2 + 2Al_2O_3 + 6H_2O \quad (1)$$

While $KAl(SO_4)_2$ salt is a good additive material for cement, Al_2O_3 is a good adsorbent for phosphate. The adsorption of phosphate on alunite calcined at 1173 K was decreased because of partial sintering in the calcination process above 1073 K.

3.2. Effect of particle size

The absorbent particle size has a considerable effect on the kinetic processes in adsorption systems. For a given mass, smaller particles have a much greater external surface area for adsorption than do larger particles [15].

Fig. 2 shows the effect of particle size on the adsorption of phosphate by alunite. It can be seen from Fig. 2 that the adsorption of phosphate from aqueous solution of concentration 10×10^{-4} mol/l has been found to increase from 25.75% to 77.88% with a decrease in the particle size of alunite from 500–710 to 90–150 μm at 298 K and pH 6. As the particle size of the adsorbent decreased, the amount of adsorbed phosphate increased. This may be explained on the basis of the surface area available for the adsorption of phosphate, which is greater in smaller particle sizes.

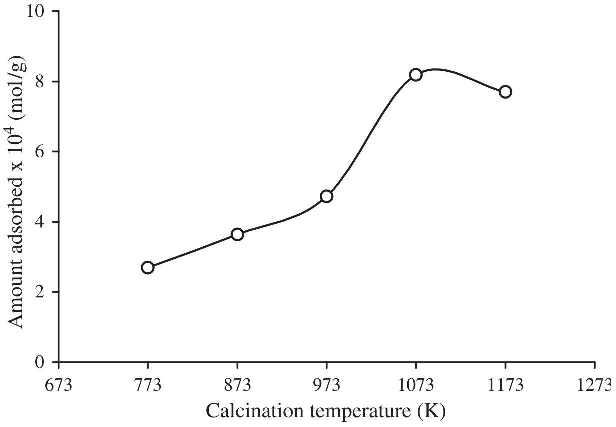

Fig. 1. Effect of calcination temperature on adsorption of phosphate by calcined alunite. Conditions: 90–710 μm particle size, 30 min calcination, 10×10^{-4} mol/l concentration, 1.0 g/100 ml dose, 60 min contact time, 298 K temperature, and pH 6.

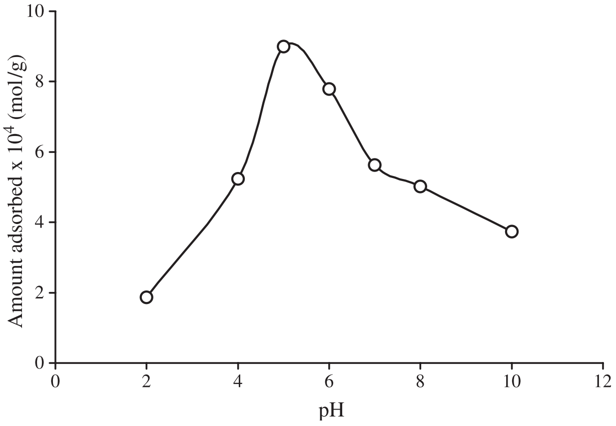

Fig. 3. Effect of pH on adsorption of phosphate by calcined alunite. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 10×10^{-4} mol/l concentration, 1.0 g/100 ml dose, 60 min contact time, and 298 K temperature.

3.3. Effect of pH

To study the influence of pH on the adsorption capacity of alunite for phosphate, experiments were performed using various initial solution pH values, changing from 2 to 10. The obtained results are shown in Fig. 3. It is found that while the adsorbed amount of phosphate increased from 1.87×10^{-4} to 8.99×10^{-4} mol/g with an increase in pH from 2 to 5, it decreased from 8.99×10^{-4} to 3.74×10^{-4} mol/g with an increase in pH from 5 to 10 (Fig. 3).

The results showed that the phosphate adsorption is strongly pH dependent. The pH dependency is both related to the amphoteric properties of the alumina surface and to the polyprotic nature of phosphate, however, several explanations to these phenomena are proposed in literature [16].

The chief constituents of alunite are metal oxides mainly of Al and Si. The surface of these metal oxides consists mainly of oxygen atoms and hydroxyl groups. It is primarily the hydroxyl groups that determine the chemistry (acid–base character) and the reactivity of these surfaces [17]. Below a pH value of about 4–4.5, the capacity decreases due to a higher solubility of alumina [16]. When pH of the solution increases, the surface becomes negatively charged and the adsorption capacity for phosphate decreases. Because negatively charged surface sites on the adsorbent unfavors of phosphate due to the electrostatic repulsion. Therefore, maximum phosphate adsorption occurred at pH 5.

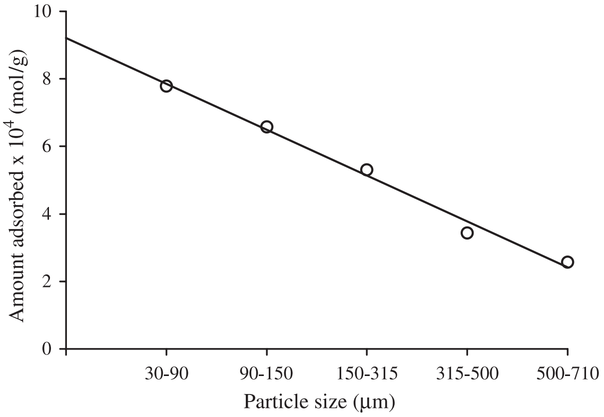

Fig. 2. Effect of particle size on adsorption of phosphate by calcined alunite. Conditions: 1073 K and 30 min calcination, 10×10^{-4} mol/l concentration, 1.0 g/100 ml dose, 60 min contact time, 298 K temperature, and pH 6.

3.4. Effects of contact time and initial phosphate concentration

To evaluate the effect of initial phosphate concentration (C_0) on adsorption, studies were conducted with initial phosphate concentrations (C_0) of 0.5×10^{-4}, 1×10^{-4}, 5×10^{-4}, 10×10^{-4}, 15×10^{-4} and 20×10^{-4} mol/l with alunite as the adsorbent material.

Based on the data, plots were prepared between the adsorbed phosphate concentrations (q_t) versus time. Fig. 4 depicts these plots at six different C_0 values. These plots indicate that the phosphate adsorbed increase rapidly in the beginning and very slowly towards the end of the run. In other words, it can be observed from Fig. 4 that the concentration of phosphate adsorbed increased with time and at some point in time reaches a constant value beyond which no more of the phosphate is removed from the solution. At this point, the amount of phosphate being adsorbed onto the adsorbent is in a state of dynamic equilibrium with the amount of phosphate desorbing from the adsorbent. A perusal of the plot shown in Fig. 4 reveals that the phosphate adsorbed is higher for greater C_0 values. This is obvious that for higher C_0 values, more efficient utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force (by a higher concentration gradient pressure) [18].

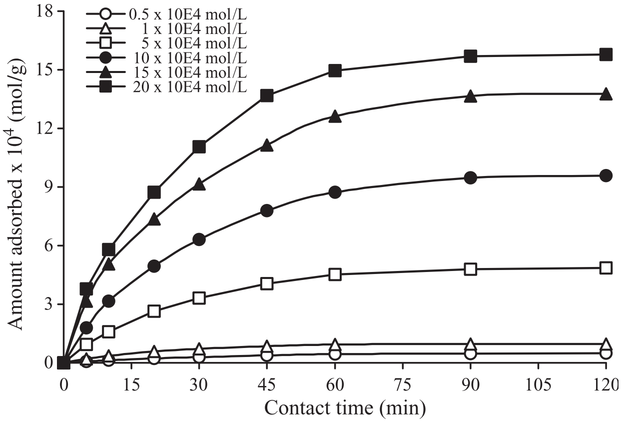

Fig. 4. Effect of contact time and initial phosphate concentration on adsorption of phosphate by calcined alunite. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1.0 g/100 ml dose, 298 K temperature, and pH 5.

The equilibrium time was found to be 60 min and independent of initial phosphate concentration. With the change in concentration of the solution from 0.5×10^{-4} to 20×10^{-4} mol/l, the percentage adsorption of phosphate decreased from 98.1% to 78.95%. The percentage uptake is highly dependent on the initial concentration of phosphate in the solution. It can be concluded that high removal at low concentration is important in terms of industrial application. The phosphate uptake versus time curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phosphate ions on the surface of the adsorbent.

3.5. Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [19]. Fig. 5 shows a plot of the phosphate loading on the adsorbent against the phosphate equilibrium concentration in the liquid phase. Several isotherm equations are available. In this study, two of them have been selected: the Langmuir and Freundlich isotherms. The linear form of the Langmuir isotherm and that of Freundlich can be presented by Eqs. (2) and (3), respectively,

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ}\frac{1}{C_e} \tag{2}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where q_e is equilibrium phosphate concentration on adsorbent (mol/g), C_e is equilibrium phosphate concentration in solution (mol/l), Q is monolayer capacity of the adsorbent (mol/g), b is adsorption constant (l/mol), K_F is the Freundlich constant, and n is the Freundlich exponent.

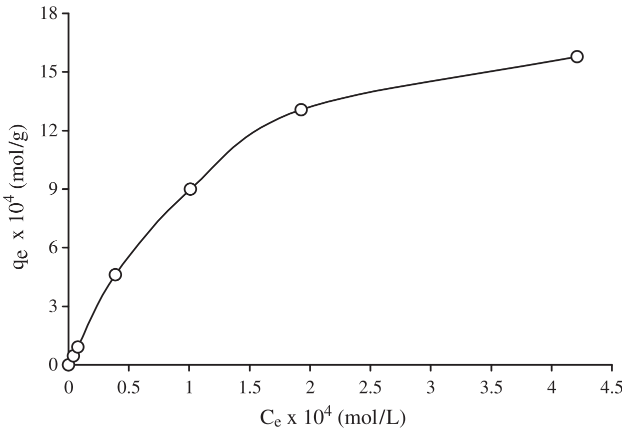

Fig. 5. Adsorption isotherms of phosphate on calcined alunite. Conditions: 90–150 μm particle size, 1073 K and 30 min calcination, 1.0 g/100 ml dose, 60 min contact time, 298 K temperature, and pH 5.

Table 2
Langmuir and Freundlich isotherm parameters

Langmuir			Freundlich		
$Q \times 10^3$ (mol/g)	$b \times 10^{-3}$ (l/mol)	r^2	K_F	n	r^2
4.697	2.562	.9995	1.598	1.208	.9870

While Langmuir isotherm parameters Q and b were obtained by plotting $1/q_e$ versus $1/C_e$, Freundlich isotherm parameters were obtained by plotting log q_e versus log C_e. The isotherm data were calculated from the least squares method. Table 2 shows the values of the parameters of the two models and the related correlation coefficients (r^2 values). It seems that the Langmuir equation best describes the equilibrium data over the concentration range used in this investigation.

4. Conclusions

Based on the experimental results in this investigation, the following conclusions can be drawn:

- The rate of adsorption increase with increased calcination temperature up to 1073 K for heat activated alunite, but the adsorbed amount of phosphate decreased at a temperature of 1173 K due to the partial sintering of the alunite surface.
- The rate of adsorption was found to increase with decreasing particle size.
- In addition, it increases with decreasing pH. Calcined alunite has a great capacity to adsorb phosphate due to having an excess positive charge on its surface with decreasing pH.
- Alunite has a considerable potential to adsorb phosphate from aqueous solutions over a wide range of concentrations.

- The initial rate of adsorption of phosphate with the alunite was high, and it declines with time until it reaches a plateau.
- The adsorption data are better explained by the Langmuir isotherm equation than the Freundlich one. The adsorption capacity, Q, was found to be 4.697×10^{-3} mol/g at optimum study conditions. Alunite can potentially be used in cement to remove phosphate.

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