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Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent

Kostantinos Karageorgiou, Maximos Paschalis, Georgios N. Anastassakis *

School of Mining Engineering and Metallurgy, National Technical University of Athens (N.T.U.A.), 9 Heroon Polytechniou Str., Technical University Campus, 157 80 Zographou, Athens, Greece

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Abstract

Phosphates are very important basic materials in agricultural and other industrial applications. Phosphorus is often present in low concentrations in wastewater, almost solely in the form of organic and inorganic phosphates (ortho- and poly-phosphates). The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication, particularly near urban areas. The usual methods of treatment are either biological or physicochemical by sedimentation. This paper studies the removal of phosphate species by adsorption onto calcite used as natural adsorbent.

The phosphate solutions were prepared artificially by adding certain quantities of K_2HPO_4 in water. The effect of equilibrium pH, phosphate/mineral ratio and contact time was studied. The results showed that pH plays an important role in the removal of phosphate species from solution, with removal being more efficient in the basic pH region. The experimental results also show that adsorption is also efficient for high ratios phosphate/adsorbent. Finally, the adsorption process is time dependant. Based on the experimental results a possible mechanism of phosphate removal onto calcite surface is proposed.

As a general conclusion, phosphate species seem to be efficiently removed from solutions using calcite as natural adsorbent. In addition, the adsorption product can be used as fertilizer for acid soils.
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Keywords: Environment; Liquid effluents purification; Adsorption; Orthophosphates adsorption; Adsorbents; Calcite; Phosphates

1. Introduction

Phosphates are very important materials to many industries. Large quantities of them are used in many industrial applications, with fertilizers being the most important. Other applications include detergents, water softening, food and drinks, metallurgy, etc. The wide use of phosphates inevitably produces large amounts of phosphate-bearing wastes, which are usually discharged into municipal and industrial water effluent streams.

Eutrophication of the water bodies is one of the most important environmental problems, which occurs in stagnant water bodies. Phosphorus has been considered as a key element causing eutrophication, which leads to abundant development of aquatic plants, growth of algae, with some kinds of them being toxic, and to balance disturbance of organisms present in water. This directly affects water quality through oxygen depletion, because of high biological oxygen demands, and acidification. This, in turn, harmfully affects fish and other aquatic life, microorganism and insects' growth as well as it causes natural resorts degradation. Consequently, the removal of phosphates from surface waters is absolutely necessary to avoid any kind of problems, particularly near urban areas. Wastes containing phosphates must meet the maximum discharge limits. In the province of Quebec (Canada), these limits are determined on a plant-by-plant basis, but a typical effluent total unfiltered phosphorus target is between 0.8 and 1.0 mg P/l [1].

Phosphorus usually occurs in wastewater and surface water in the form of organic phosphates (e.g. detergents) and inorganic phosphates (ortho- and poly-phosphates). In wastewater treatment technology, various techniques have been employed for phosphate removal. Despite the extensive experimental work carried out, phosphorus removal and recycling technologies have not been widely adopted because of the technical and economic drawbacks.

The broad categories of phosphate effluent treatment include physical [2,3], chemical [4], biological [5] and crystallization

* Corresponding author. Tel.: +30 210 7722162; fax: +30 210 7722119.
E-mail address: ganastas@metal.ntua.gr (G.N. Anastassakis).

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methods [6]. Also, flotation has been used to remove orthophosphates from solutions [7]. Chemical removal techniques are the most effective and well-established methods up to date, including phosphate precipitation with calcium, aluminum and iron salts [8–10]. However, the cost associated with the use of metal salts may hinder the widespread application. Besides, the product of chemical immobilization is metal phosphate sludge, which is disposed with relatively high phosphorus content, as the recovery of phosphorus from sludge is very difficult.

Consequently, the removal of phosphate compounds through sorption processes onto various sorbents has been tested since a long time ago. Among the adsorbents tested the following are included: aluminum and aluminum oxides [1,11,12], iron and iron oxides [13–16], fly ash [17,18], slag [19,20], red mud [21,22], bauxite [23], silicates [24,25], active carbon [26] and anion exchanger [27].

This paper studies the removal of orthophosphate species by adsorption onto calcite used as natural adsorbent investigating the effect of the key process parameters. Finally, an attempt is made to elucidate the mechanism of adsorption.

2. Experimental procedure

2.1. Reagents—materials

Artificial orthophosphate solutions were used throughout the adsorption tests. Initially, a stock solution of 100 ppm in orthophosphates was prepared by dissolving a certain amount of chemically pure $K_2HPO_4{\cdot}3H_2O$ in tap water. An aliquot of the stock solution was mixed with a certain volume of water so that a phosphate solution was prepared at the desired experimental concentration. Tap (drinking) water was used throughout the tests. Although tap water was of very low hardness, fresh phosphate solutions were daily prepared to avoid possible precipitation of phosphate species. NaOH and HCl solutions 5% (v/v) were used as pH regulators.

Calcite, picked up by hand sorting from a quarry, was used as adsorbent in the tests. The purity of calcite was 98.2% in $CaCO_3$. Minor amounts of 1.4% SiO_2 and 0.4% MgO were also detected. The initial sample was crushed in a jaw crusher and wet ground in a porcelain mill with porcelain grinding media to avoid iron contamination. The milling product was wet sieved and the fraction −0.2 mm was used for the adsorption tests, with 45% of the particles' size being less than 0.075 mm.

The particle size of calcite used for zeta-potential measurements was −5 μm. The zeta-potential tests were carried out at a solid concentration of 5% (w/v).

2.2. Equipment—procedure

The experimental procedure was as it follows: a defined volume of the phosphate stock solution, with a concentration 100 ppm in PO_4^{3-}, was diluted to the experimental concentration by adding tap water of very low hardness. The pH of the solution was then adjusted to the desired value and a defined amount of adsorbent was added. The mixture was stirred at 150 rpm for a defined period, using a stirrer with a potentiometer to regulate the stirring speed. After a certain period of stirring, pH was recorded and filtering process was applied to separate solid from liquid. The apparatus used was a Millipore No. XX 1004704 vacuum-operated system using a 0.45-μm porous filter. Then, a volume of 10 ml concentrated HCl was added to the supernatant immediately after the test. Chemical analysis of the supernatant in phosphorus was realized using an ICP-AES plasma technique. Based on the results of chemical analysis, the orthophosphate removal was calculated. A Scanning Electron Microscope JSM 6100 JEOL was used for calcite SEM analysis.

Zeta-potential measurements were carried out in an electrophoretic mass transport analyzer EMTA 1202 of Micromeritics Instrument Corporation.

3. Results and discussion

The parameters examined during adsorption tests were pH, time and orthophosphate/adsorbent ratio. The results are cited below.

3.1. Effect of pH

The effect of pH on the removal of orthophosphate species, through adsorption onto calcite, was examined in the pH region between 7.6 and 12. The tests were carried out at constant experimental conditions with an initial solution concentration 20 ppm (0.21 mM/l) in orthophosphate and 1 g of adsorbent. All the tests were carried out at constant retention time, fixed at 15 min. The effect of pH is illustrated in Fig. 1.

The results show that pH is an important factor regarding orthophosphate adsorption onto calcite. The orthophosphates uptake is comparatively lower in the slightly basic pH region (approximately 70–80%), it increases for higher pH values and becomes complete in the vicinity of pH 12. Correspondingly, the supernatant remaining concentration decreases with pH. Orthophosphates are completely removed from solution in the basic pH region around 12.

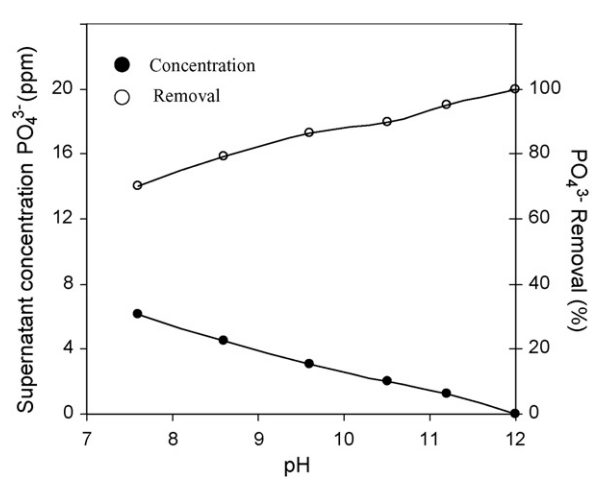

Fig. 1. Effect of pH on orthophosphates adsorption onto calcite and supernatant concentration.

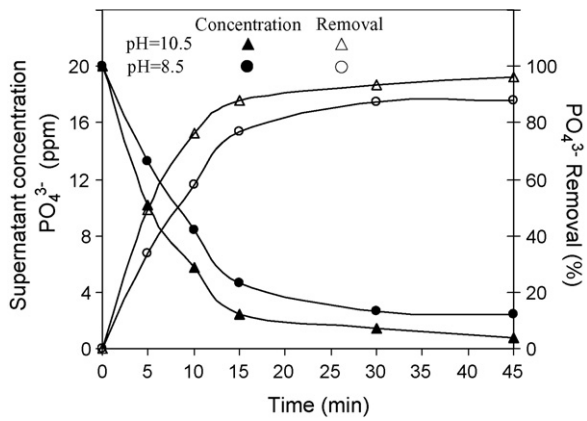

Fig. 2. Kinetics of orthophosphates adsorption onto calcite.

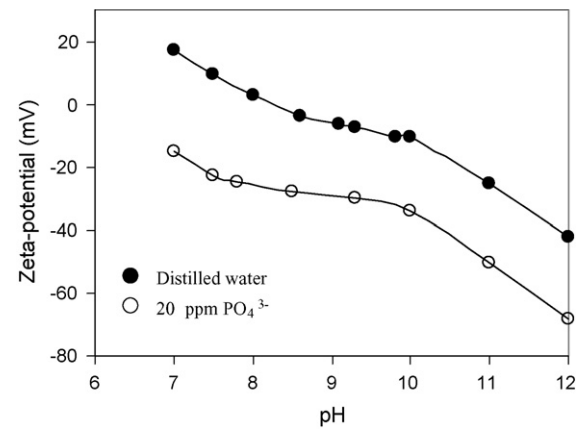

Fig. 4. Zeta-potential of calcite as a function of pH.

3.2. Effect of time

The kinetic experiments were carried out at pH values ranging from slightly to very basic. The initial solution concentration in orthophosphate was 20 ppm while the adsorbent quantity was 1 g. The results show that adsorption process is clearly time dependent (Fig. 2).

From this figure, it is observed that most of the orthophosphate uptake occurs within a time of 15 min, ranging between 88 and 95% of the totally adsorbed. For periods greater than 15 min, the uptake is further increased but with a much slower rate. Besides the uptake is not significantly higher than that for 15 min. Similarly, the supernatant concentration seems to decrease exponentially, reaching at very low to null concentration for basic pH values. Based on the kinetic results a working period of 15 min was selected as a compromise between theoretical and practical approach of orthophosphate uptake. The theoretical approach requires long equilibration time while the practical requires relatively short working period of uptake. Experiments carried out on the dissolution of calcite in water revealed that the process is very fast. This finding is in accordance with the kinetic results, as calcite dissolution is the first step for phosphate adsorption onto calcite. Also, the affinity between calcium hydrolysis complexes and orthophosphate species reinforces the relatively short effective time of adsorption.

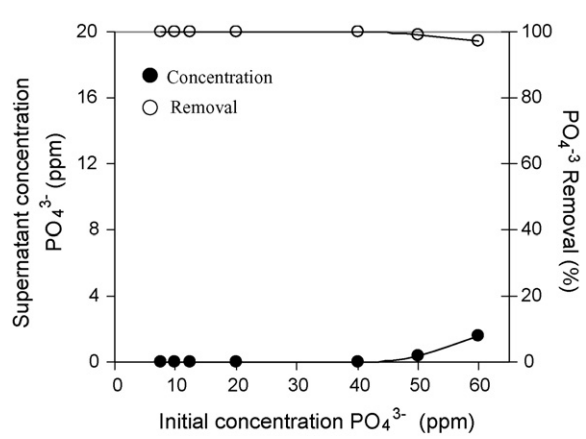

Fig. 3. Effect of initial concentration on orthophosphates removal and remaining concentration at pH 12 (adsorbent mass 1 g).

3.3. Effect of orthophosphate/solid ratio

Batch tests were carried out with various contaminant/solid ratios at pH 12. In all the cases, the solid mass was maintained constant at 1 g while the initial concentration in orthophosphates was increasing. The retention time was 15 min. The results are illustrated in Fig. 3.

As it is observed, the adsorption process is effective under the experimental conditions tested. For concentrations so high as 60 ppm in PO_4^{3-}, which corresponds to 0.1 mM PO_4^{3-}/g adsorbent, the orthophosphate removal is almost complete.

4. Discussion

From Fig. 1, it is evident that pH is the most important parameter of adsorption process. In general, pH has a very strong effect as it determines the nature and the concentration of the orthophosphate species as well as the hydrolysis products on calcite surface. In this case, the solution is composed of orthophosphate species and ionic species from calcite hydrolysis reactions. This system is also of great importance in the separation of apatite from calcite by flotation.

In most cases oxides and silicates are used as adsorbents because of their relatively low solubility and simplicity in adsorption process. Calcite is a more complex mineral, with much higher dissolution than the previous mentioned mineral groups, undergoing various hydrolysis and complex formation reactions of its constituent species. These reactions determine its electrokinetic and physicochemical properties as well as its behavior in solution.

Zeta-potential measurements of calcite in water show that the point of zero charge of the mineral occurs at about pH 8.2 (Fig. 4). When 20 ppm PO_4^{3-} is added, it is observed that the surface of calcite obtains a negative charge in the pH range examined, that is for pH between 7 and 12. From the electrokinetic results of Fig. 4, it is clearly illustrated that orthophosphate species are chemically adsorbed onto calcite for pH values greater than 8.2. For pH between 7 and 8.2, the adsorption seems

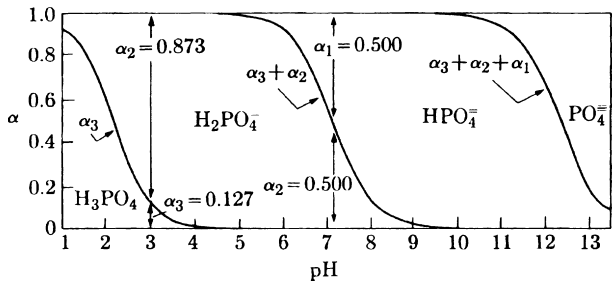

Fig. 5. Distribution diagram for phosphate present as different protonated species as a function of pH.

to be due both to electrostatic and chemical interactions. Consequently, the speciation of orthophosphate species of the solution as well as the hydrolysis reactions on calcite surface is necessary to be considered to elucidate the mechanism of adsorption.

The speciation of orthophosphates is described by the following reactions with their perspective pK at 25 °C [28]:

$$PO_4^{3-} + H_2O = HPO_4^{2-} + OH^-, \quad pK = 1.68 \tag{1}$$

$$HPO_4^{2-} + H_2O = H_2PO_4^- + OH^-, \quad pK = 6.79 \tag{2}$$

$$H_2PO_4^- + H_2O = H_3PO_4 + OH^-, \quad pK = 11.67 \tag{3}$$

$$H_2O = H^+ + OH^-, \quad pK = 14.00 \tag{4}$$

The protonation reactions (1)–(4) are also illustrated in the speciation diagram of Fig. 5 [28]. From this figure, it is clear that $H_2PO_4^-$ and HPO_4^{2-} species are present in the pH region between 5 and 10. The concentration of $H_2PO_4^-$ species is higher for pH below 7 while HPO_4^{2-} species prevail for pH between 7 and 10. For pH between 10 and 12, HPO_4^{2-} predominate over PO_4^{3-} species while, for pH higher than 12.5, the concentration of PO_4^{3-} species becomes significant and exceeds that of HPO_4^{2-}.

Considering hydrolysis reactions of calcite, it derives that cationic species, such as Ca^{2+}, $CaHCO_3^+$ and $CaOH^+$, prevail for pH less than 8, rendering the mineral surface positively charged. For pH > 8, the negative species prevail but the concentration of the positive species is still considerable. Some of the hydrolysis reactions for the cationic and anionic species are as follows [29]:

$$CaCO_3 = Ca^{2+} + CO_3^{2-}, \quad pK = 3.25 \tag{5}$$

$$CO_3^{2-} + H_2O = HCO_3^- + OH^-, \quad pK = 3.67 \tag{6}$$

$$Ca^{2+} + HCO_3^- = CaHCO_3^+, \quad pK = -0.82 \tag{7}$$

$$Ca^{2+} + OH^- = CaOH^+, \quad pK = -1.40 \tag{8}$$

Based on the above-mentioned reactions, the adsorption process could be possibly described through the following reactions occurring on calcite surface [30–32]:

$$Ca^{2+} + H_2PO_4^- = CaH_2PO_4^+, \quad pK = -1.08 \tag{9}$$

$$Ca^{2+} + HPO_4^{2-} = CaHPO_4, \quad pK = -7.0 \tag{10}$$

$$Ca^{2+} + PO_4^{3-} = CaPO_4^-, \quad pK = -6.5 \tag{11}$$

$$3Ca^{2+} + 2PO_4^{3-} = Ca_3(PO_4)_2, \quad pK = -26 \tag{12}$$

$$2Ca^{2+} + HPO_4^{2-} + HCO_3^- = Ca_2HPO_4CO_3 + H^+, \quad pK = 1.33 \tag{13}$$

$$Ca_2HPO_4CO_3 = Ca_2PO_4CO_3^- + H^+, \quad pK = 8.3 \tag{14}$$

$$10CaCO_3 + 2H^+ + 6HPO_4^{2-} + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 10HCO_3^-, \quad pK = -32 \tag{15}$$

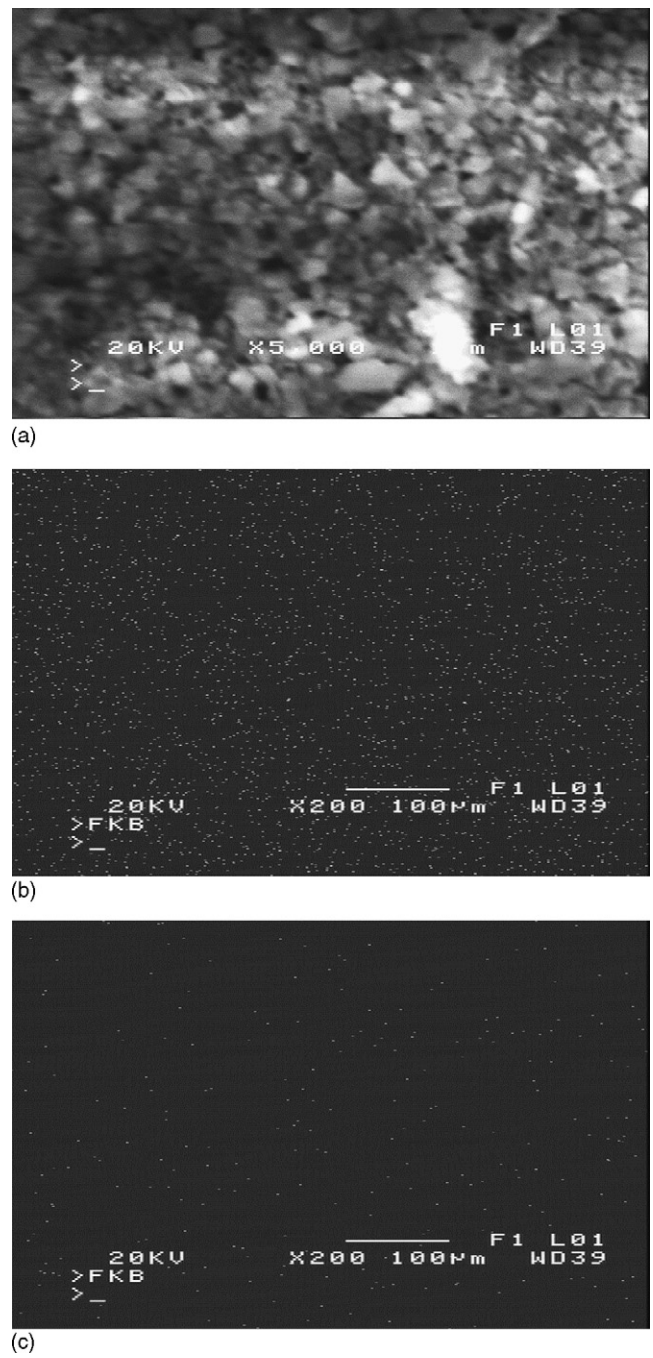

Fig. 6. SEM photo of calcite surface (a) as well as calcium (b) and phosphorous (c) mapping after adsorption at pH 12.

Consequently, specific adsorption of orthophosphate species onto calcite surface seems to be the driving mechanism of orthophosphate uptake from solution using calcite as adsorbent. This is in accordance with the results of zeta-potential measurements (Fig. 4). Also, this mechanism is supported by the results of calcite SEM analysis (Fig. 6), which clearly show that phosphate species have been adsorbed on calcite surface. This mechanism tends, in some extension, to make similar the surface of calcite to that of apatite, which is in agreement with Somasundaran's finding [33], who studied the physicochemical behavior of the mineral system calcite/apatite during flotation.

In conclusion, orthophosphate species removal from aqueous solution seems effective by adsorption onto calcite, resulting in the reduction and/or elimination of the harmful effects on the environment. In addition, there is no need for further treatment of the calcite adsorbed-phosphate product, as this product can be used as a fertilizer of acid soils.

5. Conclusions

Phosphorus is often present in low concentrations in wastewater, almost solely in the form of organic and inorganic phosphates (ortho- and poly-phosphates). The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication and its concomitant effects on living organisms and environment. This paper studied the orthophosphate species uptake from aqueous solutions using calcite as a cheap and abundant natural adsorbent.

Among the parameters studied, pH is proved to be the key variable for orthophosphate uptake. The results show that the process is more effective in the highly basic pH region, resulting to complete removal of the various orthophosphate species. Electrokinetic measurements indicate that phosphate species are specifically adsorbed onto calcite surface. Also, significant amount of orthophosphates can be adsorbed onto relatively low mass of calcite. Besides, the calcite adsorbed-phosphate product is friendly to the environment, as it does not require further treatment for the phosphate species desorption because of its potential application to acid soils fertilization.

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