



Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions

Nuray Karapınar*

General Directorate of Mineral Exploration and Research, Technology Department, 06800 Ankara, Turkey

ARTICLE INFO

Article history:

Received 20 March 2009

Received in revised form 11 May 2009

Accepted 12 May 2009

Available online 23 May 2009

Keywords:

Natural zeolite

Ammonium

Phosphorus

Seeding

Precipitation

ABSTRACT

Removal of both nutrients ammonium and phosphorus by natural zeolite has been studied in lab scale by using a mechanically stirred batch system (1000 ml). Zeolite, a mean particle size of 13 μm , was used as an adsorbent for the removal of ammonium and then as a seed material for the precipitation of calcium phosphate. A relationship was established between the uptake of ammonium by zeolite and the ratio of initial ammonium concentration to zeolite dosage. Ammonium uptake of zeolite was almost completed within initial 5 min of adsorption period. There is no pronounced effect of zeolite and ammonium, neither positive nor negative on the amount of calcium phosphate precipitation. The extent of the precipitation of phosphate increased with rising pH. It was also observed that when the system was allowed to relax at constant pH (i.e. under relatively low super saturations), a certain lag time was noted to elapse at the onset of the precipitation. At the pH 7.2, the amount of initial fast precipitation within 5 min and total precipitation within 120 min were around 34% and 93%, respectively. Precipitation of calcium phosphate on to ammonium-loaded zeolite was achieved at low super saturations ($\text{pH} < 7.5$) through secondary nucleation and crystal growth, leading to an increase in particle size.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Increasing discharge of nutrients such as ammonium and phosphorus into natural water systems strongly contributes to eutrophication. With the increased awareness and understanding of the deleterious effects of nutrients, the authorities have introduced stringent laws restricting nutrient discharges from both wastewater treatment facilities and other point source contributors, and hence efficient removal of nutrients is now required.

The traditional solution to the problem of ammonium removal is biological treatment and there have been numerous researches devoted to the various aspects of the nitrification/denitrification processes. Despite the effectiveness of biological systems, they require large reactor volumes or footprints and areas, and hence high capital costs due to the slowness of the biological conversion process for nutrient ammonium. Moreover, when exposed to the peak and variable loads, these processes may fall short in removing the influent concentration patterns and fail to achieve the required effluent quality standards unless some extra polishing units or an upgrade are provided [1]. Development of high capacity and more effective processes alternative to the conventional biological processes is of great importance for nutrient

removal/recycling operations. The application of zeolite as an ion exchanger for ammonium removal is one of the effective technologies that have received considerable attention in recent years. Zeolites are very effective in the removal of ammonium, as has been demonstrated in numerous studies worldwide which have used natural zeolite from many different deposits [1–6]. However, regeneration of zeolites and handling of the brine solutions produced are the main drawbacks for the development of zeolite-based processes because of the high cost of these operations. Therefore some studies have focused on the processes which do not require chemicals for regeneration i.e. bio-regeneration [4,7].

For phosphorus, there are a number of technologies, both established and under development, which can be used to remove/recover phosphorus from wastewaters. Amongst them, chemical precipitation, biological phosphorus removal and crystallization are the most commonly known processes, with chemical precipitation being the leading technology today. More recently, however, biological phosphorus removal has become firmly established; crystallization technology has also completed its progress towards commercialization and technologies extending chemical precipitation to assist nutrient removal are beyond the pilot stage. In the phosphate removal studies based on crystallization [e.g. [8–13]], several materials including calcite, sand, and a variety of Ca-phosphate crystals have been used as seeding material to initiate and enhance phosphate precipitation and recycling.

* Tel.: +90 312 2873430/1381; fax: +90 312 2875409.

E-mail address: karapinaruray@hotmail.com.

Realizing phosphorus removal by both precipitation (except magnesium ammonium phosphate—MAP precipitation) and crystallization does not affect the ammonium concentration of the wastewater. Therefore there is a need to develop processes to facilitate removal of nutrients, ammonium and phosphate. There are numerous studies including precipitation of magnesium ammonium phosphate as an alternative process [14]. There are two commercial processes namely the Unitika Phosnix process and The Rim-Nut process based on the crystallization of struvite (MAP) from tertiary wastewaters. The Phosnix process is based on the agitated column reactor, with ancillary chemical dosing equipment for nucleation and growth of struvite crystals. Unlike Phosnix process, the RIM-NUT is an ion exchange–precipitation process. The process consists of three stages with the first stage designed for ammonium removal by cationic resin composed of natural zeolites and the last two stages for the removal of phosphate and the nutrient precipitation process by ionic resin. The major drawback of the struvite crystallization is the high operating cost because of the magnesium addition for the precipitation of struvite.

Zeolites, naturally occurring hydrated aluminosilicate minerals, mainly consist of a three-dimensional framework structure bearing SiO_4 and AlO_4 tetrahedra. They belong to the class of minerals known as tectosilicates. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These exchangeable cations give rise to the ion-exchange properties of the material.

In this study, the removal of both ammonium and phosphorus from aqueous solutions was investigated using natural zeolites as an adsorbent for the adsorption of ammonium and the subsequent use of ammonium-loaded zeolite as seed for the precipitation of phosphate. The effect of zeolite dosage and initial ammonium concentration onto ammonium uptake of zeolite and seeded precipitation of phosphate was evaluated. Particle size measurement of seed material was used to evaluate the seeded precipitation of phosphorus precipitated homogeneously from solution or heterogeneously onto the zeolite particle. Therefore, the results given in this paper will also contribute a better understanding of seeded precipitation of phosphate. The study assumes the utilization of final ammonium and phosphate bearing zeolite product as a fertilizer.

2. Materials and methods

Zeolite (granular) marked as Type C, a natural zeolite, was obtained from ZEOLITH in Deutschland e.K. It had the following chemical composition 51.80% SiO_2 (by weight), 18.34% Al_2O_3 , 3.40% Fe_2O_3 , 0.96% MgO , 4.73% CaO , 0.35% BaO , 0.04% SrO , 0.60% Na_2O , 4.91% K_2O , and 15.14% LOI. Its given total cation and ammonium (NH_4^+) exchange capacities were max. 235 and 195 meq/100 g, respectively. The zeolite sample as received was ground to a particle size smaller than 0.060 mm prior to use in the experiments to increase both adsorption capacity and available seed surface.

Analytical grade chemicals and de-ionized water which had a conductivity of 0.7 $\mu\text{S}/\text{cm}$ were used to prepare the solutions. All the experiments were performed at $20 \pm 0.5^\circ\text{C}$.

Ammonium, phosphorus and calcium stock solutions were prepared by dissolving ammonium acetate ($\text{CH}_3\text{COONH}_4$), potassium phosphate (KH_2PO_4) and calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water, respectively. Particle size distribution analysis was determined using a laser based particle size analyzer (Galai CIS I).

All experiments were carried out by mixing the solution containing ammonium, phosphorus and calcium with the solid phase

(zeolite) in a mechanically stirred batch system (1000 ml). In the seeding experiments, zeolite dosage, ammonium concentration of the solution and the calcium/phosphorus molar ratio were kept constant at 1.0 g/l, 10.0 mg/l and 5.01, respectively. To initiate the precipitation on the zeolite surface, the procedure was followed as given in Karapinar et al. (2006). pH was adjusted to the experimental values by slow addition of sodium hydroxide to improve heterogeneous nucleation after mixing of all components. Once a given super saturation condition (relative super saturation 12.0–16.0 for Hydroxyapatite, HAP) was achieved the system was allowed to relax. During the relaxation period, pH of the solution was kept constant at its initial value, and, if necessary, sodium hydroxide was added. During the allowed period of relaxation, 15- and 2-ml aliquots of solution were removed for analyses at predetermined intervals. The 15-ml sample solution was filtered using a membrane filter having a pore size of 0.45 μm (Sartorius AG) and then analyzed for ammonium, calcium and phosphorus. The 2-ml sample solution was for particle size measurements. Change in the particle size of the suspension during the relaxation was characterized by both particle size measurement and microscopic examination.

A computer programme PHREEQC Version 2 has been used to calculate the saturation-index (SI) with respect to calcium phosphates of the chemically defined precipitation system. The equilibrium constants used in calculations were taken from Song et al. [15].

Ammonium was determined according to DIN 38406-E5. Calcium was analyzed using EDTA titrimetric method (DIN 38406 E3, 1982) while phosphorus was analyzed using a spectrophotometric method (DIN EN 1189, 1996) at a wavelength of 700 nm with a Lamp 2 UV/VIS Spectrophotometer (PerkinElmer, Germany).

3. Results and discussion

3.1. Ammonium removal by natural zeolite

Fig. 1 shows removal of ammonium from synthetic wastewater solutions at different zeolite dosages and initial ammonium concentrations. Unless otherwise stated a reaction time of 60 min was applied for ammonium uptake by the zeolite and during reaction period no pH adjustment was exercised. The pHs of suspensions

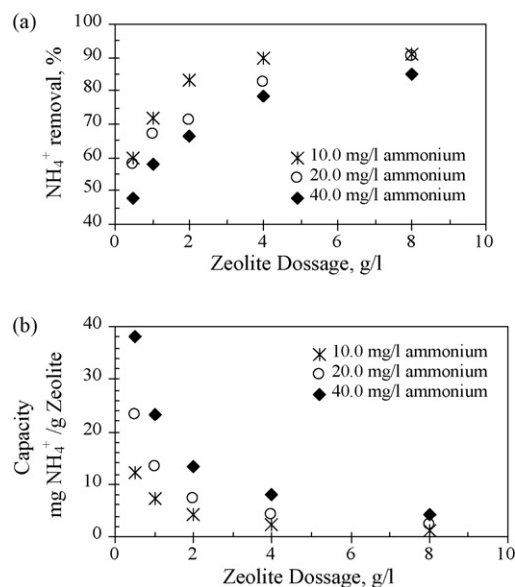


Fig. 1. Ammonium removal at different zeolite dosages (0–8 g/l) and initial ammonium concentrations (10–40 mg/l).

Table 1

Final pH values of suspension at different concentrations of ammonium and zeolite.

Ammonium, mg/l	pH ^a
10	6.0–8.5
20	6.4–8.3
40	6.5–7.8
80	6.5–7.4
100	6.6–7.3
160	6.7–7.1
200	6.7–7.0

^a The pH range represents the range of zeolite dosage (0.5–8.0 g/l).

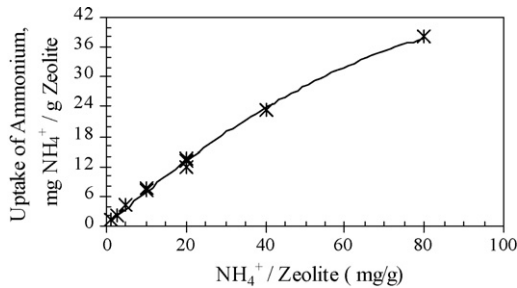


Fig. 2. Relationship between ammonium uptake capacity of zeolite and $\text{NH}_4\text{-N/zeolite}$.

developed depending on the concentration of ammonium and zeolite are shown in Table 1.

As expected, the ammonium uptake behavior of zeolite used in this experiments is quite similar to that of zeolite used in other studies; at all ammonium concentrations tested, the amount of ammonium removed increased with increasing zeolite concentration (Fig. 1a), while at the same time the uptake of ammonium by zeolite ($\text{mg NH}_4^+/\text{g zeolite}$) decreased (Fig. 1b) indicating that there is a correlation between the uptake of ammonium by zeolite ($\text{mg NH}_4^+/\text{g zeolite}$) and the ratio of initial ammonium concentration to zeolite dosage (Fig. 2). The ammonium uptake by zeolite is a very rapid process and was almost completed within the minutes of contact time (Fig. 3).

3.1.1. Effect of P and related cations onto ammonium uptake of Zeolite

With regard to the objective of this study, ammonium uptake of zeolite was investigated at different phosphorus and calcium concentrations where the calcium/phosphorus molar ratio and initial concentration of ammonium were kept constant at 5.01 and 10.0 mg/l, respectively. The experiments were carried out at its own pH developed after mixing all components (ammonium acetate,

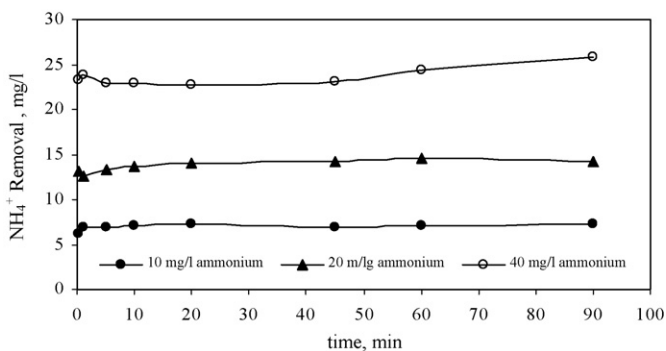


Fig. 3. Ammonium removal as a function of the contact time at a zeolite dosage of 1.0 g/l.

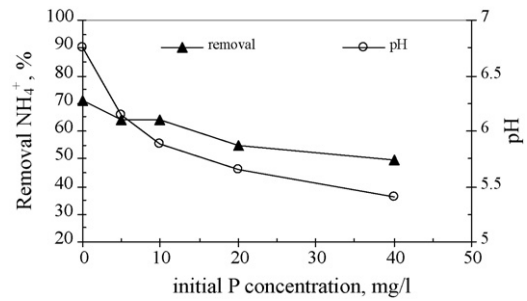


Fig. 4. The effect of P onto ammonium removal by zeolite (ammonium concentration = 10 mg/l, zeolite dosage = 1.0 g/l, the molar ratio of Ca/P = 5.01).

potassium phosphate, calcium chloride and zeolite). In these experiments, zeolite was added at last into the stirred solution. Fig. 4 shows that the uptake of ammonium by zeolite decreased in the presence of P. This effect was because of the presences of K (potassium phosphate) and Ca (calcium chloride) as competing ions in solution. It is well known that ammonium uptake by zeolite is through cation exchange mechanism and the competitive roles of K and Ca are common in cation exchange reactions. An increase in P concentration means also an increase in K and Ca concentrations, leading a decrease in ammonium uptake of zeolite. The decrease in uptake capacity of zeolite was recorded to be around 10% at 10 ppm P while it increased to almost 30% at 40 ppm P. No Ca-phosphate precipitation was observed under these pH conditions.

3.2. Ca-phosphate precipitation

Since ammonium uptake of zeolites was widely studied and the phenomena have been well known, in this study, the emphasis was given on the seeded precipitation of phosphorus in aqueous solution including ammonium.

3.2.1. The effect of ammonium on calcium phosphate precipitation

Fig. 5 shows the effect of ammonium on Ca-phosphate precipitation at pH 9.0. The increase in the concentration of ammonium in the range of 10–60 mg/l produced no significant effect on the precipitation of Ca-phosphate. This was consistent with the calculated saturation indices (Fig. 5).

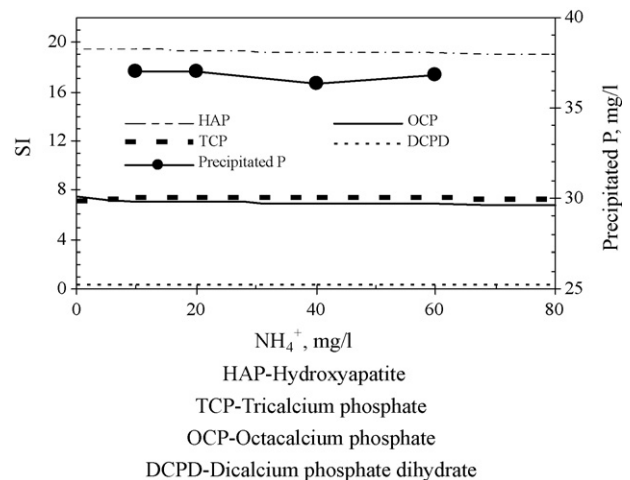


Fig. 5. The effect of ammonium onto Ca-phosphate precipitation and saturation indices of Ca-phosphate phases (P = 40 mg/l, the molar ratio of Ca/P = 5.01, pH = 9.0).

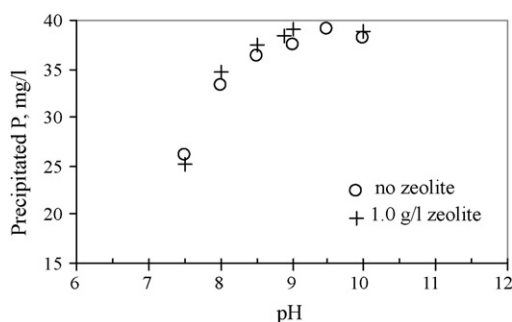


Fig. 6. The effect of pH on Ca-phosphate precipitation in the presence and absence of zeolite ($P = 40$ mg/l, and molar ratio of $Ca/P = 5.01$, reaction time = 1 h).

3.2.2. Ca-phosphate precipitation in the presence of zeolite

Fig. 6 illustrates the dependence of precipitation of calcium phosphate on pH (7.5–10) in the presence and absence of zeolite. The addition of zeolite appeared not to affect the formation of calcium phosphate precipitate. However, the extent of the precipitation of phosphate increased with increasing alkalinity in a pH range of 7.5–9.0; thereafter, it almost leveled off (Fig. 6). Since the solution condition was more favorable for the precipitation, no effect of the seed on the amount of precipitation could be observed.

In the present study, the composition of precipitate was not investigated. However the calculated molar ratios of Ca/P of the precipitate formed under working conditions (with and without zeolite) were given in Fig. 7, where the molar ratios of Ca/P of the precipitates determined to be around 1.5.

Since the Ca-phosphate precipitation is a base consuming process, an increase in the amount of precipitate by increasing pH was expected. The pH dependence of precipitation was considered in the light of its effect on the supersaturated conditions of solution [12,15]. In other words, an increase in the pH makes the solution conditions favorable for precipitation. In this regard, whether the precipitation took place onto seed surface needs to be resolved. Previous investigations on magnetite-seeded precipitation of phosphate showed that, at relatively lower pHs precipitation occurred heterogeneously on the surface of seed particles whereas by improving the solution conditions for precipitation (e.g. the increase in the saturation index) homogeneous nucleation in the solution was unavoidable [12]. In addition to achieve high precipitation efficiency, the objective of seeded precipitation of phosphate at least in this study was to load the precipitate onto the seed surface. In this regard, Karapinar et al. [12] reported an inverse relationship between total precipitation and seeded precipitation efficiency. They also noted that at low pHs, all precipitates could take place on the seed surface through secondary phase nucleation and growth [13]. Therefore, to load the phosphate onto zeolite particles, the same procedure was followed in this study.

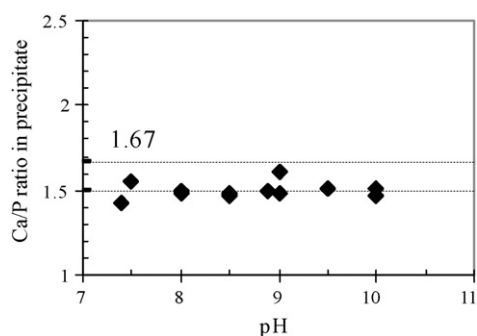


Fig. 7. The calculated Ca/P molar ratios of precipitates, $P = 40$ mg/l, the molar ratio of $Ca/P = 5.01$ (reaction time = 1 h).

Table 2
Lagtime required for zeolite-seeded precipitation of Ca-phosphate.

pH	T_L , lagtime (s)
6.9	52
7.0	28
7.1	31
7.2	35
7.5	49

In the seeded precipitation experiments, loading of precipitate onto the seed surface would be controlled by two mechanisms; nucleation and growth. Provided that the precipitate formed/encrusted on the surface of the seed, this would then lead to an increase in the size of seed. Therefore, loading efficiency of Ca-phosphate onto zeolite was evaluated by variation in the particle size of seed particles under experimental conditions.

In the seeding precipitation experiments, regardless the operative process in precipitation either homogeneous or heterogeneous nucleation, rapid precipitation was obtained at all pH values. However, when the system was allowed to relax at constant pH (i.e. under relatively low super saturations), a certain lag time was noted to elapse at the onset of the precipitation. The lag times recorded at different pH values were given in Table 2.

Regardless of the seed type, the same tendency for pH-dependence of lag time was also observed in a previous study during the magnetite-seeded precipitation of Ca-phosphate [13]. These authors attributed the effect of pH on the lag time mainly to the initial fast precipitation and to the residual concentration of phosphorus. At the end of the precipitation in the pH range of 6.9–7.5, the total amount of precipitate formed under lower super saturation conditions was nearly the same or even higher than that obtained under higher super saturation conditions (Fig. 8).

Since the efficiency of seeded precipitation (the ratio of precipitate onto seed to total precipitation) is a function of variation of size of the seed material, measured particle size of the seed during the relaxation time could provide an explanation of zeolite-seeded precipitation of phosphate. The measured particle size after relaxation period is given in Fig. 9. For all relaxing experiments, particle size of zeolite is greater than that of zeolite itself, meaning that particle size is getting bigger with the precipitation of Ca-phosphate. Results also showed that an increase in relaxing pH from 6.9 to 7.5 leads to decrease in particle size.

pH tendency of measured particle size can be explained by the amount of fast precipitation during the relaxation. It is known from previous study that favorable solution conditions for precipitation (due to increase in saturation index by the increase in pH), homogeneous nucleation in solution was getting higher leading to

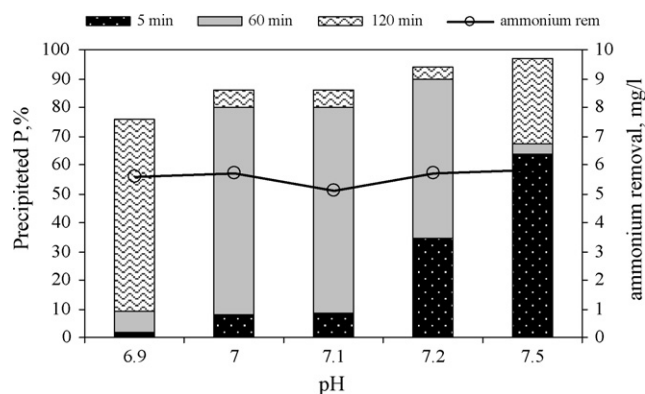


Fig. 8. Ca-phosphate precipitation during the relaxation (ammonium = 10 mg/l, $P = 40$ mg/l, the molar ratio of $Ca/P = 5.01$, zeolite dosage = 1.0 g/l).

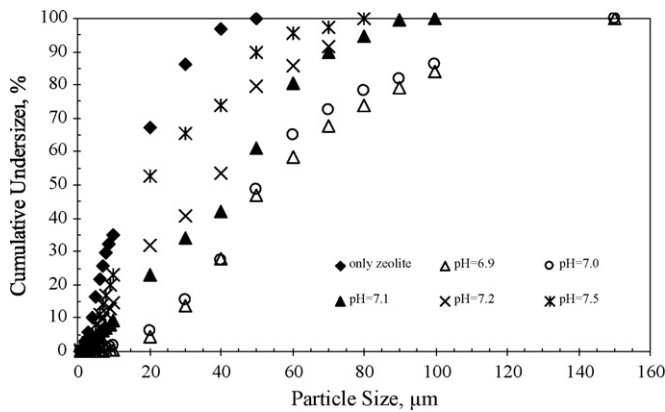


Fig. 9. Particle size distributions of zeolite particles after precipitation tests over a relaxation period of 120 min.

decrease in phosphate loaded on seed although total precipitation is increased. This means that when the solution conditions are getting more favorable for precipitation (an increase in the amount of fast precipitation), calcium phosphate precipitation was mainly controlled by nucleation process rather than the growth of precipitate nucleated either homogeneously or heterogeneously, leading new small particles in solution. According to Fig. 8, the amount of initial fast precipitation is increasing with the increase in pH.

Fig. 10 shows the appearance of zeolite particles before (a) and after (b) precipitation tests at pH 7.0. They also revealed that precipitate was loaded onto zeolite surface with an increase in particle size of zeolite particles (Fig. 9). However, under high super saturation conditions (i.e. at pH 9.5), a more voluminous precipitate in which some zeolite particles were entrapped was obtained. It

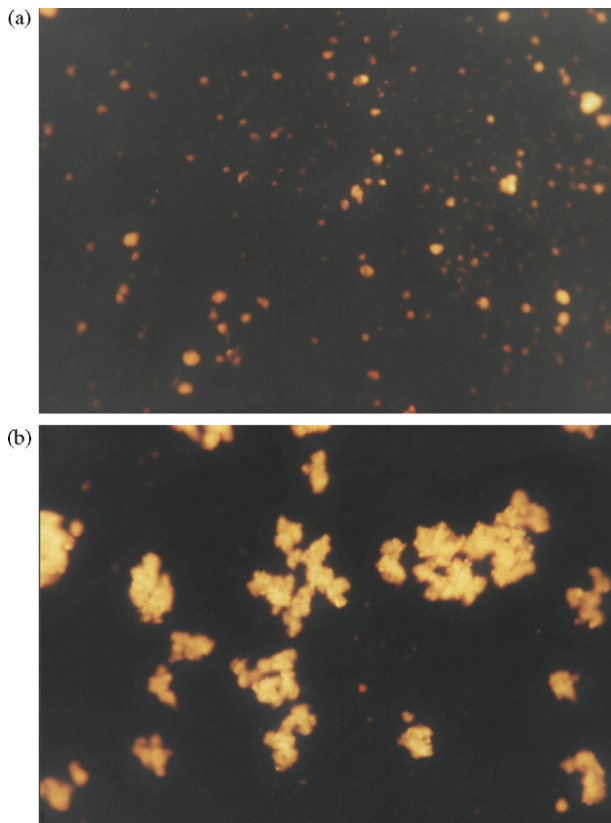


Fig. 10. (a) Appearance of zeolite particles before precipitation at pH 7.0. (b) Appearance of zeolite particles after precipitation at pH 7.0.

should be noted that particle size of precipitates with and without zeolite at high super saturations could not be undertaken because of the transparency and fine nature of the precipitates.

4. Conclusion

It is well known that zeolite has a high affinity for ammonium. In this study, zeolite was also tested for use as a seed material to precipitate phosphate in the form of Ca-phosphate. Results showed that zeolite can be used to remove both ammonium and phosphate from aqueous solutions. The highest ammonium removal efficiency was achieved at the lowest used initial ammonium concentration. Results indicated that the removal efficiency and the uptake of ammonium by zeolite are both dependent on the initial ammonium and zeolite concentrations, indicating rise in uptake of ammonium by zeolite for higher ratios. While existence of competing cations such as K and Ca in the solution was reducing the ammonium uptake by zeolite, there was no considerable effect of ammonium on the precipitation of phosphate. By setting conditions available for secondary nucleation and growth mechanism (i.e. relaxation of suspension at low super saturations), phosphate precipitation was loaded onto zeolite particle surfaces. The total amount of precipitate formed under relatively lower super saturation conditions (pH 6.9–7.5) was nearly the same or even higher than that obtained under high super saturation conditions. The loading of phosphate on the seed surface was confirmed by an increase in the particle size of zeolite.

This study highlights that zeolite can be suitably used as an adsorbent/seed material for the removal of both nutrients ammonium and phosphorus from the wastewaters. However, the method should be tested by using natural wastewaters including both nutrients. In addition, the usage of zeolite enriched by phosphorus and ammonium as a fertilizer should also be investigated.

The findings of this study will also provide a better understanding of seeded precipitation of phosphate in the field of phosphate removal and recycle technologies.

Acknowledgements

This work was supported by a grant from Deutsche Forschungsgemeinschaft (DFG) on the proposal of The Scientific and Technical Research Council of Turkey (TUBITAK). The author would like to thank DFG and TUBITAK.

References

- [1] B.B. Beler, Clinoptilolite and multipurpose filters for upgrading effluent ammonium quality under peak loads, *Water Sci. Technol.* 37 (9) (1998) 235–242.
- [2] J. Hlaway, Gy. Vigh, V. Olasz, J. Inczedy, Investigations on natural Hungarian zeolite for ammonium removal, *Water Res.* 16 (1982) 417–420.
- [3] N.A. Booker, E.L. Cooney, A.J. Priestley, Ammonium removal from sewage using natural Australian zeolite, *Water Sci. Technol.* 34 (9) (1996) 17–24.
- [4] M. Gren, A. Mels, O. Lahav, S. Tarre, Biological-ion exchange process for ammonium removal from secondary effluent, *Water Sci. Technol.* 34 (1) (1996) 449–458.
- [5] T.C. Jorgensen, L.R. Wetherley, Ammonium removal from wastewater by ion exchange in the presence of organic contaminants, *Water Res.* 37 (2003) 1723–1728.
- [6] A.H. Englert, J. Rubio, Characterization and environmental application of a Chilean natural zeolite, *Int. J. Miner. Process* 75 (2005) 21–29.
- [7] J.Y. Jung, Y.C. Chung, H.S. Shin, D.H. Son, Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process, *Water Res.* 38 (2004) 347–354.
- [8] P.G. Koutsoukos, G.H. Nancollas, Crystal growth of calcium phosphates—epitaxial considerations, *J. Cryst. Growth* 53 (1981) 10–19.
- [9] E.C. Moreno, K. Varughese, Crystal growth of calcium apatites from dilute solutions, *J. Cryst. Growth* 53 (1981) 20–30.
- [10] J.F. De Rooij, J.C. Heughebaert, G.H. Nancollas, A pH study of calcium phosphate seeded precipitation, *J. Colloid Int. Sci.* 100 (2) (1984) 350–358.

- [11] D. Donnert, Investigations on phosphorus removal from wastewater. Progress Report KFK 4459, Kernforschungszentrum Karlsruhe, 1998.
- [12] N. Karapinar, E. Hoffmann, H.H. Hahn, Magnetite seeded precipitation of phosphate, *Water Res.* 38 (2004) 3059–3066.
- [13] N. Karapinar, E. Hoffmann, H.H. Hahn, P-recovery by secondary phase nucleation and crystal growth of calcium phosphates on magnetite mineral, *Water Res.* 40 (6) (2006) 1210–1216.
- [14] S.G.J. Brett, G.K. Morse, J.N. Lester, Phosphorus Removal and Recovery Technologies, Selper Publications, London, UK, 1997.
- [15] Y. Song, H.H. Hahn, E. Hoffmann, Effects of solution conditions on the precipitation of phosphate for recovery. A thermodynamic evaluation, *Chemosphere* 48 (10) (2002) 1029–1034.