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Seed selections for crystallization of calcium phosphate for phosphorus recovery

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Abstract

Seed induces and promotes the crystallization of calcium phosphate, and acts as carrier of the recovered phosphorus (P). In order to select suitable seed for P recovery from wastewater, three seeds including Apatite (AP), Juraperle (JP) and phosphate-modified Juraperle (M-JP) were tested and compared. Batch and fixed-bed column experiments of seeded crystallization of calcium phosphate were undertaken by using synthetic wastewater with 10 mgP/L. It showed that AP had bad enduring property in the crystallization process, while JP had better performance for multiple uses, and M-JP was a hopeful seed for P recovery by crystallization of calcium phosphate.

Key words: crystallization; seed; phosphorus recovery; Juraperle; Apatite

Introduction

In recent years phosphorus (P) recovery from wastewater and animal manure has drawn much attention of the water industry, the P industry and the policy-makers (Brett *et al*., 1997; Driver *et al*., 1999). The substantial difference between the traditional P removal and the P recovery from wastewater is that P removal stresses getting a P free effluent by transferring P to sludge with chemical and biological processes, but P recovery stresses getting a P-containing product that can be reused either in agriculture or in P industry. It is commonly considered that crystallization processes can recover P either as calcium phosphates that are similar to phosphate rocks, or as magnesium ammonium phosphate that is a slow release fertilizer. Seeded crystallization is an effective process for P recovery from wastewater, in which the seed not only induces and promotes the crystallization of phosphate, but also acts as a carrier of P recovered.

So far a variety of seeds have been tested in the experimental studies of calcium phosphate crystallization including phosphate rock, bone charcoal, magnesia clinker, zirconium hydroxide, pumice stone and sand (Stratful *et al*., 1999), and it is reported that bone charcoal, magnesia clinker and zirconium hydroxide gave the best performance, whilst pumice stone gave the worst. In recent studies and practices for P recovery, sand has been used in the DHV's Crystalactor process (Piekema and Gaastra, 1993; Giesen, 1999) in full-scale, but carbonate has to be removed before the crystallization process for P recovery. Besides, although sand is cheap and easily available, it has the disadvantage of possessing high dead weight. More studies are needed in selecting seeds for P recovery from wastewater, so the present study devotes to the selection and comparison of three seeds potentially available to P recovery from wastewater. Batch and column experiments were undertaken with artificial wastewaters for seeded crystallization of calcium phosphate; chemical analysis and instrumental method were employed to characterize the seeds.

1 Materials and methods

1.1 Seed materials

Apatite (AP), Juraperle (JP) and its phosphate-modified form phosphate-modified Juraperle (M-JP) were taken as seeds in the crystallization of calcium phosphate. AP is a Jordan phosphate rock with average particle size of 1.5 mm and a specific surface area (SSA) of 1.0 m^2/g determined by measuring the N_2 isotherm at 77 K with a Quantachrome Autosorb1-MP device (Quantachrome Instruments, USA) and calculated with the Brunauer-Emmett-Teller (BET) method (Brunauer *et al*., 1938); JP is a German calcite with average particle size of 1.5 mm

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and a SSA of 0.4 m^2/g (BET). To obtain seeds, 100 g JP was put into 5-L bottles containing 2.5 L phosphate solutions whose concentrations were 75, 200, 600, 800 mgP/L, respectively. The bottles were first intensively shaken manually for 2 min and then were shaken on a SM-25 shaking machine (Edmund Buehler, Germany) at 75 r/min and 25±0.5°C for 50 h. Afterwards, M-JP was separated from solution by using 2772 1/2 Folded Filters (Schleicher & Schuell, Germany) and air dried at the above temperature. The M-JP seeds were sieved and only the particles with grain sizes larger than 0.355 mm were used as seeds in the crystallization experiments.

1.2 Batch and column experiments

In batch experiment synthetic water I (SW-I) was used to study the efficiencies of AP and JP on the crystallization of calcium phosphate. SW-I was hard water prepared referring to the municipal water and wastewater of Karlsruhe of Germany, with 10 mgP/L phosphate addition without organic matter; its composition is shown in Table 1. Calculated by using PHREEQC programme (Parkhurst and Appelo, 1999; Song *et al*., 2002), the saturation indices of SW-I with respect to hydroxylapatite and to calcite were 11.37 and 0.36, respectively. The batch experiments were initiated by completely mixing 500 ml SW-I and 2, 5, and 10 g/L AP or JP seed in a plastic bottle, respectively, and then the bottles were shaken on a SM-25 shaking machine at 75 r/min and 25±0.5°C. The composition of the solution was measured with samples taken at 4, 24, 48 and 72 min. After the batch experiments, the seed was separated from solution with 2772 1/2 Folded Filters, air-dried at 25±0.5°C.

Using the secondary effluent of an activated sludge wastewater treatment plant and supplementing phosphate into 10 mgP/L prepared SW-II (Table 1). In continuous flow-through column experiment SW-II was used to study the efficiency of the M-JP on the crystallization of calcium phosphate. A plexiglas column with a diameter of 3.0 cm was filled with 220 g M-JP seed to reach a fixed bed height of 20 cm. The SW-II was pumped into the column from the bottom at a flow rate of 140 ml/h and up flew through the fixed bed, so the hydraulic retention time was 1.0 h. The composition of the influent and effluent was measured with samples taken at intervals.

1.3 Chemical analysis and instrumental measurement

The water sample was filtrated by a 0.45-μm MF-Millipore Membrane (Millex® -HA, Ireland). P concentration was measured by phosphomolybdenum blue method (DIN EN 1189-D11, 1998) with a MPM 1500 Spectrophotometer (WTW, Germany) at the wavelength of 690 nm. Dissolving around 0.3 g seed sample into nitrate acid in a steel cell at 110°C overnight, diluting the solution and measuring P concentration, the P content loaded on the seed has been calculated. Before and after crystallization experiments the seeds were observed at 133.32 Pa water vapour pressure with a XL 30 ESEM Environmental Scanning Electron Microscopy (Philips, The Netherlands).

2 Results and discussion

2.1 Apatite as seed

It could be preferable to use calcium phosphate rock as seed for the crystallization of calcium phosphate considering the following reuse process of the recovered material. In order to primarily understand the effect of the Jordan AP on the crystallization of calcium phosphate, different seed concentrations were adopted in the batch experiments, and the results are shown in Fig.1a. It shows that AP can greatly increase the efficiency of phosphate removal from SW-I; with 0, 2, 5, 10 g/L AP and at the reaction time of 48 h, the P removal efficiencies are 18%, 50%, 93% and 98%, respectively; seeded crystallization is much more efficient than un-seeded one. This can be also reflected by the change of solution pH value during the crystallization.

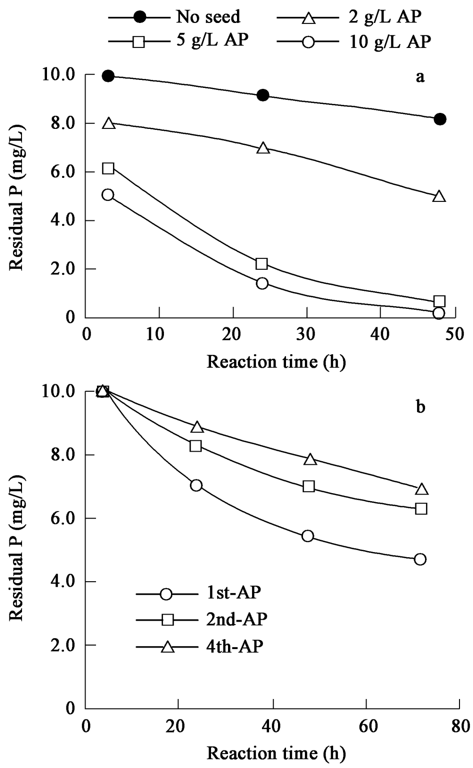

Fig. 1 Effects of AP concentration (a) and the reused AP seeds (2 g/L AP) (b) on the crystallization of calcium phosphate. Batch experiments with SW-I in (a): pH_s was 7.95, and the pH_e values for the reactions with 0, 2, 5 and 10 g/L AP were 8.28, 7.91, 7.85 and 7.78, respectively; in (b): pH_s was 7.86, and the pH_e values for reactions with 1st-AP, 2nd-AP and 4th-AP were 8.17, 8.20 and 8.11, respectively.

Table 1 Composition of synthetic waters (SW) (mg/L, at 25°C)

SW	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}-P	HCO_3^-	pH	DOC
I	98.7	12.6	98.8	11.5	176	45.4	10.0	262	7.53	–
II	90.0	342	95.8	12.3	46.8	15.9	10.0	63.0	7.60	18.0

The pH value at the starting of the experiment (pH_s) was 7.95, and the pH values at the end of the experiment (pH_e) with 0, 2, 5, 10 mg/L AP were 8.28, 7.91, 7.85, 7.78, respectively. pH decrease indicates the extent of the crystallization reaction of phosphate, since it is a base uptake process. A suitable seed must be also enduring considering the possible inhibitions resulted from some wastewater composition, such as carbonate and organic matter. Fig.1b shows the efficiencies of the reused AP seeds on the crystallization of calcium phosphate from hard water SW-I. With the one time or multiple used AP, the phosphate removal efficiencies decrease at 2 g/L AP seed concentration and the reaction time of 72 h, with the first-, the second- and the fourth-time use of the seed, the P removal efficiencies are 54%, 37% and 31%, respectively. It shows that the enduring property of the AP seed is not good in promoting the crystallization of calcium phosphate. SW-I is only hard water, in case that organic matter also exists, the crystallization of phosphate would be more difficult, so AP can not meet the request of seeded crystallization of calcium phosphate from wastewater for recovery.

2.2 Juraperle as seed

Considering the influence of carbonate on the crystallization of phosphate, JP was tested as seed for the crystallization of calcium phosphate. Fig.2 shows the original and the multiple used JP on the crystallization of calcium phosphate, and the comparisons between the efficiencies of JP and AP. Different from AP, the multiple used JP seeds have better performance than the original one in promoting the crystallization of calcium phosphate from hard water, and this phenomenon was also reported in the past (Berg *et al*., 2002a, b; Song *et al*., 2004). It is interesting to compare the efficiencies of JP and AP at the same experimental round. For the first time use, AP is much more efficient than JP; for the second time use, AP is still more efficient than JP, but the preponderance becomes smaller; for the fourth time use, the efficiency of JP gets very close to the efficiency of AP. These results manifest that the enduring property of JP in the crystallization of calcium phosphate is better than that of AP. The P contents of the one time, two times and four times used JP seeds were determined to be 0.8, 1.7 and 2.1 mg/g, respectively. The former studies (Berg *et al*., 2002a; Song *et al*., 2004) observed the coverage of phosphate on the JP seed, and this can explain the efficiency increase of the reused JP seed. The above results also remind us of the modification of JP with phosphate, i.e., by covering the surface of the JP particles with newly formed phosphate so as to increase the positive effect of the seed on the crystallization of calcium phosphate.

2.3 Modified Juraperle as seed

In the modification of JP, different phosphate solutions were used. Chemical analysis gives the P content of the

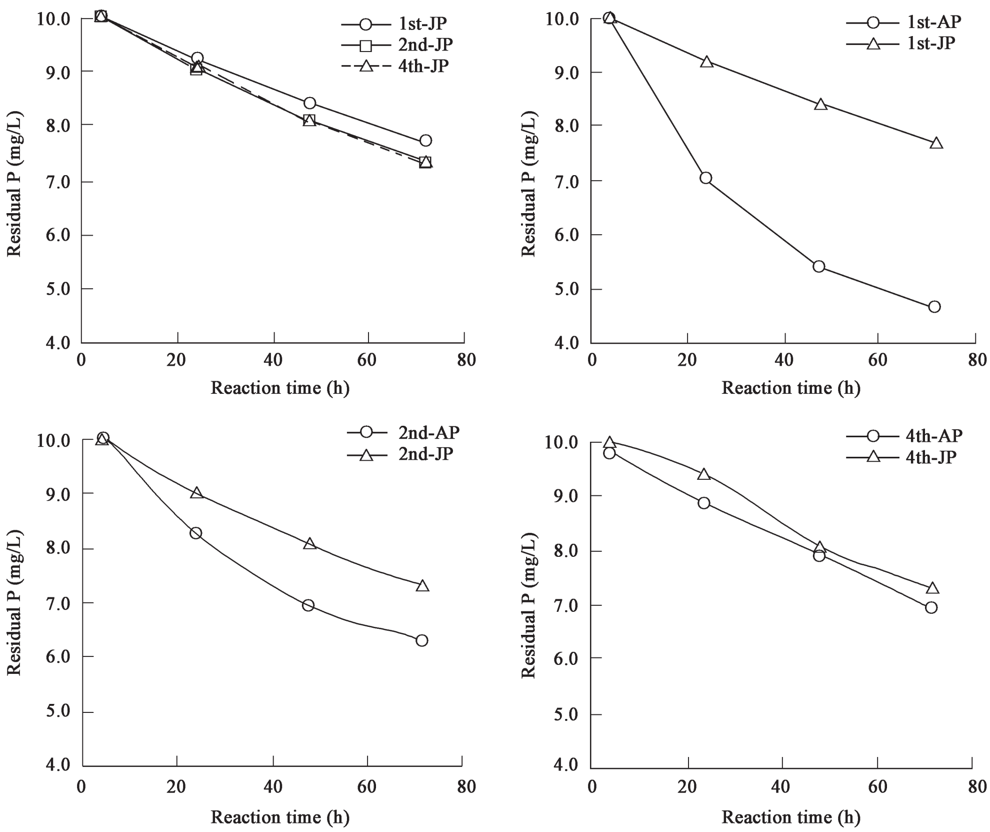

Fig. 2 Effects of the reused JP seeds (2 g/L JP) concentration on the crystallization of calcium phosphate, and the efficiency comparisons of JP and AP. Batch experiments were with SW-I; pH_s was 7.86, pH_e values for the reactions with 1st-JP, 2nd-JP and 4th-JP were 8.26, 8.25 and 8.24, respectively; pH_e values for the reactions with AP were the same as in Fig.1.

Table 2 P content of the phosphate-modified JP (mg/g)

M-JP	JP	JP-75	JP-200	JP-600	JP-800
P used for modification(mg/L)	–	75	200	600	800
P content of M-JP (mg/g)	0.29	0.66	0.96	2.1	5.1

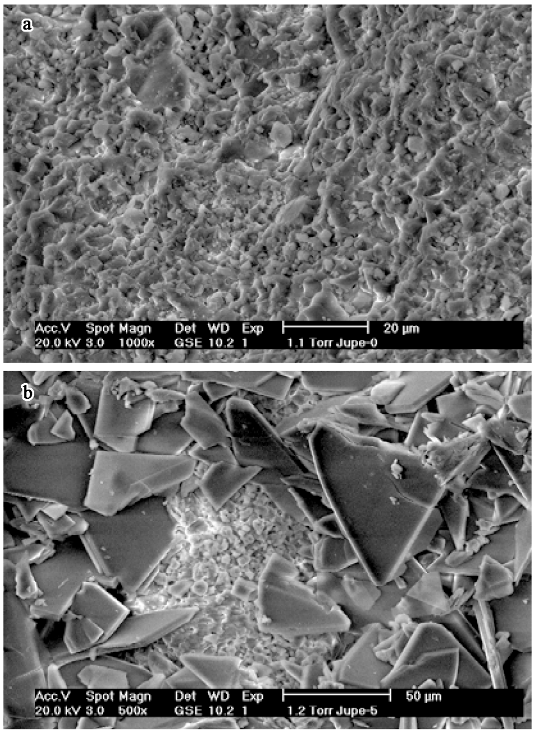

Fig. 3 ESEM images of the original JP (a) and the JP-800 (b).

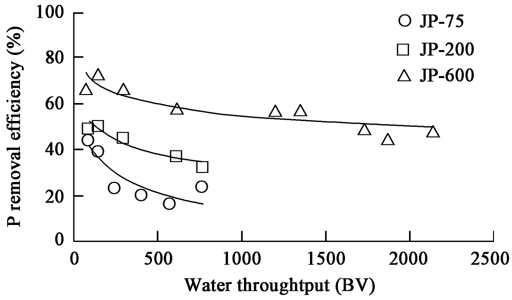

Fig. 4 P removal efficiencies of the fixed-bed columns with different M-JP seeds. Continuous flow-through column experiments with SW-II; pH_s was 7.69, pH_e values for the reactions with JP-75, JP-200 and JP-600 were 7.93, 7.85 and 7.81, respectively.

modified JP in Table 2. In Fig.3 the ESEM images of the original JP (a) and the JP-800 (b) prove that big phosphate crystals appear on the surface of the M-JP seed.

In order to understand the efficiency of the M-JP seeds, continuous flow-through column tests have been undertaken using SW-II. Fig.4 gives the P removal efficiencies of the column tests with different M-JP seeds. It shows that with more P on the M-JP, the P removal efficiency of the fixed-bed column becomes higher. Although with the increase of the water throughput (in Bed Volume, BV) of the test, the P removal efficiencies decrease gradually; the column packed with JP-600 still has a P removal efficiency of around 50%. Because SW-II contains DOC, it proves that the M-JP is resistant to the DOC concentration of 18 mg/L.

The above studies have selected three seeds for the crystallization of calcium phosphate. The seeded crystallization process of calcium phosphate from wastewater is complicated. It may be influenced by the solution composition including the concentrations of phosphate and the inhibitors, the seed composition and the seed surface property etc. In the present study much attention was paid to the composition of the seed, and further study is being undertaken, especially on the optimisation of the seed modification and characterization. JP is a relatively cheap material (25 EUR/t) and the modification process is simple, once the crystallization process is triggered, it is expected to proceed till the seed enriches enough P for recovery purposes. In the on-going experiment using M-JP (Fig.4 JP-600) as seed to crystallize calcium phosphate from SW-II containing 10 mgP/L, the loaded P has accounted for about 1% (8.5 mg/g) seed weight after a water throughput of 2100 BV. The phosphate industry requires that the P content of the phosphate materials should be greater than 10.9% (Schipper *et al.*, 2001). Therefore, the limited quantity of P loaded on the M-JP is still far less than the requirement of the phosphate industry. However, the present experiment only used a P concentration of 10 mg/L, and the water throughput tested was still very limited; with larger water throughput, the P load on the M-JP would be increased to approach the request of P recovery.

3 Conclusions

Seed selection is important for the crystallization of calcium phosphate from wastewater, both for the process and for the reuse of the recovered material. In the present study three seeds were tested. It shows that Apatite does not have good enduring property in the solution with carbonate, so it is not a suitable seed for efficient P removal and recovery from wastewater. Juraperle, especially the used Juraperle has good performance in the crystallization process of calcium phosphate because of the accumulation of the newly formed phosphate on its surface. Phosphate-modified Juraperle is a hopeful seed for the crystallization of calcium phosphate for P recovery.

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