Effect of humic substances on the precipitation of calcium phosphate

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Abstract: For phosphorus (P) recovery from wastewater, the effect of humic substances (HS) on the precipitation of calcium phosphate was studied. Batch experiments of calcium phosphate precipitation were undertaken with synthetic water that contained 20 mg/L phosphate (as P) and 20 mg/L HS (as dissolved organic carbon, DOC) at a constant pH value in the range of 8.0—10.0. The concentration variations of phosphate, calcium (Ca) and HS were measured in the precipitation process; the crystalline state and compositions of the precipitates were analysed by powder X-ray diffraction (XRD) and chemical methods, respectively. It showed that at solution pH 8.0, the precipitation rate and removal efficiency of phosphate were greatly reduced by HS, but at solution pH $\geqslant 9.0$ the effect of HS was very small. The Ca consumption for the precipitation of phosphate increased when HS was added; HS was also removed from solution with the precipitation of calcium phosphate. At solution pH 8.0 and HS concentrations $\leqslant 3.5$ mg/L, and at pH $\geqslant 9.0$ and HS concentrations $\leqslant 10$ mg/L, the final precipitates were proved to be hydroxyapatite (HAP) by XRD. The increases o solution pH value and initial Ca/P ratio helped reduce the influence of HS on the precipitation of phosphate.

Keywords: calcium phosphate; phosphorus recovery; precipitation; humic substances; initial Ca/P ratio; solution pH value

Introduction

Phosphorus (P) recovery from wastewater is becoming a great concern of both water industry and phosphate industry. The technological development of P recovery from wastewater requires scientists to have a better understanding of the precipitation of calcium phosphate. One of the main potential inhibitors of calcium phosphate precipitation from wastewater is the organic matter, so currently there is a particular need for research on calcium phosphate precipitation in organic rich systems that simulate wastewater environments (van der Houwen and Valsami-Jones, 2001). In the former studies aiming at understanding the precipitation mechanisms of calcium phosphate in bio-chemical systems, much attention was paid to the effects of bio-chemicals, such as amino acids (Spanos *et al.*, 2001), proteoglycans (Paschalakis *et al.*, 1993), glucose (Dalas and Koutsoukos, 1989), phytate and phosphonate (Koutsoukos *et al.*, 1981) etc., so the bio-chemical conditions such as the solution pH of 7.4 and the temperature of 37°C were used in the experiments. Although a few bio-chemicals such as phospholipids can promote the precipitation of calcium phosphate (Dalas *et al.*, 1990), more often the organic bio-chemicals have inhibitory effects on the precipitation reaction. For P recovery from wastewater, it is vital to understand the effects of the organic substances, which most often appear in wastewater, on the precipitation of calcium phosphate. The recent study of van der Houwen *et al.* (2001) investigated the effects of two organic ligands, citrate and acetate, on the precipitation of calcium phosphate.

It showed that citrate had a pronounced inhibition to the precipitation of calcium phosphate, while the acetate had negligible effect.

There are a lot of organic substances in wastewater; humic substances (HS) are an importan type among them. A recent study showed that aquatiHS appeared to be one of the major fractions amon; the dissolved organic matter (DOM) in effluents c wastewater treatment plants (Imai *et al.*, 2002 accounting for 3% —28% of the total DOM. For recovery from wastewater, it is necessary to g information about the effect of the HS concentratio on the precipitation of calcium phosphate under th solution conditions of P recovery. The present stud used Brown Water from the Black Forest th: contained HS to synthesize wastewater samples. Th Brown Water was characterised elsewhe: (Abbt-Braun *et al.*, 1991; Frimmel and Abbt-Brau 1999). The effect of the HS concentration up to 2 mg/L (as dissolved organic carbon, DOC) on tl precipitation of 20 mg/L phosphate (as P) as calciu phosphate was studied; this would improve o understanding of the calcium phosphate precipitatit for P recovery.

1 Materials and methods

1.1 Source of HS

There are a variety of HS sources, but in t present study, an HS-containing Brown Water samp was used as the HS source, whose parameters ; listed in Table 1. The Brown Water was filtrated using 0.45 μm membranes before utilization, and HS concentration was instrumentally measured a

Table 1 Parameters of Brown Water from the Black Forest, Kaltenbronn, Germany

Parameter	Value	Parameter	Value
pH	6.30	Absorbance (254 nm), cm^{-1}	2.576
Ca, mmol/L	0.20	DOC, mg/L	50
Alkalinity, mmol/L	0.36	Conductivity, μS/cm	54.6

counted as mg/L of DOC.

1.2 Batch experiments

The precipitation of calcium phosphate was initiated by the rapid mixing of $CaCl_2$ and KH_2PO_4 solutions. In the experiments 1000 ml of 476.9 mg/L $CaCl_2$ was added to 1000 ml of 175.4 mg/L KH_2PO_4 within 30 s, to get an initial P concentration of 20 mg/L and Ca to P molar ratio (Ca/P) of 3.33. At solution pH 9.0 and an HS concentration of 20 mg/L, varying the concentration of $CaCl_2$ solution, the Ca/P ratios of 1.67 and 5.00 were also used. In order to prepare 20, 10, 3.5 and 0 mg/L of HS additions, the KH_2PO_4 stock solutions contained 40, 20, 7.0 and 0 mg/L of HS before mixing. KNO_3 was added to the $CaCl_2$ solution prior to mixing to keep the ionic strength of the precipitation system around 0.02 mol/L, which was equivalent to wastewater. The precipitation reaction was undertaken at pH values of 8.0, 9.0 or 10.0. Prior to mixing, the pH value of each reagent solution was adjusted to the defined value by the addition of 0.45 mol/L NaOH, and the pH value of the mixture was monitored with a pH 191 pH-meter (WTW GmbH, Germany) and kept at the above defined constant value by NaOH supplement. The initial mixing was under strong stirring by a RZR 1 blade-paddle stirrer (Heidolph, Germany) for 3 min; afterwards, solutions were stirred at a constant reproducible rate. Aliquots of 15 ml for Ca, P and HS analyses were removed at frequent intervals after mixing, and filtrated with 0.45 μm cellulose nitrate filters (Sartorius AG, Germany). All the above reagent solutions were prepared from analytical grade reagents. The water used in the experiments was deionised water with a conductivity of 7 ×10^{-4} mS/cm. All the experiments were performed in a double-walled Plexiglas beaker, which was kept at a constant temperature of (20.0 ± 0.3)℃ with a WK 230 thermostatic controller (Lauda, Germany).

1.3 Chemical and instrumental analyses

The Ca concentration was analysed by complexo-metric method (Deutsches Institut fuer Normung e. V., 2002), and the P concentration was analysed by molybdenum heteropolyphosphate complex method (Deutsches Institut fuer Normung e. V., 1998a) with a Lambda 2 UV/Vis Spectrometer (Perkin Elmer, Germany) at the wavelength of 700 nm. The HS concentration (as DOC) was also analysed according to German standard methods (Deutsches Institut fuer Normung e. V., 1998b) with a Shimadzu TOC-5000 Total Carbon Analyser, equipped with an ASI-5000 Autosampler (Shimadzu Corporation, Japan).

At solution pH 8.0, the reaction time was 420 min and 540 min for the situations without and with HS additions, respectively; at solution pH 9.0 and 10.0, the reaction time was always 120 min. After the accomplishment of the precipitation experiments the reacted mixture was filtrated with S & S 5891 Filter Paper (Schleicher & Schuell, Germany). The precipitates were first dried at a room temperature of (20 ± 0.5)℃, and afterwards dried to constant weights in a drying box. The crystalline state of the precipitates was detected with X-ray diffraction (XRD). To start XRD measurements, the precipitate sample was filled into a glass capillary holder with a diameter of 0.5 mm, and then the measurements were undertaken on a Huber Guinier camera equipped with a Gemonochromater and a Huber 670 image plate (Huber Diffraktionstechnik GmbH, Germany). Diff-ractograms were recorded with Cu-radiation (Cu $K_{\alpha 1}$ = 0.15406 nm) over an angular range of 8—100° 2θ with a step width of 0.005° 2θ per second counting time. The compositions of the precipitates were measured by chemical analyses: about 0.1 g sample was dissolved by the hydrochloric acid of 2.0 mol/L, and then was prepared to a constant volume of 100 ml; the concentrations of Ca, P and HS were measured by using the above methods, and finally the compositions of the precipitates were calculated.

2 Results and discussion

2.1 Effect of HS on the precipitation of phosphate

At an initial Ca/P ratio of 3.33, with HS additions of 0, 3.5, 10 and 20 mg/L, and at pH of 8.0, 9.0 and 10.0, the residual phosphate concentrations in solutions are plotted with respect to the reaction time in Fig.1.

At solution pH 8.0 and without HS addition, after a first rapid precipitation within 30 min, the precipitation reaction advanced gradually, but an acceleration phenomenon appeared at 270 min, so the kinetic curve of phosphate precipitation had a sigmoid shape. This phenomenon has been reported in our former studies (Song et al., 2002a, b), which is attributed to the formation of a new calcium phosphate phase other than the initially formed one in the precipitation process with reference to the kinetic study of the precipitation of calcium phosphate (van Kemenade et al., 1987). With 3.5 mg/L HS addition the precipitation of phosphate was quite similar to, but faster than that without HS addition within 240 min and the acceleration was postponed to 345 min. With 10 and 20 mg/L HS additions, no acceleration phenomenon was observed within 540 min; after a
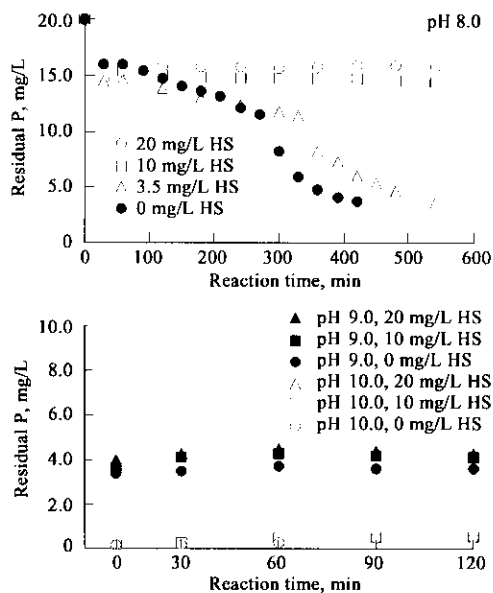
Fig.1 Effect of HS concentration on the precipitation of phosphate

rapid precipitation within 30 min, the phosphate concentration did not vary much any more; with 10 mg/L HS addition, the residual phosphate concentration was a little lower than that with 20 mg/L HS addition. In general, with the increase of HS addition in solution the precipitation rate and efficiency of calcium phosphate decreased; HS distinctly inhibited the precipitation of calcium phosphate at solution pH 8.0.

At solution pH values of 9.0 and 10.0, rapid precipitation of phosphate occurred within 10 min and the residual phosphate concentrations decreased to low levels; afterwards the phosphate concentrations only changed slightly. At solution pH 9.0 the precipitation efficiencies were all at about 80%; the precipitation efficiency slightly decreased with the increase of HS addition; with 10 and 20 mg/L HS additions, the precipitation efficiencies of phosphate decreased by 3% and 5%, respectively. The results show that the inhibitory effect of HS on the precipitation of phosphate is very small at solution pH 9.0. At solution pH 10.0, the precipitation efficiencies of phosphate without and with HS additions were nearly the same; all were about 96%. The inhibitory effect of HS on the precipitation of phosphate was so small that it almost could be negligible.

The effect of HS on the precipitation of phosphate is closely related to the solution pH value. This can be understood from two aspects: when the solution pH increases from 8.0 to above 9.0, the thermodynamic driving force for the precipitation of calcium phosphate increases significantly (Song *et al.*, 2002c), and then the phosphate removal rate and efficiency increase greatly, even with HS in the system. On the other hand the inhibitory effect of HS on the precipitation of phosphate is attributed to the

combination of HS with Ca and the blocking function of the HS species to the active growth sites of the initially nucleated precipitates of calcium phosphate, and these should not be closely related to the solution pH. Thererore, the inhibitory effects of HS on the precipitaiton of phosphate was obvious at solution pH 8.0 and not so obvious at solution pH $\geq$ 9.0.

2.2 Effect of HS on the Ca consumption

The residual Ca concentrations of the phosphate precipitation reactions are shown in Fig. 2. At solution pH 8.0, without and with an HS addition of 3.5 mg/L, the kinetic curves of the precipitation of Ca were sigmoid curves. Clearly when the precipitation reactions accelerated, more Ca was needed to precipitate phosphate from the solution. It is noticeable that from the residual Ca concentration the acceleration occurred at about 180 min, instead of 270 min when the precipitation of phosphate began to accelerate. The formation and transformation of calcium phosphates are complicated. There are at least four calcium phosphates, $CaHPO_4 \cdot 2H_2O$, $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, $Ca_3(PO_4)_2$ and $Ca_5(PO_4)_3OH$ that may form in a saturated solution, and once a calcium phosphate compound forms, it usually begins to transform into other forms soon (Eanes *et al.*, 1965). In the present study, the discrepancy of the variations of the Ca and phosphate concentrations just reflects the formation and transformation of the calcium compounds in solution although it would be rather difficult to recognize them.
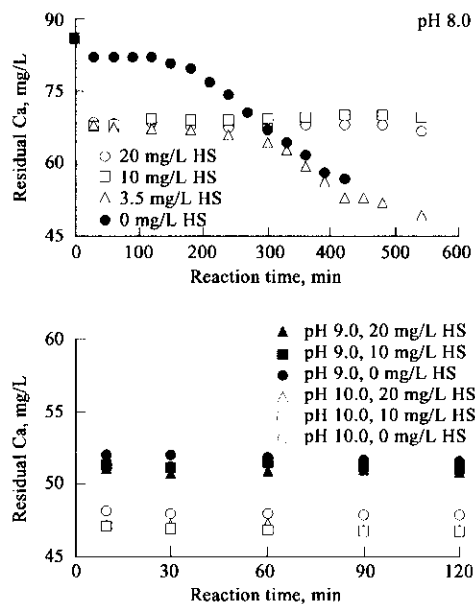

Fig. 2 Effect of HS concentration on the Ca consumption for phosphate precipitation

With 3.5 mg/L HS addition, the residual Ca concentration was much lower than that without HS addition, especially before the occurrence of the acceleration of the reaction. At solution pH 8.0 and

with HS additions of 10 and 20 mg/L, the Ca concentrations kept nearly constant after the rapid precipitation within 30 min, but with 10 mg/L HS addition the residual Ca concentration was higher than that with 20 mg/L HS addition. With the increase of HS addition to solution the Ca consumption for the precipitation of phosphate increases.

At solution pH 9.0 and 10.0, rapid precipitation of Ca occurred within 10 min, corresponding to the precipitation of phosphate; with the increase of solution pH value, the residual Ca concentration was lowered. At each solution pH value, the residual Ca concentrations were very close, but with the increase of HS addition the precipitated Ca increased slightly, especially at solution pH 9.0. The comparison of the precipitation of phosphate and Ca indicates that more Ca is needed to precipitate phosphate when HS are added to solution. This should be due to the combination of HS and Ca. This combination firstly could reduce the concentration of the free Ca ions available for the precipitation reaction of calcium phosphate, and secondly might block the active growth sites of the initially nucleated precipitates of calcium phosphate, thus inhibiting the further growth of the precipitate crystallites.

2.3 HS removal with the precipitation of calcium phosphate

During the above batch experiments it was observed that the HS in solution was removed with the precipitation of calcium phosphate. Fig.3 shows the residual HS in solution with respect to the reaction time.

Under all the three tested pH values, the curves of the residual HS concentrations have the same shape; after a rapid precipitation, the residual HS concentrations do not vary much any more. At solution pH 8.0 and HS additions of 3.5, 10 and 20
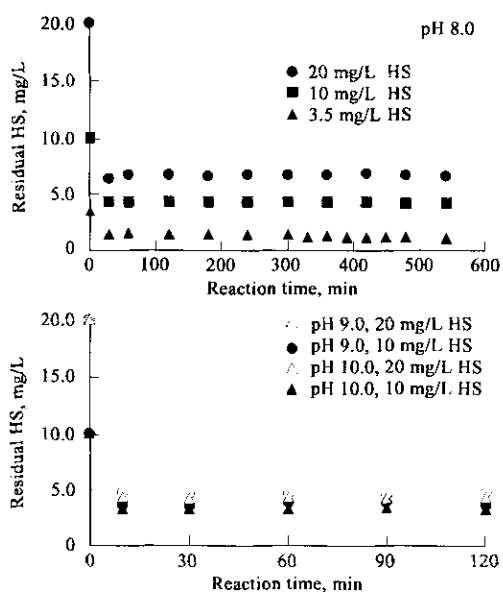

Fig.3 Removal of HS in the precipitation process of calcium phosphate

mg/L to the solutions, the removal efficiencies of HS at a reaction time of 60 min were 55%, 58% and 66%, respectively, and they did not vary much with the prolongation of the reaction time. At solution pH 9.0 and HS additions of 10 and 20 mg/L in solutions, the removed HS at a reaction time of 120 min were 61% and 76%, respectively; while at solution pH 10.0 the corresponding values were 67% and 78% , respectively. With the increase of solution pH value, the removed HS increased.

In order to understand the mechanism of the HS removal from the present precipitation system, comparison experiments were once undertaken: in batch experiments phosphate was not added, but all the other solution parameters were kept as the same as the phosphate precipitation experiments. It showed that there was no HS removal from solution. This result ruled out the possibility of the coagulating effect of Ca on HS removal. The comparison experiments showed that the formation of the calcium phosphate precipitate was responsible for the HS removal from solution. The newly produced calcium phosphate precipitate had large specific surface area, thus having good adsorption ability. The dissolved HS had negative charge at the experimental conditions. By the combination with Ca ions, the negative charge of HS could be reduced and then the HS be readily adsorbed by the newly formed calcium phosphate precipitate. Therefore, the HS removal in the present system is attributed to adsorption mechanisms.

2.4 Approaches to reducing the influence of HS on the precipitation of calcium phosphate

As stated in former studies (Song et al., 2002a, b, c), the precipitation of calcium phosphate from solution is a base for Ca uptake process, so both higher pH value and higher initial Ca/P ratio favour the precipitation of calcium phosphate. In the present precipitation system with HS addition, these two approaches have been studied to increase the precipitation of phosphate in terms of rate and efficiency. Fig.4a shows the effect of the solution pH value on the precipitation of phosphate with 20 mg/L HS addition. At solution pH 8.0, 9.0 and 10.0, the precipitation efficiencies of phosphate at a reaction time of 120 min were 21% , 78% and 97% , respectively. Obviously a higher solution pH helps to precipitate a higher amount of phosphate from solution and this phenomenon is similar to that without HS addition; therefore, increasing solution pH value is an effective approach to reduce the influence of HS on the precipitation of calcium phosphate. However, a possible problem is that at higher solution pH more HS may be also removed from solution together with calcium phosphate, thus decreasing the relative P content of the precipitate. This will be discussed further together with the results of the
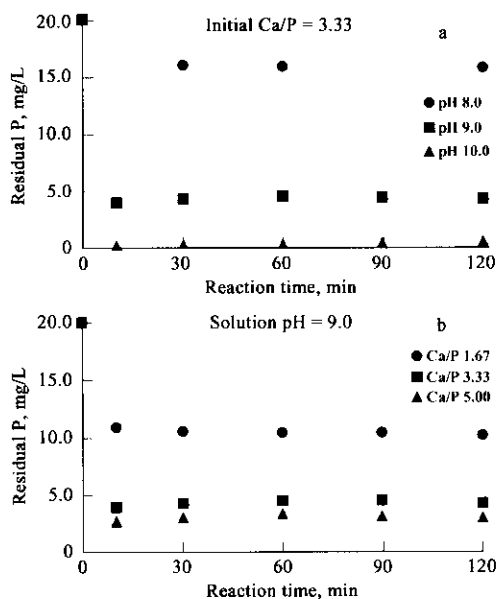
Fig.4 Effects of (a) solution pH and (b) initial Ca/P ratio on the precipitation of phosphate with 20 mg/L HS in solution

Fig.5 XRD patterns of the precipitates

composition analyses of the precipitates.

Fig.4b shows the effect of the initial Ca/P ratio on the precipitation of phosphate at solution pH 9.0 and HS addition of 20 mg/L. At initial Ca/P ratios of 1.67, 3.33 and 5.00 and a reaction time of 120 min, the precipitation efficiencies of phosphate were 49%, 78% and 84%, respectively. A higher initial Ca/P ratio also helps to increase the precipitation efficiency of phosphate. However, when the initial Ca/P ratio is increased the same problem as increasing pH value may also exist, i.e. with the increase of the initial Ca/P ratio more HS will be removed together with calcium phosphate, thus decreasing the relative P content of the precipitate.

The above studies show that both higher solution pH value and higher initial Ca/P ratio help increase the precipitation rate and the efficiency of phosphate removal, thus helping reduce the influence of HS. However, if both are too high, the removed HS from solution will also increase, thus decreasing the relative P content of the precipitate, so a comprehensive consideration is needed to design the practical conditions for the precipitation of phosphate as calcium phosphate from wastewater.

2.5 Crystalline states and compositions of precipitates

The XRD patterns of the precipitates obtained at solution pH 8.0—10.0 are shown in Fig. 5.

At solution pH 8.0 only the precipitates from solutions without HS and with an HS addition of 3.5 mg/L were examined by XRD, because with HS additions of 10 and 20 mg/L little precipitate could be gathered. It shows that the XRD patterns all correspond to hydroxyapatite (HAP); the addition of HS up to 3.5 mg/L does not affect the formation of
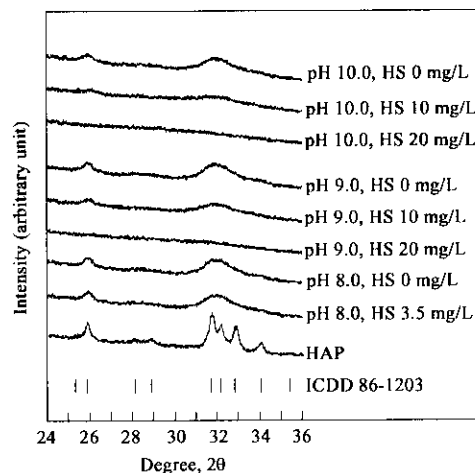
HAP.

At solution pH 9.0, the precipitates obtained from solutions without HS and an HS addition of 10 mg/L have XRD patterns corresponding to HAP; however, the precipitate obtained at the HS addition of 20 mg/L does not show the existence of HAP. This result indicates that the presence of HS in solution inhibited the formation of HAP, although a part of phosphate could be precipitated at such solution conditions. The inhibition of HS on the precipitation of calcium phosphate should be due to its blockage to the active sites of the newly formed crystallites, thus influencing their growth and transformation. At solution pH 10.0, the HS addition up to 10 mg/L does not affect the formation of HAP, whereas the HS addition of 20 mg/L inhibits the formation of HAP. It also shows that with 10 mg/L HS addition in solution and at pH 9.0— 10.0, the XRD peaks of the precipitates are weaker than that without HS addition; this also indicates the inhibition of HS on the formation and transformation of calcium phosphate.

In the practice of P recovery, the composition of the precipitate is an important parameter to evaluate the quality of the recovered product. The air-dried precipitates obtained from the batch experiments were chemically analysed and the compositions are listed in Table 2.

At solution pH 8.0—10.0 and without HS addition, the precipitates have Ca and P contents of $(35.0 \pm 0.2)\%$ and $(17.9 \pm 0.2)\%$, respectively; at a certain HS addition and different solution pH values, the precipitate compositions are also similar, indicating that the increase of solution pH does not substantially affect the compositions of the precipitates. At each solution pH value, with the increase of HS in solution, both the Ca and the P contents of the precipitate significantly decrease, while the HS content increases.

The changing tendencies of P and HS in the

Table 2 Compositions of the precipitates

No.	Solution conditions			Composition		
	pH	Initial Ca/P ratio	HS, mg/L	Ca, %	P, %	HS, %
1	8.0	3.33	-	35.2	18.1	-
2	8.0	3.33	3.5	33.7	16.2	2.0
3	9.0	3.33	-	35.2	18.1	-
4	9.0	3.33	10	31.4	14.8	4.1
5	9.0	3.33	20	26.8	12.3	6.3
6	10.0	3.33	-	34.8	17.7	-
7	10.0	3.33	10	29.2	14.1	3.8
8	10.0	3.33	20	28.0	12.3	6.1

precipitate were identical with the analyses of the solution compositions; the increase of the HS addition in solution inhibited the precipitation of P and caused more HS precipitation. However, the changing tendency of Ca in the precipitates were different from the analyses of the solution compositions; although the increase of the HS addition in solution caused more Ca consumption during the precipitation of calcium phosphate, less Ca were found in the precipitates. This discrepancy could be attributed to the complicate composition of the Brown Water, there should exist organic matter other than HS in Brown Water; these organic matter caused the increase of Ca consumption, but were not precipitated; for further studies, the compositions of the Brown Water must be closely examined so as to make it clear how the organic matter other than HS affect the precipitation of calcium phosphate.

3 Conclusions

In this paper, the effect of dissolved HS on the precipitation of calcium phosphate was studied. At solution pH 8.0 the precipitation rate of phosphate was greatly reduced by HS and the precipitation efficiency also decreased; at solution pH $\geqslant$9.0 the effect of HS on the precipitation of phosphate was very small. The Ca consumption in the precipitation process increased with HS addition. At solution pH 8.0 and HS concentrations $\leqslant$3.5 mg/L, and at solution pH $\leqslant$9.0 and HS concentrations $\leqslant$10 mg/L, the final precipitates were proved to be HAP. The increases of the solution pH and the initial Ca/P ratio can enhance the precipitation efficiency of phosphate, so they are two methods to reduce the influence of the HS on the precipitation of calcium phosphate.

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