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Phosphorus release from coprecipitants formed during orthophosphate removal with Fe(III) salt coagulation: Effects of pH, Eh, temperature and aging time

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ABSTRACT

Although Fe(III) salts coagulation has been widely used for phosphate removal, knowledge about the phosphorus release from the formed Fe-P coprecipitants is limited. This paper investigated the effects of Fe/P molar ratio, aging time, pH, Eh, and temperature on the release of phosphorus and iron in coprecipitants using batch tests. At neutral pH, three kinds of coprecipitants were prepared: unaged FP-1 (Fe/P = 3), FP-2 (Fe/P = 6) and aged FP-2 for 3 months (Fe/P = 6). Results showed that solution pH (4–10) affected the release of phosphorus obviously while its effect on Fe release was slight. Alkaline condition (pH 10) resulted in the greatest release rate of phosphorus due to the desorption of adsorbed phosphorus mainly via ligand exchange, which finally reached about 10% after 48 h. Under near-neutral pH and oxidizing conditions (Eh > 200 mV), P release rates were below 10% and proper aging was favorable for inhibiting P release. Under reducing conditions, the release rates of iron and phosphorus were higher than those under oxidizing conditions. As the Eh ranged from −261 mV to −194 mV, remarkable P release rates (> 15%) began to occur after 48 h. Higher Fe/P molar ratio benefited to control the P release. With the rising of water temperature from 10 °C to 40 °C, P release rates increased. Under reducing conditions and at different temperatures, good linear correlation between Fe and P release hinted the predominant role of Fe for P release. Surface property analyses of coprecipitants including XRD, zeta potentials and FTIR were further conducted.

1. Introduction

For a long time, eutrophication has become one of globally environmental problems and caused the widespread concern of researchers [1,2]. The algae overgrowth directly resulted from eutrophication may deteriorate natural water quality. In order to effectively control the eutrophication of water bodies (lake or reservoir), nutrient (especially phosphorus) removals are generally considered to be an important strategy. As has been demonstrated by many practices of eutrophication prevention, phosphorus removal is generally accepted to be more effective compared to nitrogen [3]. In the practices of lake or reservoir restoration, various methods of phosphorus control have been applied, which include reducing input of phosphorus into water bodies, enhancing phosphorus sedimentation and so on [4]. On the other hand, in order to curb the discharge of phosphorus from municipal secondary effluent into water bodies, it is also very necessary to develop robust water treatment technologies for phosphorus removal.

Till now, several methods of phosphorus removal have been investigated including biological processes, coagulation, adsorption, membrane technology and so on [3–5]. Among these methods, phosphorus removal using iron or aluminum salts as coagulants is a common practice to decrease the phosphorus concentrations from aqueous solutions in natural waters or engineered systems [6–8]. However, since aluminum was known as a potent neurotoxicant [9,10], iron salts gained more interests for phosphorus removal in water treatment processes compared to aluminum salts. As widely used coagulants, iron salts had the advantages of safety, low cost and high efficiency. Thus, extensive studies on iron salts coagulation for phosphorus removal were

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carried out by many researchers in recent years [7,11,12]. Furthermore, phosphorus usually occurs in surface water and wastewater in the form of inorganic phosphates, organophosphorous and polyphosphate. Among these three forms, it is accepted that phosphorus was generally present as phosphate, which approximated 50% of total soluble phosphorus in municipal wastewater and was the main species to remove [13,14]. In Fe(III) salt coagulation for phosphate removal, the Fe/P molar ratio usually needed to be higher than that by sole chemical precipitation (i.e. Fe/P molar ratio > 1). This was attributed to the complexity of chemical reactions such as precipitation between phosphate and ferric ion, complexation and adsorption on hydrous ferric oxides. Besides, to meet stringent effluent nutrient discharge requirements, the addition of excess Fe(III) (Fe/P molar ratio > 3, or even higher) was also needed to reach a low residual phosphate concentration [8,15].

In the case of chemical phosphate removal using Fe(III) salts, as for the lakes and reservoirs restoration, the water bodies served as a settling basin. The Fe–P coprecipitant covered the top layer of sediment and persisted in water bodies for a long time [3]. Even in municipal wastewater treatment plants, dissolved orthophosphate was converted into solid Fe–P coprecipitants and retained in sedimentation facilities, where the solids retention time usually reached up to several hours and then were separated from water with the discharge of sludge.

Recent studies showed that in water environments, Fe–P coprecipitants were often exposed to different environmental conditions such as pH, redox potential (Eh), temperature and etc. These environmental conditions might influence the mobilization and subsequent release of phosphorus in coprecipitants [16,17]. As a result, this might reinforce the eutrophication. Unfortunately, little was known about the behaviors of phosphorus release from coprecipitants affected by these environmental conditions.

To this end, this paper designed several Fe-P coprecipitants with different Fe/P molar ratio and aging time using common $FeCl_3$ coagulant at neutral pH. The main objectives are to explore the release behaviors of phosphorus and iron from Fe-P coprecipitants under various physicochemical conditions such as aging time, pH, Eh and temperature. And the surface properties of coprecipitants were also analyzed.

2. Materials and methods

2.1. Preparation of Fe–P coprecipitant

Unless otherwise specified, all chemicals used in this study were analytical grade, which were provided by Sinopharm Chemical Regent Co., Ltd. (Beijing Chemical Company). Deionized water was produced by a GWA-UN water purifier (Persee, Purkinje General Co., China). Fe-P coprecipitant was prepared with $FeCl_3$ and KH_2PO_4. The step was briefly described as follows. The $FeCl_3$ solution and KH_2PO_4 solution were mixed using two preseted Fe/P molar ratios (3:1, 6:1). Under gently magnetic stirring, NaOH solution was rapidly added into the above-mentioned mixture until pH became 3, and then was slowly added until pH was kept constant at 7. This pH value was selected, mainly because the pH of optimum coagulation for phosphate removal was near to neutral [7]. Then the solution was stabilized for 24 h. The final concentration of Fe was 0.2 mol/L in the suspension. A portion of the obtained suspension was immediately collected and freeze dried. The remaining suspension was aged for 3 months at room temperature, and then was collected and freeze dried. As for the two preseted Fe/P molar ratios (3:1 and 6:1) in preparation procedure, the obtained dry coprecipitant samples were separately written as FP-1 and FP-2. All samples were stored in desiccators for further batch tests.

2.2. Batch experiments

Batch experiments were carried out to investigate the release behaviors of Fe and P under various environmental conditions. The coprecipitant samples and deionized water were mixed to obtain a suspension, in which coprecipitant content was 2 g/L. Experiments were carried out on a rotary shaker or magnetic stirrer. During the whole process, solution pH was kept constant by adjustment at regular time intervals using HCl and NaOH solutions. Samples were collected at different time intervals and immediately filtrated using 0.45 μm filter membrane. The concentrations of iron and phosphorus in filtrates were measured. All batch tests were run in duplicate and average values were used for data processing.

The experiments on pH effect were conducted in a 1 L beaker at three different pH values (pH 4.0, 7.0 and 10.0). The concentration of coexisting ions (silicate) was 5 mmol/L. The solution was stirred by a magnetic stirrer for 48 h. At different time intervals (5 min to 48 h), 5 mL sample was withdrawn. After filtration using 0.45 um filter membrane, P and Fe concentrations in the filtrates were measured.

To investigate the release of Fe and P at different Eh ranges, sodium ascorbate ($C_6H_7NaO_6$) and sodium citrate ($Na_3C_6H_5O_7·2H_2O$) were used as reducing agents. The experiments were performed in 50 mL centrifuge tubes with 30 mL reducing agents of different concentrations and 0.05 g coprecipitant. To avoid the introduction of oxygen during sampling, some nitrogen was blown into the tubes and the tubes were immediately sealed after sampling. It was concluded in previous studies that the Eh value in sediments of natural lakes was in the range of about −300 to 300 mV [18]. Thus, in current study, solution Eh was controlled in two ranges (reducing conditions: −300 mV to −100 mV, oxidizing conditions: +100 mV to +300 mV). The tubes were placed on a rotary shaker and shaken for 10 days (240 h) in dark. At different time intervals, pH and redox potential were determined. Samples were immediately filtrated with 0.45 um filter membrane, and then Fe and P concentrations were measured.

In the experiments on the temperature influence, solution temperatures were adjusted to 10 °C, 25 °C and 40 °C, respectively. A certain amount of coprecipitant was put into deionized water to form suspensions (2 g/L), and then suspensions were shaken on a rotary shaker for mixing. Samples were taken at different time intervals (5 min to 48 h). Concentrations of Fe and P were measured after samples were filtrated with 0.45 um filter membranes.

2.3. Determination and characterization

The coprecipitant samples were firstly acid-digested using Microwave Digestion-Extractor (ETHOSE, Milestone, Italy) for the measurement of contents of total P and total Fe. The concentrations of phosphorus were measured by the ascorbic acid-molybdate blue method via a UV–vis spectrophotometer (Persee-T6, Purkinje General Co., China). Iron concentrations were measured with an Atomic Absorption Spectrometer (AAnalyst 800, Perkin-Elmer, USA). The pH and Eh values were measured by Multi-parameter tester (S220, METTLER TOLEDO, Switzerland). As for different suspensions, zeta potentials were measured by a zeta potential instrument (NANO ZS, Malvern, UK). The specific surface area of coprecipitant samples was measured using a Nova 6000 analyzer (Quantachrome, USA). FTIR and XRD analyses were measured using Fourier Transform Infrared Spectrometry (TENSOR 27, BRUKER, Germany) and an X-ray powder diffractometer (B max-2500, Rigaku, Japan), respectively. The release rates of Fe and P were calculated via following Eqs. (1)–(2).

$$\text{Fe release rate}\%) = \frac{R_{Fe}}{T_{Fe}} \times 100\% \tag{1}$$