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Chemical behavior of different species of phosphorus in coagulation

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HIGHLIGHTS

- Phosphorus removal in wastewater was tested through coagulation process.
- Chemical reactions between coagulants and phosphate species were observed.
- The size and reactivity of various phosphates play a role during the coagulation.
- Ortho-P is better removed than poly-P when the coagulant concentration is high.

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ABSTRACT

Phosphorus is one of the elements that have a significant impact on such environmental problems as eutrophication or algal bloom. Phosphorus compounds in water can be hydrolyzed to orthophosphate that is the only form of phosphorus that algae can assimilate. In this study, phosphorus removal in terms of orthophosphate and total phosphorus from wastewater was studied using alum or ferric ions as coagulants. It was observed that alum shows higher phosphorus removal efficiency than ferric ions in the same mole ratio concentrations. The proportion of orthophosphate among total phosphorus did not change significantly during coagulation process when the coagulant concentration is low. However, the proportion becomes gradually decreased as the coagulant concentration increases. Not only the electrolyte concentration difference in solution, but the characteristics of orthophosphate and polyphosphate such as reactivity and ionic size might also cause the differences in the removal rate. Orthophosphate that has greater reactivity than other phosphorus species would be involved in chemical reactions dominantly when large amounts of coagulants are applied. However, the effect of reactivity was diminished due to the large ionic size of polyphosphate and low concentration of electrolyte in low coagulant concentration during the coagulation process.

1. Introduction

Phosphorus is one of the essential elements for many living organisms. Dissolved phosphorus compounds in aqueous solution can be classified into three species types which are orthophosphate (PO_4^{3-}, ortho-P), polyphosphate (a chain link molecule of ortho-P such as $P_3O_{10}^{5-}$, poly-P), and organic phosphorus which consists of carbon compound in molecules (Tchobanoglous et al., 2003). Even though phosphorus is a beneficial element to an ecosystem, the excess amount of phosphorus in a natural water body can cause serious environmental problems (Smith et al., 1999; Rosenberg, 1995; Nixon, 1995; Karydis et al., 1983). One of the significant issues is eutrophication mainly caused by ortho-P. Ortho-P is the chemically or enzymatically hydrolyzed form of phosphorus and the only form of phosphorus that can be assimilated by algae, bacteria and plant (Correll, 1998). Many countries have developed the regulations on the total maximum daily load of phosphorus for watersheds or limited the phosphorus concentration in wastewater effluent (Wei et al., 2008). Therefore, the removal of phosphorus has become an important issue during last few decades (Babatunde et al., 2008; E. de-Bashan and Bashan, 2004; Yeoman et al., 1988).

Several processes have been studied to decrease the phosphorus concentration in the wastewater treatment plant effluent discharged into a natural water system. However, phosphorus control needs to be further improved to meet newly amended regulation that has been becoming stricter. For example, in Korea, the standard for discharged water from wastewater treatment plants has been

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lowered from 2 to 4 mg/L in 2010 to 0.2–4 mg/L in 2012.

Physical, biological and chemical processes have been studied to remove phosphorus from wastewater (Morse et al., 1998). One of the general methods used in wastewater treatment plant is a chemical process, especially a coagulation process. Metal salts as coagulants are added to the wastewater, causing the transformation of dissolved inorganic phosphate to the particulate form of phosphate. The suspended solid is subsequently separated by gravity (Morse et al., 1998). Previous studies on coagulation process are mostly related to the types and concentrations of the coagulants, and the conditions of wastewater to enhance the phosphorus removal efficiency. Aluminum sulfate (Omoike and Vanloon, 1999; Galaneau and Gehr, 1997; Hano et al., 1997) and iron (III) chloride (Clark et al., 1997; Caravelli et al., 2010; Mamais et al., 1994; Zhou et al., 2008) are widely used coagulants in conventional wastewater treatment plant for decades (Rybicki, 1997). The efficiency of phosphorus removal by each of these coagulants was reviewed previously (Daigger and Sigmund, 1991; Aguilar et al., 2002).

Even though many researches on coagulation have been conducted, there are limited studies on the chemical behaviors of ortho-P or poly-P (Razali et al., 2007; Lojklema, 1980; Gao et al., 2013; Georgantas and Grigoropoulou, 2007). In the previous study by Georgantas and Grigoropoulou, alum and aluminum hydroxide were used for ortho-P and metaphosphate (one form of poly-P) removal from aqueous solution. It was found that the different phosphate species have different affinities with the surface sites of aluminum hydroxide, and ortho-P was dominantly removed compared to metaphosphate due to an orientation effect and a charge per phosphorus atom.

The objective of this research is to characterize the chemical behaviors of phosphorus species during coagulation process in wastewater treatment system. A lab scale coagulation experiment was performed in different coagulant concentrations using wastewater from wastewater treatment plant in order to observe the removal phenomena of each phosphorus species. The study would provide a further understanding of how different species of phosphorus behave in different concentration of coagulants. Therefore, the results of the study might be helpful in enhancing conventional coagulation process efficiency in the wastewater treatment plant.

2. Materials and methods

2.1. Chemicals and materials

As coagulants, alum ($Al_2(SO_4)_3 \cdot 18H_2O$, Sigma–Aldrich) with purity of 98% or higher and ferric chloride(($FeCl_3$, Kanto Chemical Co. Inc.) with purity of 96% or higher were used. A multi-meter (Orion, STAR A329) and a turbidimeter (LaMotte, 2020) were used to analyzed the pH, conductivity, and turbidity of the wastewater samples. A heating block reactor (DRB200, HACH) was used for digestion of the samples to measure the total phosphorus (T-P) concentration, and a colorimeter (DR900, HACH) was used to measure the ortho-P and T-P concentrations.

2.2. Sample preparation

Wastewater samples had been obtained from two wastewater treatment plants. The collection points of the samples were indicated in Fig. 1. A lab scale coagulation test was conducted using the effluent samples of a secondary treatment process in a wastewater treatment plant by three depths of a storage tank that are named as upper (U), middle (M), and lower (L). The influent and effluent water samples of the advanced treatment process were additionally collected from the different wastewater treatment plant and named as input (I) and output (O) samples. The sample I and O were collected to investigate the change of the chemical species of phosphorus during the coagulation process in a real wastewater treatment plant. Therefore, the results of the lab scale coagulation experiments were compared with the analytical result of the samples from real wastewater treatment plant. After obtaining the wastewater samples, the samples were sealed and stored in a refrigerator at 4 °C until any experiment or chemical analysis.

Two sets of each sample were prepared. A set of wastewater samples was filtered using 0.45 μm filter for the comparison with unfiltered samples before coagulation process. Since the colorimeter determines the phosphorus concentration by shooting the light through the sample cell, the phosphorus concentration would not be detected appropriately if the light is shot to the large particles in the sample. Thus, the samples after the coagulation process in lab scale were required to be filtered using 0.45 μm filter before the measurement. The other set of wastewater samples without filtration process was prepared for analyzing ortho-P and T-P concentration before and after an advanced treatment in wastewater treatment plant.

For the coagulation experiment in a lab scale, the wastewater samples had been in a chemical reaction in shaking incubator that was kept at 25 °C for 20 min. Alum and ferric chloride were prepared in different concentrations as mole ratios of 1:1, 1:2 and 1:3 for P: Al or Fe. The coagulants were added and shaken at the mixing speed of 150 rpm for 1 min followed by 30 rpm for 10 min. They were then allowed for 30 min for settling down before the supernatant samples were obtained for the chemical analysis.

2.3. Analytical procedure

Before measuring the ortho-P and T-P concentration, all the samples were measured for pH, conductivity and turbidity using a multi-meter and a turbidimeter.

The ortho-P concentration in the wastewater was determined by a colorimeter (DR900, HACH) using ascorbic acid method (Method 8048, HACH) that is equivalent to the Standard method 4500-P-E. During the procedure, ortho-P reacts with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid, then, reduces the complex, which results in the molybdenum blue color. The difference in color results in the difference in the absorption of light which passes through the sample cell. The colorimeter detects the absorbed light and estimates the concentration. The measurement of wavelength was 610 nm in this study. T-P concentration was also measured by colorimeter using acid persulfate digestion method (Method 8190, HACH) which is equivalent to the Standard method 4500-P B&E. The heating procedure with sulfuric acid and persulfate is included in the test for the digestion of phosphorus in different species into ortho-P, and the identical colorimetric analytical procedure is applied.

3. Result

3.1. Basic characteristics

Basic characteristics of wastewater samples had been measured before coagulation experiments in a laboratory. Every measurement was at least in triplicates. The result indicates that the collected samples were in the neutral pH range from 6.5 to 7 and conductivities were around 490 μS/cm. Turbidity increases from 0.26 to 1.91 as the depth of the collection point increases. The sample L was only used in following experiments since no difference was found between samples in all parameters except turbidity.

After the lab scale coagulation experiments with different