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Effect of phosphate releasing in activated sludge on phosphorus removal from municipal wastewater

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ABSTRACT

Aluminum and ferric salts are commonly used in municipal wastewater treatment plants (WWTPs) for phosphorus (P) removal. In this study, on-site jar tests were conducted to determine the removal of different P species from the fresh samples in the presence and absence of activated sludge (AS) with different doses of alum, poly-aluminum chloride, and ferric chloride at different pH. The soluble P (SP) concentration in the samples was about 0.63 mg/L. When the mixed liquor containing AS was treated with 8 mg/L of Al, SP could be reduced to 0.13 mg/L, while it was reduced to 0.16 mg/L with only 1 mg/L of Al after sedimentation removal of AS from sample. Chemical analysis determined that AS contained 59.8 mg-P/g-TSS and 43.8 mg-Al/g-TSS and most of the P was associated with the aluminum hydroxide. We discovered that the phosphate in the AS could readily be released from it, which was mainly responsible for ineffective removal of P to low levels in mixed liquor even with very high alum dose. This study provides new insight into the behavior and fate of P in the wastewater treatment plants that use alum to enhance P removal in the final effluent.

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Introduction

With the rapid economic development and continued growth in human population, phosphorus (P) resources are being consumed with an unprecedented speed, due to both industrial uses and ever-increasing food demands. Eventually, excessive P is released into natural water bodies and causes a significant environmental problem known as eutrophication, which is characterized by uncontrolled growth of plants and algae in water ecosystems. Due to the increasingly serious P pollution, extensive efforts have been made to limit and recover P from wastewater with different techniques. The US EPA (US Environmental Protection Agency) had reported that municipal and industrial wastewater are the significant sources of P to surface waters throughout the country, therefore treating wastewater

and regulating P discharge limit in final effluent in municipal and industrial wastewater treatment plants (WWTPs) is one of the well-known solutions to prevent eutrophication.

P in a wastewater treatment system can be classified as soluble phosphorus (SP) and particulate phosphorus (PP). Therein to, SP can be divided into soluble PO_4^{3-} , soluble polyphosphate and soluble organic phosphate (SOP) (Li and Brett, 2015; Park et al., 2016). Usually, the discharge criteria are based on the total phosphorus (TP) concentration including both SP and PP. Municipal WWTPs currently are subject to the discharge limit with 1.0 mg/L of TP proposed by the US EPA. In the future, limits will be improved to a much more stringent level, 0.23 mg/L daily maximum TP.

Numerous technologies for P removal have been studied at laboratory, pilot- and full-scale in order to ameliorate current P

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problem and limit P to the satisfied discharge level. According to different removal mechanisms, phosphorus treatments can be briefly categorized as physicochemical and biological treatments (Zhao et al., 2012). Chemical coagulation with aluminum (Alum, AlCl_3), iron (FeCl_3 , FeCl_2 , $\text{Fe}_2(\text{SO}_4)_3$), calcium (CaCl_2 , CaO) and magnesium (MgCl_2 , $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is the most common physicochemical treatment for phosphorus removal from municipal wastewater (Georgantas and Grigoropoulou, 2007; Zelmanov and Semiat, 2015; Martí et al., 2010). The process of phosphorus removal using Al and Fe salts is complex, but well-studied in synthetic systems. When Al salts are employed, different soluble monomers (Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$), polymeric species ($\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$), and amorphous $\text{Al}(\text{OH})_3$ are formed rapidly through hydrolytic reactions under the effect of pH, temperature, and concentration (Maher et al., 2015; Huang et al., 2015). The overall process can be described as precipitation, coagulation–flocculation, and adsorption on the formed precipitants/metal hydroxide, while adsorption is recognized as the dominant mechanism.

Although massive studies have assessed phosphorus removal by different kinds of coagulants, only limited research has been done in fresh mixed liquor collected from aeration tank and limited work was aimed to study how the compositions of AS affect P removal process, particularly the residual metal precipitates adsorbing phosphate ions.

In this study, the phosphorus profile in a WWTP was monitored from October 2015 to May 2016. P removal in terms of TP, SP, soluble PO_4^{3-} , SOP and PP, as well as the pH effect on P removal in fresh samples in the presence and absence of AS, were investigated by using three kinds of inorganic metal coagulants: alum, poly-aluminum chloride (PAC) and FeCl_3 . P release from AS under various pH conditions and the influence of the presence of AS on P removal were also studied in order to explore the major reason causing the significant difference in P removal in the presence and absence of AS.

1. Materials and methods

1.1. Biological and chemical materials

AS was obtained from an aeration tank operated with a volume of 928 m^3 and retention time of 8 hr in the WWTP. The mixed liquor samples collected near the aeration tank effluent spot at different time were used to characterize the parameters of TSS, VSS, soluble TOC, Zeta potential and the chemical composition of AS. The characteristics of the mixed liquor sample are as follow: TSS 5000 mg/L, VSS 3800 mg/L, soluble TOC 10.0 mg/L, zeta potential -6.7 mV, Al 43.8 mg/g TSS, Fe 1.5 mg/g TSS, Ca 10.4 mg/g TSS, Mg 2.8 mg/g TSS, P 59.8 mg/g TSS. The relatively high Al content was caused by the return of activated sludge undergoing alum treatment in secondary clarifier.

The working solution for alum, PAC and FeCl_3 were prepared by commercial alum products provided by Chemtrade Logistics Inc., commercial PAC product purchased from USALCO LLC., and laboratory-grade FeCl_3 chemical purchased from Fisher Scientific. In this work, all the coagulant dosages were in the unit of mg/L as Al or Fe.

1.2. Experimental procedure

Uniform mixed liquor containing AS and supernatant samples after removal of sludge by settling were used in different tests. All experiments were conducted on site by a conventional jar test with a six paddle stirrer at room temperature. The operating conditions, after a pre-determined amount of coagulant was added into a 1-L beaker, were referred the standard method ASTM D2035 as follows: rapid mixing at the speed of 120 r/min for 1 min, slow mixing at the speed of 40 r/min for 4 min, then settling for 1 hr. The supernatant was collected from the treated samples for TP analysis and a portion of it was passed through a 0.45 μm membrane filter (A Chemtek Inc.) for analysis of soluble PO_4^{3-} and SP. pH values were governed in the same range of 6.0–6.6 to examine the effect of coagulant dose on P removal.

The study of P removal at different initial pH values was carried out by adding 4 mg/L of coagulant as Al or Fe into a series of samples at pH 5.0, 6.0, 7.0, 8.0, and 9.0. A blank control test without any coagulant addition was performed in order to check the impact of pH on AS itself. 0.1 mol/L hydrochloric (HCl) and sodium hydroxide (NaOH) were used to adjust pH. The pH of the samples was not further regulated during the reaction, therefore the final pH values of supernatants were recorded and plotted against residual P concentrations of different P species.

P released from AS in the original sample at various pH values and in deionized water at neutral pH was also evaluated. When the experiment was conducted in deionized water, in order to maintain the same activity of the sludge as in the original sample, AS was collected by settling so that there was still some wastewater content in the sludge. Therefore, P concentration at time zero did not start from 0 mg/L. The supernatant samples passed through 0.45 μm membrane filters were collected for analysis of soluble PO_4^{3-} and SP.

1.3. Analytical methods

TSS and VSS analyses of the original samples were performed following Standard Method 2540D (Rice et al., 2012). Zeta potential analysis for the original samples was carried out using a Zeta Nano Sizer Malvern Instrument.

AS dried at 103°C was digested according to EPA Method 3051 (Microwave Assisted Acid Digestion). The digested solution was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent Technologies) and total organic carbon analyzer (PHOENIX 8000).

The soluble PO_4^{3-} concentration was quantified by a spectrophotometer (HACH, DR6000) using the USEPA PhosVer 3 Method (Method 8048, HACH), which is accepted for reporting wastewater analysis and is equivalent to Standard Method 4500-P. TP and SP were both determined following USEPA PhosVer 3 with the acid persulfate digestion method (Method 8190, HACH). Heating the samples for half an hour at 150°C was included in the digestion procedure. The PP concentration was obtained from the subtraction between the TP and SP concentrations, while SOP was the difference between SP and soluble PO_4^{3-} . In this study, all the P concentrations in different species were in the unit of mg/L as P.

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