



Kinetics and capacities of phosphorus sorption to tertiary stage wastewater alum solids, and process implications for achieving low-level phosphorus effluents



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ABSTRACT

The role of adsorption and/or complexation in removal of reactive or unreactive effluent phosphorus by already formed chemical precipitates or complexes has been investigated. Potential operational efficiency gains resulting from age of chemically precipitated tertiary alum sludge and the recycle of sludge to the process stream was undertaken at the Iowa Hill Water Reclamation Facility which employs the DensaDeg[®] process (IDI, Richmond, VA) for tertiary chemical P removal to achieve a filtered final effluent total phosphorus concentration of <30 µg/L. The effect of sludge solids age was found to be insignificant over the solids retention time (SRT) of 2–8 days, indicating that the solids were unaffected by the aging effects of decreasing porosity and surface acidity. The bulk of solids inventory was retained in the clarifier blanket, providing no advantage in P removal from increased solids inventory at higher SRTs. When solids recycle was redirected from the traditional location of the flocculation reactor to a point just prior to chemical addition in the chemical mixing reactor, lower effluent soluble P concentrations at lower molar doses of aluminum were achieved.

At laboratory scale, the “spent” or “waste” chemical alum sludge from P removal showed high capacity and rapid kinetics for P sorption from real wastewater effluents. Saturation concentrations were in the range of 8–29 mg soluble reactive P/g solids. Higher saturation concentrations were found at higher temperatures. Alum sludge produced without a coagulant aid polymer had a much higher capacity for P sorption than polymer containing alum sludge. The adsorption reaction reached equilibrium in less than 10 min with 50% or greater removal within the first minute.

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1. Introduction

The control of phosphorus (P) in effluent discharges from waste water treatment facilities (WWTF) to prevent eutrophication of receiving waters is well known. Regulatory initiatives are further contributing to the addition of stringent effluent P limits to discharge permits. Accordingly, many WWTFs are facing increasingly stringent effluent P standards and as a result the effluent limit of 0.1 mg P/L total phosphorus (TP) or lower is being achieved. Since

the reliable performance limit of enhanced biological phosphorus removal (EBPR) is commonly accepted at about 0.1 mg P/L in the dissolved form, these facilities will need to utilize tertiary chemical phosphorus removal (CPR) to reliably achieve limits lower than 0.1 mg TP/L (ultra-low limits) (Pagilla and Urgun-Demirtas, 2007). Aluminum salts in the form of sulfate seems to be the preferred choice of precipitant for achieving very low effluent P levels (Araldos and Pagilla, 2010; Pagilla and Urgun-Demirtas, 2007).

The chemistry of Al added to water is complex, but has been well studied. The complexity comes from the formation of different monomeric and polymeric Al species formed as a function of water pH, temperature, and other ions present. It was shown that the mostly monomeric soluble Al species are formed in the pH range found in water (6–8), with the dominant species shifting from Al^{3+} to $Al(OH)_2^+$ and porous, amorphous $Al(OH)_3(s)$ to $Al(OH)_4^-$ as pH

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increases (van Benschoten and Edzwald, 1990). It is further known that the solubility profile as a function of pH shifts lower and minimum solubility occurs at a higher pH as temperature is decreased from 25 °C to 4 °C (van Benschoten and Edzwald, 1990). The mechanistic basis for P removal using chemical precipitant addition is generally considered to be more complex than simple precipitation. The overall mechanisms of chemical P removal from water by addition of Al and Fe salts include direct precipitation as metal phosphates, co-precipitation as metal hydroxy precipitates, surface complexation on polymeric metal hydroxyl precipitates, and adsorption of phosphate on solid surfaces (Galarneau and Gehr, 1997; Tanada et al., 2003; Babatunde and Zhao, 2010). The form of phosphate species (orthophosphate, condensed phosphate, or organic phosphate) present in the water also plays a role in the mechanism of P removal. The role of adsorption and/or surface complexation in removal of reactive or unreactive phosphorus to the already formed chemical precipitates or complexes has been reported. Omoike and van Loon (1999) showed that the most likely mechanism involves sorption of P species on $\text{Al}(\text{OH})_3(\text{s})$ formed by Al salt addition to water for P removal, and further precipitation/complexation of P onto the Al hydroxyl precipitate for additional P removal.

It is well proven that alum sludge from water treatment plants have high capacity for wastewater effluent P removal depending on the structure and/or age of the sludge solids (Huang and Chiswell, 2000; Ippolito et al., 2003; Georgantas et al., 2006; Babatunde and Zhao, 2010). The role of mixing, pH, contact time, precipitated solids concentration in the mixing tank, and feed secondary effluent characteristics could influence this process of tertiary P removal. The use of waste alum sludge formed in water treatment plants to remove P from wastewater and lake water has been reported (Galarneau and Gehr, 1997; X. Yang et al., 2006, 2008; and Babatunde and Zhao, 2010). The aluminum hydroxide flocs found in the sludge adsorb the phosphates in the water. The sorption capacity and rate are decreased with increasing age of the Al hydroxide flocs, due to loss of porosity and acidity of the surfaces (Georgantas and Grigoropoulou, 2007; Berkowitz et al., 2006; Babatunde and Zhao, 2010; Galarneau and Gehr, 1997; Y. Yang et al., 2006, 2008; Zhao and Yang, 2010). The precipitates formed initially are amorphous and porous with high surface area and surface acidity, providing high capacity for phosphorus removal.

Based on these past studies and their findings, it can be hypothesized that tertiary CPR in WWTPs involves surface complexation and adsorption of reactive and some unreactive P species on the formed aluminum hydroxide precipitates when the alum salts are dosed in excess of stoichiometric requirements for precipitation reactions alone. Hence, the role of precipitated solids in overall P removal and pH control needs to be understood well to optimize the solids recycle to the chemical mixing tank and the alum dose added.

The investigation of such variables and the process along with careful analytical measurements would explain the basis for precipitation/solids contact P removal from wastewater effluents. Such information could be used to enhance the process and optimize the operating conditions of tertiary P removal by chemical addition.

This paper presents lab scale and full scale investigations of some of the above listed parameters on tertiary P removal with specific focus on role of precipitated sludge solids in enhancing P removal and/or reducing the dose of coagulant to be added to achieve the desired P removal.

2. Materials and methods

The study was conducted on-site at two facilities owned and operated by the Upper Blue Sanitation District (UBSD),

Breckenridge, CO, USA; the Farmers Korner Waste Water Treatment Facility (FKWWTF) and the Iowa Hill Water Reclamation Facility (IHWRF).

2.1. Facility process descriptions

The lab scale experiments described in this section were conducted at the process control laboratory of the FKWWTF. The FKWWTF is a 4.99 MGD (18.9 MLD) advanced wastewater treatment plant consisting of conventional activated sludge followed by the DensaDeg process (Degremont Technologies, Richmond, VA) for CPR, final filtration through dual media sand anthracite filters, and disinfection/dechlorination by hypochlorite and bisulfite. The process includes a flash mix reactor (FMR) for chemical addition and mixing, draft tube reactor (DTR) for flocculation, and a solids contact clarifier equipped with lamellar settling tubes. The tank volumes of the three units in this process are 16,300 L, 79,100 L, and 140,600 L respectively. Precipitated solids are recycled from the clarifier to the DTR. Sodium hydroxide (NaOH, 25% w/w) and alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, 48.5% w/w) are dosed immediately upstream of the FMR. A low charge, high molecular weight cationic liquid polymer (Aqua-Ben, 720 E) is dosed to the DTR tank at an average of 1 ppm active. Excess chemical sludge is wasted from the clarifier and is further processed in sludge treatment.

Full scale work was conducted at the IHWRF, a 1.5 MGD (5.7 MLD) advanced wastewater treatment plant employing an anaerobic-aerobic activated sludge configuration for EBPR and separate stage nitrification in a biological aerated filter. Tertiary CPR at the plant is also accomplished with the DensaDeg[®] process. The volumes of the FMR, DTR, and the clarifier in the DensaDeg process are 12,200 L, 32,600 L, and 95,100 L, respectively. Sodium hydroxide (NaOH, 25% w/w) is dosed immediately upstream of the FMR for pH control, alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, 48.5% w/w) is introduced to the bottom of the FMR, and a low charge medium molecular weight cationic dry polymer (Aqua-Ben, 1655N) is dosed to the DTR, also at an average of 1 ppm active. Settled solids are recycled from the clarifier to the DTR under normal operations. The system was modified so that recycled solids could be returned to the DTR or the FMR during this study. Wastewater characteristics of the CPR unit process influent and effluent are given in Table 1 and the operation and CPR performance of both facilities has been previously documented (Maher et al., 2011; Bott and Parker, 2011).

2.2. Phosphorus analysis

Total phosphorus (TP) determinations were prepared by the persulfate digestion method, Standard Methods for the Examination of Water and Wastewater, 21st edition, 2005 4500-P B. 5. Reactive phosphorus (RP) was then determined by the ascorbic acid method, SM 4500-P E. on a Spectronic 20 Genesys Spectrophotometer for the full scale investigation and a Hach DR 2800 spectrophotometer for the lab study, both at a path length of 5 cm. During the full scale trials, soluble phosphorus fractions were determined by vacuum filtration through a 0.45 μm membrane filter (Pall GN-6 47 mm, P/N 66068). At lab scale, soluble phosphorus fractions were determined by series vacuum filtration through a 7 cm number 2 qualitative filter (Whatman 1002-070) and 0.45 μm membrane filter (Pall GN-6 47 mm, P/N 66068). Samples were analyzed for total phosphorus (TP), total reactive phosphorus (tRP), soluble total phosphorus (sTP), and soluble reactive phosphorus (sRP) (Gu et al., 2011). Soluble non-reactive phosphorus (sNRP) was calculated as the difference between sTP and sRP.

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