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REMOVAL OF PHOSPHORUS AND ORGANIC MATTER REMOVAL BY ALUM DURING WASTEWATER TREATMENT

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Abstract—Ferron reagent and FTIR spectroscopy were used for the identification and characterization of the aluminum species formed during dephosphorization of simulated wastewater with and without organic matter. Evidence from FTIR spectroscopy showed the formation of aluminum hydroxyphosphate, hydroxy-Al–tannate and aluminum complexes containing both phosphorus and tannic acid. The surface reactivity of the solid products is proportional to the rate of reaction with ferron. The measured reactivities indicate that aluminum solid species with different surface properties were formed depending on solution components and method of precipitation. Tannic acid was found to inhibit phosphorus removal and the extent of inhibition increased with increasing concentration. When prehydrolyzed aluminum is exposed to tannic acid, the organic matter forms a coating on the surface of the inorganic solid during the aging process. Coprecipitation of aluminum, phosphate and tannic acid, which is synonymous with the addition of alum before or in the aerator, produces some soluble complex and some hydroxy-Al–phosphate–tannate complex, in the form of solid with very small particle size. This system gives high residual aluminum. The results suggest that it is advantageous to add at least a portion of the alum at the exit of the aerator. This enhances phosphorus removal by coprecipitation under conditions where the concentration of organic matter is relatively low and enhances removal of organic matter by postprecipitation onto the recycled sludge in the aerator. © 1999 Elsevier Science Ltd. All rights reserved

Key words—coprecipitation, postprecipitation, wastewater, surface reactivity, tannic acid, residual phosphorus, residual tannic acid

INTRODUCTION

Phosphorus is present in low concentrations in wastewater but its release to a receiving water body is of environmental significance because it is an essential, often limiting nutrient for plants and microorganisms, and is therefore a cause of eutrophication. Phosphorus removal from wastewater is a complex process due to differences in its forms and in the composition of wastewater. The amount of phosphorus in typical raw domestic sewage is also highly variable, but the approximate concentrations of the various forms have been estimated (Jenkins *et al.*, 1971) as orthophosphate (5 mg P L⁻¹), tripolyphosphate (3 mg P L⁻¹), pyrophosphate (1 mg P L⁻¹), and organic phosphates (1 mg P L⁻¹). Apart from the organic phosphorus species, other organic constituents, both soluble and in solid form, span a wide range of chemical structures and molar masses. A considerable amount of general information is available, related to the classification of dissolved organic matter in wastewater (Painter

et al., 1960; Bunch *et al.*, 1961). In the latter paper it was shown that the soluble fraction of secondary effluents contained ether extractables (10%, of which 65% was organic acids), carbohydrates and polysaccharide (5%), protein (10%), tannins and lignins (5%) and anionic surfactants (for example, alkylbenzene sulfate) (10%). Studies conducted by Manka and Rehman (1971) indicated that 40–50% of the total organic content of secondary effluents from trickling filters of a municipal wastewater plant consisted of humic substances. Other organic components identified in the same effluent included: ether extractables (fatty acids, 8.3%), carbohydrates (11.5%), proteins (22.4%), tannins (1.7%) and anionic detergents (13.9%).

Alum, [Al₂(SO₄)₃·nH₂O] is a coagulant used extensively in wastewater treatment. When alum is added to water, it dissociates to give trivalent Al³⁺ ions, which hydrate to form the hexaquoaluminum ion Al(H₂O)₆³⁺. In water containing only carbonate or bicarbonate species as a source of alkalinity, the aquo aluminum ion, Al(H₂O)₆³⁺ undergoes a series of rapid hydrolytic reactions to form soluble monomeric and polymeric species as well as solid Al(OH)₃.

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It has been shown that the initial OH/Al molar ratio, temperature, rate of addition of base, presence of different anions and aging period of solutions all have an influence on the extent and rate of the hydrolytic processes (Van Benschoten and Edzwald, 1990). The solid amorphous hydrous aluminum oxide, often designated as $\text{Al}(\text{OH})_3$ is able to remove suspended solids by a variety of mechanisms and is also able to incorporate soluble phosphorus into its structure via coprecipitation or adsorption onto the surface. The soil and geological sciences literature have shown that hydrous aluminum oxides are capable of binding phosphates in soils (Bowden *et al.*, 1980; Hsu, 1989) and one of the mechanisms involves the specific sorption of phosphates by replacing the coordinated $-\text{OH}_2$ or $-\text{OH}$ groups of aluminum or iron(III) oxides (Rajan *et al.*, 1974). It has been suggested that the precipitation of phosphate using aluminum salts is governed by the integration of $\text{Al}-\text{OH}-\text{Al}$ and $\text{Al}-\text{PO}_4-\text{Al}$ types of linkages into an aluminum hydroxyphosphate rather than by precipitation of discrete phases such as $\text{Al}(\text{OH})_3$ or AlPO_4 (Hsu, 1975).

In the activated sludge wastewater treatment process, addition of chemical coagulants can occur at various points, including: immediately upstream of the primary clarifier, in the aeration chamber during aeration, immediately after the aeration chamber but prior to final clarification and at more than one point simultaneously (Bowker and Stensel, 1990). Depending on the particular plant, each of these locations has advantages and disadvantages. Because the complexing components of wastewater, including some organic compounds, compete with hydrogen carbonate and phosphate species for the aluminum ions, the possible effect of organic matter on phosphorus removal is one factor that should be considered in determining the point of addition of the coagulant.

We have estimated concentrations for dissolved organic carbon (DOC) in a typical activated sludge wastewater treatment plant for raw sewage feed, primary clarifier feed, primary clarifier effluent, recycled sludge, aerator mixed liquor, aerator effluent and plant effluent (Duffy *et al.*, 1994). Concentrations were found to range from 62 mg C L^{-1} in the raw sewage feed to 7.8 mg C L^{-1} in the plant effluent. The differences in organic matter concentration in the various parts of the plant may influence dephosphorization efficiency, the residual aluminum concentration in the effluent and the physical and chemical characteristics of the sludge. Moreover, BOD levels in the effluent are strictly regulated.

The purpose of the present study was to contribute to a better understanding of the interaction between aluminum, organic matter and phosphorus in the wastewater treatment process. More specifically, laboratory experiments using simulated wastewater were carried out in order to understand the

effect of soluble organic matter (and therefore point of addition of coagulant) on the removal of phosphorus from wastewater by alum. Tannic acid (TA) was used as a surrogate for soluble organic matter. Tannic acid is a water-soluble hydrophilic acid with a molar mass of $1701.23 \text{ g mol}^{-1}$. It contains saccharide and aromatic as well as $-\text{COO}-$ and phenolic $-\text{OH}$ groups, making it similar in some ways to soluble fulvic acid. It has been used as a model compound for soluble organic matter in studies on drinking water treatment (Julien *et al.*, 1994; Cathalifaud *et al.*, 1997) as well as in several studies in the field of soil science (Lawrence, 1980; Alberts, 1982; Violante and Huang, 1984; Goh *et al.*, 1986; Goh and Huang, 1986; Inskip and Silvertooth, 1988; Buondonno *et al.*, 1989; Dentel *et al.*, 1995). The concentration of TA used in this study, 17 ppm (9.1 mg C L^{-1}), was close to the concentration of soluble organic matter (9.8 mg C L^{-1}) found in the aerator of the Kingston Township Wastewater Treatment Plant.

To measure possible interactions and effects of the various wastewater components, controlled precipitation was carried out under specified conditions and direct measurements of residual phosphorus, aluminum and TA were made. A kinetic procedure (Duffy and vanLoon, 1994), in which aluminum present in solid-phase species formed a soluble aluminum–ferron complex with ferron reagent, was used to measure reactivity of the solids precipitated from the systems investigated. The reactivity of the precipitate with ferron reagent gives an indication of the surface structure (the surface speciation and its microtopography). In order to combine with ferron, $\text{Al}-\text{OH}$, $\text{Al}-\text{PO}_4$ or Al –organic matter bonds at the interface between the hydrolytic product and the adjacent solution must be broken. Aluminum that is present in weakly bonded labile forms therefore would be expected to react rapidly, whereas aluminum that is strongly bound and inert in the solid would react much more slowly. An amorphous precipitate with a large surface area would also be expected to react more rapidly than a more crystalline product due to the high surface concentration of aluminum ions — able to react with the ferron reagent in solution. Any aluminum species in a solid solution mixture that are present in soluble form react even more rapidly than that readily available on the surface of an amorphous solid.

In additional experiments, examination of the solid phase materials was done using Fourier transform infrared (FTIR) spectroscopy.

MATERIALS AND METHODS

All chemicals used were obtained from BDH and were reagent grade, except the alum, which was commercial grade, obtained from the Kingston, Ontario Water Purification Plant. Distilled deionized water (DDW) was used for all sample preparations.

This paper describes two types of experiments —

coprecipitation experiments, which are synonymous with the addition of alum before or at the aerator, and *postprecipitation experiments*, which are synonymous with addition of coagulant at the aerator exit outlet, prior to the recycling of sludge. The synthetic wastewater was made up of NaHCO_3 (100 mg L^{-1} as CaCO_3) and also contained other components — KH_2PO_4 (5.0 mg P L^{-1}) and tannic acid (TA, $\text{C}_76\text{H}_{52}\text{O}_{46}$, 17 mg L^{-1}) which were added as described below. Alum (4.3 mg Al L^{-1}) was used as a coagulant in all the experiments. The solution volume was 1 L and a constant mixing speed of 380 rpm was maintained using a mixer equipped with dual blades. For all the experiments, aging periods — the time taken between formation of the precipitate and initiating the ferron test or analysis of residuals — ranged from 5–120 min. The alkalinity used in this study is typical of that found in wastewater. The pH of all the aged solutions ranged from 6.6 to 7.8, which is within the range of 6.0–9.0 specified for secondary effluent from wastewater facilities (Holmes *et al.*, 1993).

In the coprecipitation studies, alum was added to the synthetic wastewater containing (i) orthophosphate ions (AIP[†]), (ii) tannic acid (AITA) and (iii) both orthophosphate and tannic acid (AIPTA). The postprecipitation experiments were carried out as follows: (i) adding phosphate to prehydrolyzed alum that had been allowed to age for 5 min in the absence of tannic acid (Al5P) or to a prehydrolyzed coprecipitate of aluminum and tannic acid that had aged for 5 min (AITA5P), (ii) introducing tannic acid to similarly aged prehydrolyzed alum (Al5TA) or coprecipitated aluminum and phosphate (AIP5TA), and finally (iii) introducing tannic acid and orthophosphate as a mixture to prehydrolyzed alum (Al5PTA systems). For comparison, a control experiment, involving synthetic wastewater to which only alum (4.3 mg Al L^{-1}) had been added, was also carried out. In all cases, the molar ratio of Al:P was approximately 1:1. Under actual plant treatment conditions, a several-fold excess of aluminum is usually added to ensure complete phosphorus removal. We opted for the near stoichiometric ratio in order to be able to observe differences in phosphorus removal efficiency between the various conditions.

Samples obtained under conditions described above gave only small amounts of solids and filtration of the 1-L mixture generally took several hours. Thus, for infrared analysis, an additional set of 5-min aged solids was obtained using ten times the amounts of all chemicals as specified above, but only 100-ml volumes of solution. Before recording the FTIR spectra, the solids obtained after filtration through Millipore[®] membrane filters ($0.45 \mu\text{m}$ pore size) were oven-dried at 105°C . Fourier transform infrared (FTIR) spectra were recorded from 4000 to 350 cm^{-1} (100 scans) on samples in KBr pellets using a Bomen MB-100 instrument.

Direct measurements of residual phosphorus and TA were made after filtration of samples through Millipore[®] membrane filters (0.22 and $0.45 \mu\text{m}$ pore size). The residual phosphorus concentrations of the solutions were determined by the phosphomolybdate blue method while residual TA concentrations were determined spectrophotometrically at 278 nm using an Ultrospec 3000 (Pharmacia

Biotech Ltd) spectrophotometer, after acidification of the solution to pH 2.0.

For the kinetic procedure, 0.250 mL of the aged suspension was added to 1.50 mL of ferron reagent and 1.00 mL of DDW in a 1-cm glass cuvet and the contents well mixed, after which the absorbance at 370 nm was monitored continuously (vs a blank) until all the aluminum had reacted to form the ferron–Al complex. To quantify the rate of reaction of aluminum in the mixtures with ferron, the time required to recover 50% of the solid phase aluminum, designated as t_{50} , was determined. Increasing t_{50} values are indicative of decreasing reactivity of aluminum in the solid phases. As an additional factor the percentage of aluminum that reacted within the first 30 s was measured and this (presumably composed of soluble species) is referred to as “fast reacting aluminum”. Details of the procedure including the preparation of ferron reagent are described elsewhere (Duffy and vanLoon, 1994).

RESULTS AND DISCUSSION

The ferron test and FTIR spectroscopy

Data showing the % fast reacting aluminum and the values of t_{50} obtained from the ferron experiments are shown in Table 1 Table 2. Similarly, the FTIR spectra of selected solid samples are presented in Fig. 1.

Coprecipitation studies

Precipitation of aluminum alone. As has been observed previously, (Duffy and vanLoon, 1994), the ferron reactivity of the solid hydrous aluminum oxide Table 1 decreases as it ages in contact with the solution over the time period between 5 and 90 min. The decrease in surface reactivity has been attributed to a reduction in the specific surface area of the precipitate due its gradual transition from amorphous to a more crystalline aluminum hydroxide (Duffy and vanLoon, 1994). While the t_{50} value increased, the amount of initial fast-reacting component also increased somewhat as the solid material aged, accounting for between 6.6% after 5 min aging and 29.7% after 90 min aging, of the total aluminum. Parallel to the increase in highly reactive aluminum, the concentration of residual aluminum increased from 4% (5 min aged) to 27% (120 min aged), confirming that one or more soluble species of aluminum was the reactive form. While aging, the pH of the mixture increased from 6.78 to 7.90. Aluminum hydroxide, an amphoteric compound, exhibits minimum solubility in the pH 6.0–6.5 range and above these pH values, the solubility increases, with the preponderant species on the alkaline side being $\text{Al}(\text{OH})_4^-$ (Sposito, 1989).

The FTIR spectrum of the “simple” aluminum hydrous oxide solid is shown in Fig. 1. The amorphous nature of the freshly precipitated solid phases is indicated by broad, relatively featureless infrared absorption bands (not shown) in both the -OH stretching and deformation regions (Nail *et al.*, 1975). An absorption band that can be attributed to Al–O vibrations of aluminum in octahedral co-

†The symbol AIP refers to a situation in which alum is added to a solution containing phosphate so that the aluminum (Al) and phosphorus (P) are coprecipitated. The symbol Al5P means that aluminum is precipitated alone by hydrolysis, the precipitate is allowed to age for 5 min and then phosphate is added to the mixture. In this case, phosphorus is removed from solution by postprecipitation processes. The other symbols can be interpreted in a similar way.

Table 1. % fast reacting aluminum species (FR) and t_{50} values obtained from ferron tests on coprecipitation systems after different aging periods

Systems	Aging time (min)							
	5		30		60		90	
	% FR	t_{50}	% FR	t_{50}	% FR	t_{50}	% FR	t_{50}
Al	6.6	1715	4.5	2918	13	3527	29.7	4254
AIP	7.0	2887	5.0	4050	6.5	4713	7.2	5134
AITA	22.2	247	22.1	488	22.6	510	27.2	633
AIPTA	7.9	2453	12.3	2700	13.3	2448	15.9	2717

Table 2. % fast reacting aluminum species (FR) and t_{50} values obtained from ferron test on postprecipitation systems after different aging periods

Systems	Aging time (min)							
	5		30		60		90	
	% FR	t_{50}	% FR	t_{50}	% FR	t_{50}	% FR	t_{50}
AISP	3.7	4108	3.7	5287	4.4	5740	1.5	6000
AIP5TA	5.5	9822	13.2	5550	11.3	5022	13.0	4599
A15TA	15.7	3824	21.1	767	26.6	768	28.6	615
AITA5P	15.2	954	14.8	1376	9.9	1521	18.2	1691
A15PTA	4.7	17100	3.1	11400	8.7	7500	11.8	6300

ordination is seen in the region $400\text{--}750\text{ cm}^{-1}$ (Tarte, 1967). It is interesting to note the presence of two absorption bands at 1505 and 1438 cm^{-1} . These are characteristic of the presence of carbonate as a unidentate complex with aluminum (Serna *et al.*, 1977).

AIP systems. The surface reactivity of this solid was significantly smaller than that of "pure" hydrous aluminum oxide Table 1. Like the pure material however, reactivity decreased with aging time.

The infrared spectrum (Fig. 1) of this solid had an intense surface H–O–H bending vibration maximum around 1634 cm^{-1} and a very strong broad absorption at 1086 cm^{-1} . The presence of a strong band between 1100 and 1040 cm^{-1} has been attributed to P–O stretching vibrations in inorganic orthophosphates and the position of this band depends on the species of phosphate and associated ions (Corbridge and Lowe, 1954). The spectrum of AIP was nearly identical to that of wavellite (Ferraro, 1982), $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ indicating that the solid phase is a form of aluminum hydroxyphosphate combining both Al–OH–Al and Al– PO_4 –Al linkages (Hsu, 1975; Duffy and vanLoon, 1994) rather than a mixed material containing aluminum hydroxide and aluminum phosphate individually.

The aluminum hydroxyphosphate was very unreactive to ferron, highly insoluble and residual concentrations of aluminum were generally less than 4% of the initial concentration of aluminum.

AITA systems. When TA was coprecipitated with hydrous aluminum oxide, the precipitate that formed exhibited very high reactivity as indicated by the small t_{50} value Table 1. This property can be

attributed to the presence in the solid of transitional pores and macropores, which provide easy access for penetration and degradation of the bonds between TA and aluminum. Previous studies (Ng Kee Kwong and Huang, 1981) have demonstrated that the specific surface of aged products of hydrolysis of aluminum was about five times larger when carried out in the presence of TA, compared to hydrolysis without organic matter present. The ferron test also showed that there was more fast-reacting aluminum (greater than 20% of the recovered aluminum) than in either of the precipitation conditions already discussed above. The concentrations of residual aluminum were similar (18–27%) to the % fast reacting aluminum, again indicating that it is a soluble form of the metal that reacts "instantaneously" with ferron.

Compared with the spectrum of pure TA, that for TA that had been precipitated by alum with or without orthophosphates showed absorption band shifts (1712 cm^{-1} to $1700 \pm 4\text{ cm}^{-1}$), reduction in some band intensities (peaks at 1712 and 1200 cm^{-1}) and the presence of new band at 1371 cm^{-1} . Reduction in the intensity of the carboxylic acid group (1713 cm^{-1}) has been attributed to its dissociation while the new bands at about 1600 and 1375 cm^{-1} were also reported to indicate formation of carboxylate ions to which metal ions were bonded via electrovalent linkages (Schnitzer, 1969; Tan *et al.*, 1971; Goh *et al.*, 1986). Tannic acid has been used as a surrogate for organic matter in previous studies (Violante and Huang, 1984; Inoue and Huang, 1986) on interactions with aluminum minerals in soils. The series of absorption

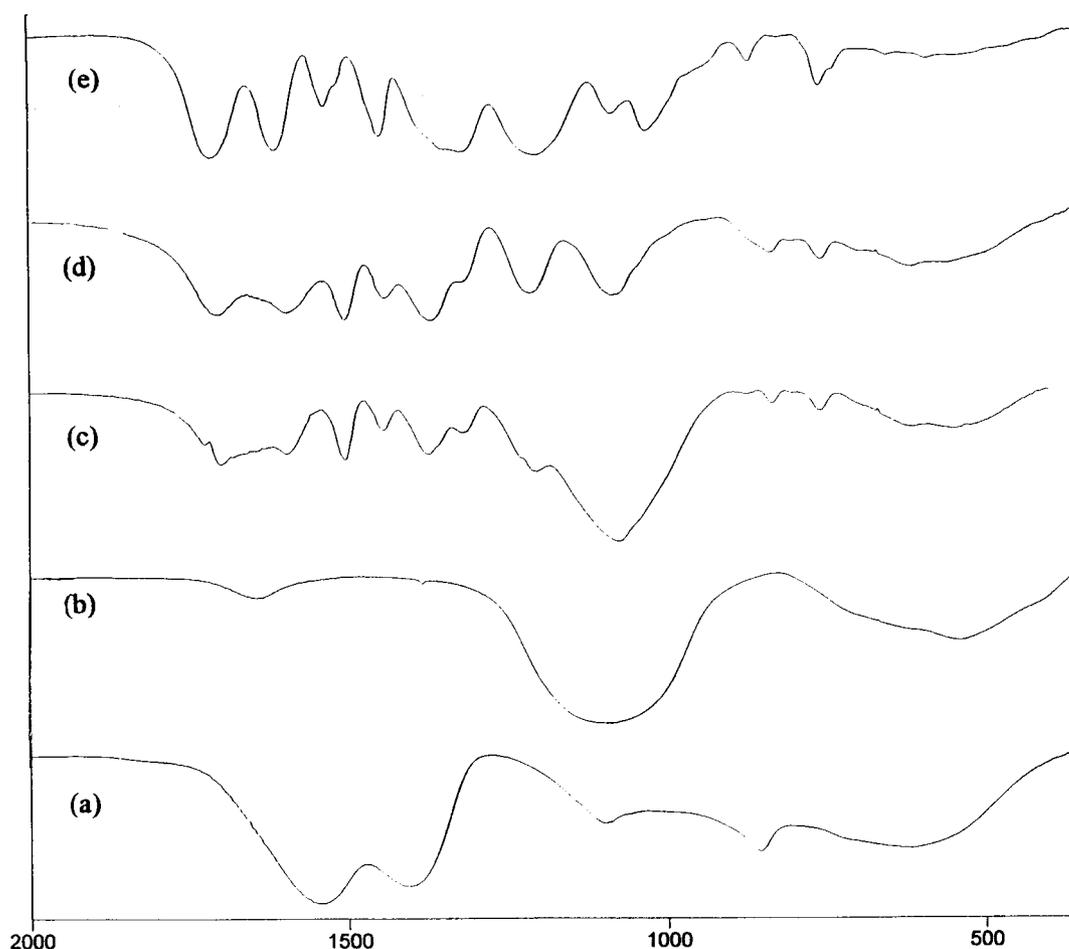


Fig. 1. Fourier transform infrared (FTIR) spectra of solid samples in the region 2000–400 cm^{-1} . (a) Al, (b) AIP, (c) AlPTA (d) AITA, (e) TA.

bands that they observed between 1700 and 1000 cm^{-1} in the spectra of TA with allophane and imogolite were also different from those of pure TA and were in positions nearly identical to those observed in the present AITA system (Fig. 1). Huang *et al.* attributed these bands, on samples obtained after very long reaction times, to the presence of hydroxy-Al-tannate complexes.

AlPTA systems. The values for t_{50} in the AlPTA system indicate a solid that is different from either AITA or AIP. Not surprisingly, the t_{50} for AlPTA was higher than that for the fast-reacting AITA but lower than that of AIP. Furthermore, unlike these two-component cases, the reactivity of the AlPTA solids did not change significantly over a 90-min aging period. The AlPTA solids were very fine and large fractions passed through 0.45- μm (84%) and even 0.22- μm (64%) membrane filters. The small, colloidal size of the particles when aluminum, TA and phosphorus are precipitated together is likely to result in poor settling with inefficient suspended solid removal during wastewater treatment. How-

ever, when the ratio of aluminum to tannic acid was increased, the precipitate that was formed settled readily, probably as a result of more complete neutralization of the negative charge associated with TA and phosphate. Therefore, additional coagulant can be used to remove these fine particles and the optimal conditions required for their removal are being further investigated.

When the concentration of TA in AlPTA system was increased from 2.5 to 100 ppm, the percent fast-reacting aluminum increased and the solids that were formed became more reactive. The presence of a new peak at 318 nm in the absorption spectra of the filtrate obtained from the 100 ppm TA system indicates that the soluble aluminum exists predominantly as aluminum-tannate complexes. This TA concentration (53.6 mg C L^{-1}) is lower than concentration of 62 mg C L^{-1} soluble organic matter measured in raw sewage feed at the treatment plant (Duffy *et al.*, 1994) in Kingston township and the plant value may be characteristic of other facilities as well.

The reactions involving hydroxyl ions, TA and orthophosphates with aluminum ions are parallel and competitive. At low TA concentrations, the TA and phosphates are incorporated into the network of the hydrous aluminum oxides floc. However, as the TA concentration increases, a higher concentration of soluble complexed aluminum species are formed and a higher concentration of residual aluminum remains unprecipitated. The interaction of organics to form complexes with soluble metal species prior to precipitation has been suggested as the first step in for the removal of organic matter in from wastewater (Semens and Field, 1980); and from drinking water (Gregor *et al.*, 1997). Precipitation occurs either when the binding capacity of the natural organic matter (NOM) has been satisfied or the solubility of the Al-NOM complex is exceeded (Gregor *et al.*, 1997).

The FTIR spectra of AIPTA (Fig. 1) has peaks that are characteristic of both aluminum tannate and aluminum phosphate linkages. The shift of the orthophosphate band from 1086 cm^{-1} (AIP system) to 1074 cm^{-1} (AIPTA system) indicates the presence of tannate as an associated ion in the complex. Similar shifts in an equivalent absorption in a metal-phosphate-fulvic acid complex compared to the corresponding absorption in the pure metal phosphate have been reported (Levesque and Schnitzer, 1967).

Postprecipitation studies

A15P system. This system is characterized by the smallest amount of fast-reacting aluminum and it has surface reactivity even lower than that found in AIP. The reactivity decreased still further while aging. This finding is consistent with phosphates first binding to the surface of freshly precipitated hydrous aluminum oxide (Duffy *et al.*, 1994) and subsequently being incorporated into the solid. The presence of phosphate concentrated at the surface of the precipitation product is likely to hinder the ability of ferron to degrade the solid phase product in order to react with aluminum.

The infrared spectrum of A15P is similar to that of AIP except for the more intense H-O-H bending vibration with a maximum around 1640 cm^{-1} which may indicate a higher concentration of waters of hydration. The carbonate bands found in the original hydrolytic aluminum precipitates were present but exhibited reduced intensities.

A15TA systems. The A15TA solid that had aged for 5 min reacted only very slowly with ferron as indicated by the large value of t_{50} . In one sense, this is surprising because the AITA solid was very reactive, for reasons discussed above. However, we suggest that the initial slow reactivity be due to a surface coating of TA onto the prehydrolyzed aluminum hydroxide floc; evidence for this is discussed under A15PTA system. The increased reac-

tivity as the solid aged is due to the surface TA interacting slowly with underlying inorganic material, eventually forming a product similar to the structurally-distorted material from the AITA coprecipitation case. The proportion of very fast reacting species likewise increased with time, approaching that of AITA.

The FTIR spectrum of A15TA confirms the presence of functional groups of tannate in the solid. In order to compare the degree of interaction between TA and the aluminum in A15TA and AITA, the height of the band near 1448 cm^{-1} was used to normalize absorption bands associated with formation of carboxylate ion and binding to aluminum in the region of $1800\text{--}1000\text{ cm}^{-1}$. The data analysis reveals that the new bands (at about 1600 and 1375 cm^{-1}), associated with the formation of carboxylate ions in the hydrolytic products, had relatively higher intensities in AITA systems compared to A15TA, indicating a higher degree of chemical binding in the former case. It has been shown that large organic molecules, whether charged or not, are strongly retained by physical forces on the surface of clay minerals (Greenland, 1965).

Based on ferron and FTIR data for A15TA, therefore we propose that the initial reaction of TA, a high molar mass compound, with prehydrolyzed aluminum involve the formation of an organic coating on the solid. It is interesting that slightly more TA was removed by postprecipitation than by coprecipitation. More will be said about this below.

AIP5TA, AITA5P and A15PTA systems. Three other cases of postprecipitation were also studied. Reaction of TA with precipitated aluminum hydroxyphosphate (AIP5TA) resulted in a precipitate, which exhibited very low reactivity, although it increased somewhat with aging as had the A15TA system Table 2. The solid AIP5TA products were much less reactive than the already unreactive A15TA precipitate irrespective of age.

Interestingly, the AIP5TA solids differed significantly in reactivity from those obtained in the AITA5P system. The latter material was much more reactive and reactivity also showed an opposite trend with aging. As well, the % fast-reacting aluminum species in the latter system were higher indicating that part of the aluminum ion remained in solution as Al-tannate complex. The marked differences in surface reactivity between AIP5TA and AITA5P would appear to be due to differences in the chemical modification of the aluminum on the surface of the solid phases.

For AIP5TA as for A15TA, we postulate that the postprecipitation addition of TA results in coating the initially-formed aluminum hydroxyphosphate solid followed by slow structural distortion as the TA reacts with the precipitate, substituting for the original Al-OH and Al-O-P bonds. The displace-

ment of phosphate from the solid by TA was shown by increased soluble residual orthophosphate as aging proceeded (Fig. 2a). On the contrary, the solid produced in the AITA5P system showed decreases in surface reactivity with aging and a simultaneous increase in both phosphorus (Fig. 2b) and TA removal (Fig. 3a) from the simulated wastewater. However, phosphorus removal in this system was the least efficient of all the cases. The low phosphate removal in the AITA5P compared to

AIP5TA shows that the surface of the initially formed hydroxy-aluminum-tannate solid is apparently resistant to replacement by phosphorus.

Solid AI5PTA was by far the least reactive of the materials investigated; however, like AI5TA and AIP5TA where TA was removed by postprecipitation, there was an increase in surface reactivity with aging (Tables 1 and 2). In addition, the % fast-reacting aluminum species also increase gradually with aging. The increase in soluble aluminum con-

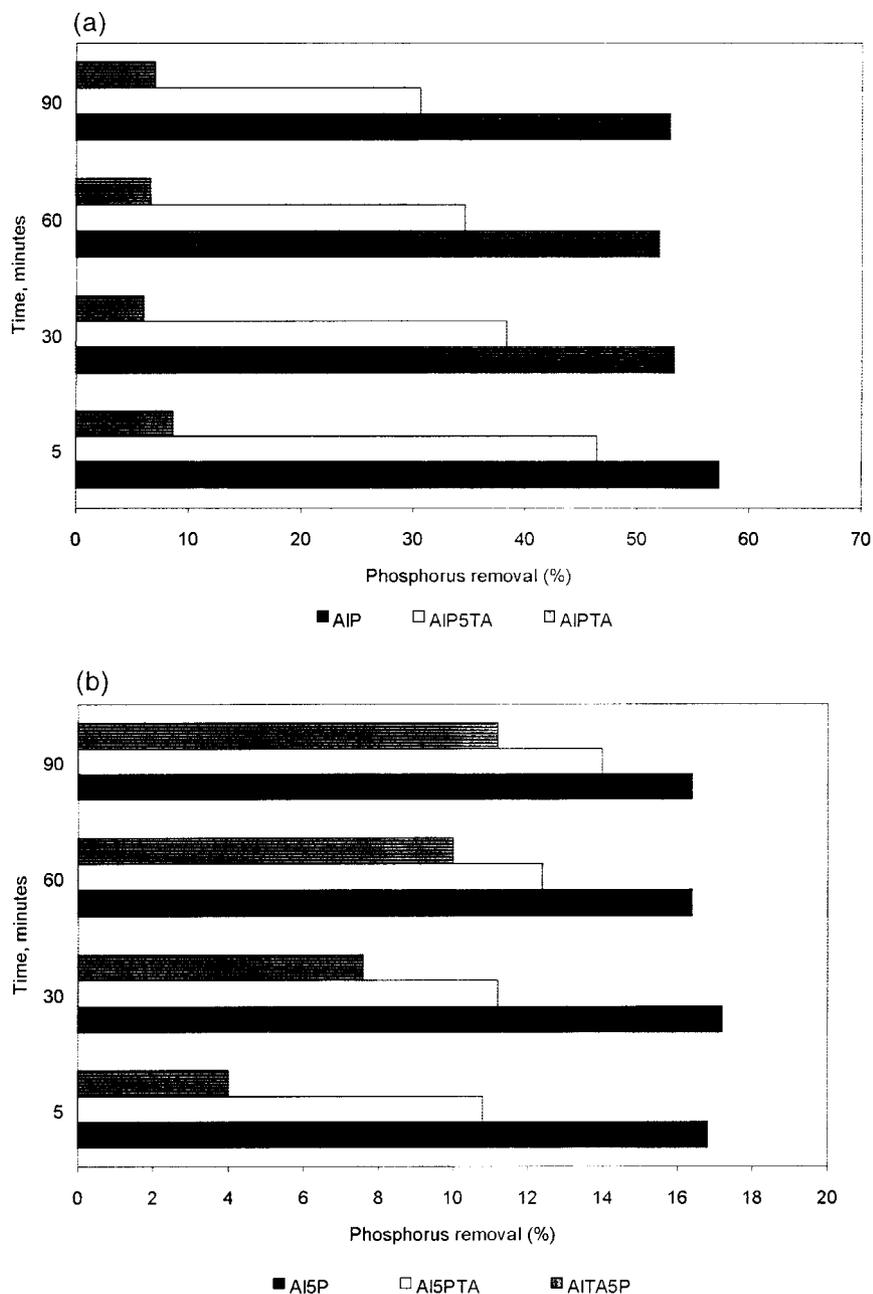


Fig. 2. (a) Phosphorus removal (%) in coprecipitation systems. In the case of AIP5TA, phosphorus is removed by coprecipitation. (b) Phosphorus removal (%) in postprecipitation systems.

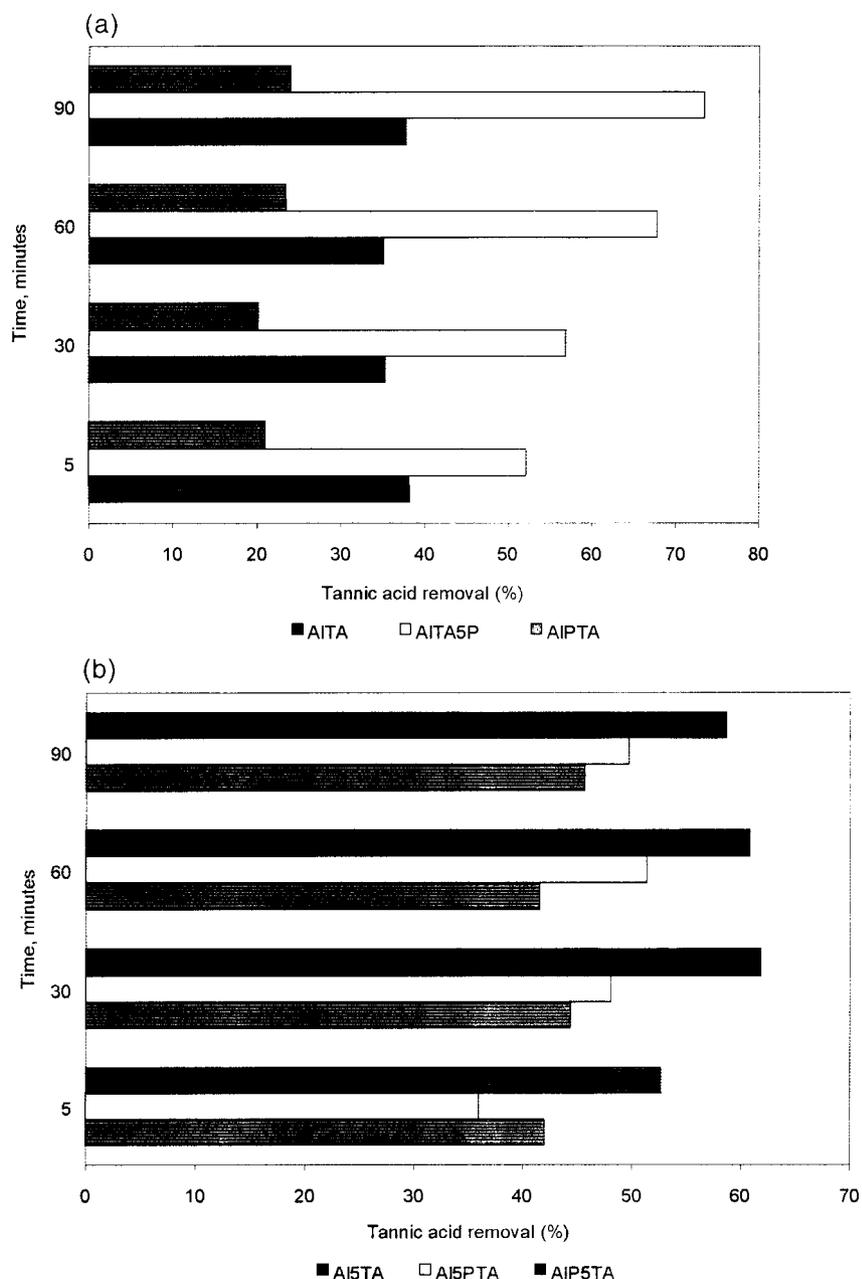


Fig. 3. (a) Tannic acid removal (%) in coprecipitation systems. In the case of AITA5P tannic acid is removed by coprecipitation. (b) Tannic acid removal (%) in postprecipitation systems

tinued with further aging and fast-reacting aluminum made up 28% of the total after 15 h. Twenty-four percent of the aluminum was in solution or was a fine enough solid to pass through a 0.22- μm membrane filter.

Again, we postulate that the low reactivity of the solid phases is due to the TA coating, an effect that is in some way enhanced even more by the simultaneous presence of phosphorus. The inhibitory effect of the coating in various TA postprecipitation systems was especially important over short aging

periods and in cases where the concentration of TA was large.

Direct evidence for organic coatings on the AI5PTA solid was obtained using atomic force microscopy (Omoike *et al.*, 1998). By this technique, it was possible to demonstrate that the surface of AI5PTA solid had remarkably different viscoelastic properties than the aluminum and AIP5TA solids. The viscoelastic properties of the latter two were similar to those of the mica substrate, a relatively hard mineral. On the contrary, the viscoelastic

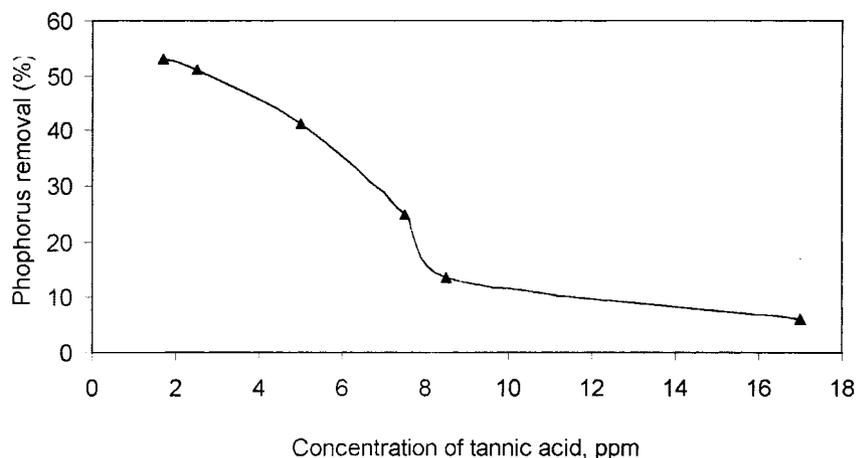


Fig. 4. Influence of increasing tannic acid concentration on phosphorus removal: AIP5TA system, aged for 30 min.

properties of the Al5P5TA surface were characteristic of a "soft", organic material. Images obtained from pure TA and Al5P5TA showed similar change in contrast both in phase and height data, as a function of set point and tip oscillation amplitude. Therefore it appears that the TA in Al5P5TA was in the form of a coating on the harder inorganic material. The ferron data indicate that a similar coating was formed in the two other cases where TA was removed by postprecipitation.

Residual phosphorus and tannic acid

Data on residual phosphorus and TA are presented in Figs 2 and 3. Phosphorus was removed to a greater extent when coprecipitated rather than postprecipitated onto prehydrolyzed solid. For example, more than twice as much phosphorus was removed as AIP (Fig. 2a) compared to Al5P (Fig. 2b) at the aging periods investigated. Where phosphorus and TA were present during coprecipitation (AIP5TA), the competition between them interfered with the removal of both components but TA appeared to have a larger inhibitory effect on phosphorus than did phosphorus on TA. The competition was evident in postprecipitation experiments as well. When TA was added to 5 min aged coprecipitates of aluminum and phosphate, the % phosphorus removal showed a significant decrease.

While TA removal was adversely affected when TA and phosphate were simultaneously coprecipitated, removal of the organic material was enhanced when precipitated onto an AIP rather than aluminum solid. Furthermore, when phosphate was added to a 5 min aged coprecipitate of aluminum and TA, the amount of TA that was removed from solution continued to increase steadily as the mixture aged.

Phosphorus and organic removal were much poorer in the AIP5TA system compared to the other

phosphorus and TA-containing systems and this, in large part, is due to the fine nature of the precipitate. It was this system that had the greatest loss of solid material during filtration.

In general, phosphorus was better removed by coprecipitation, while TA was usually more efficiently taken from solution by precipitation onto a prehydrolyzed solid. Of all the cases, the AIP5TA system gave best compromise results for phosphorus and organic removal. This finding has practical implication in wastewater treatment plants where coagulants are used to remove both phosphorus and organic matter. The addition of coagulant at the aerator exit where the concentration of organic matter is relatively low should be highly effective in removing (by coprecipitation) any inorganic phosphate that remains in the waste stream. The sludge produced at this point would consist in large part of aluminum hydroxyphosphate and hydrous aluminum oxide. This sludge, when recycled into the aerator, is capable of efficiently removing soluble organic matter by postprecipitation onto the solid precipitate. The simultaneous biological processes, in the aerator add to the efficiency of removal of both organic matter and phosphorus.

The influence of concentration of TA on phosphorus removal was examined for the AIP5TA system. As shown in Fig. 4, increase in the concentration of TA inhibited the removal of phosphorus from the simulated wastewater (53% removal where there was little or no TA to 6% removal in the presence of 17 ppm TA). In part, the poorer removal efficiency is due to the increase in solubility of aluminum when complexed with the organic ligand. This was indicated by spectrophotometric measurements (not shown) on the filtrate, which revealed a peak due to soluble complexed aluminum ion at 318 nm and reduced size of the uncomplexed TA peak at 278 nm. The peak at

318 nm increased as the concentration of TA in the system increased.

CONCLUSIONS

Phosphorus and dissolved organic matter removal during wastewater treatment is a complex process. However, the results of these experiments support the following conclusions.

1. The product of the coprecipitation of aluminum and orthophosphate ions is an aluminum hydroxyphosphate; a low reactivity solid and residual aluminum concentration after the completion of the aging process is very low.
2. Soluble and colloidal hydroxy-Al-tannate complexes are formed as a result of the coprecipitation of aluminum and TA. However, the efficiency of removal of TA is greater by postprecipitation onto prehydrolyzed aluminum rather than by coprecipitating it with the coagulant. The TA forms a coating on the surface of the inorganic solid.
3. Coprecipitation of aluminum, TA and orthophosphate produces a soluble hydroxy-Al-tannate complex and a solid, which has very small particle size. Separation of the suspended particles in this system is difficult and residual aluminum was high. In the three component mixture, the presence of TA, especially at high concentration, inhibited phosphorus removal. This system is synonymous with the addition of alum before or in the aerator. It should be emphasized that experiments in this study were carried out under conditions where the molar ratio of aluminum to phosphorus was approximately 1:1. In the more usual situation in wastewater treatment plants, an excess of aluminum is added to the water. This enhances the efficiency of charge neutralization of the negative colloids and it is likely that flocculation and settling of the precipitate would be more complete.
4. Recycled sludge contributes to phosphorus and dissolved organic matter removal in the activated sludge process. In water treatment practice, therefore, there is some justification for addition of a portion of the alum at the exit outlet of the aerator to enhance phosphorus removal both through coprecipitation under conditions where the concentration of organic matter is relatively low and also by postprecipitation onto the recycled sludge in the aerator.

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