

Effect of Tannins on Phosphate Removal Using Alum

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Received 27.05.2002

Abstract

Phosphate removal from wastewater can be achieved either through chemical removal, advanced biological treatment or a combination of both. Chemical phosphate removal involves the addition of aluminum, iron and calcium salts to achieve phosphate precipitation. The effectiveness of tannin obtained from valonia as a coagulant aid was investigated using various doses, together with $\text{Al}_2(\text{SO}_4)_3$ in a jar test. Jar tests were conducted in a synthetic water containing varying concentrations (1-20 mg/L) of phosphate. $\text{Al}_2(\text{SO}_4)_3$ was effective in the removal of phosphate from synthetic water. Both ($\text{Al}_2(\text{SO}_4)_3$ + tannin) and ($\text{Al}_2(\text{SO}_4)_3$ + AN913, synthetic anionic polyelectrolyte) were more effective than $\text{Al}_2(\text{SO}_4)_3$ alone. Tannin and AN913 as coagulant aids gave similar phosphate removals in cases of high phosphate concentrations (10-20 mg/L). However, tannin was more effective than AN913 in cases of low phosphate concentrations (1-5 mg/L).

Key words: Tannins, Polyelectrolyte, Coagulant aid, Phosphate removal, Chemical precipitation.

Introduction

Phosphorus is found in wastewater in three principal forms: orthophosphate ion, polyphosphates or condensed phosphates and organic phosphorus compounds. Prior to the development of synthetic detergents, phosphorus concentrations in wastewater typically varied from 2 to 4 mg/L. Most of the phosphorus was contributed by human wastes as a result of the metabolic breakdown of proteins. With the advent of synthetic detergents, which use large amounts of polyphosphate builders, phosphorus concentrations have risen to average values of the order 8 mg/L. Large variations on an hourly basis in the influent concentrations of phosphorus are often due to the wash-day phenomenon, when condensed phosphate concentrations can increase to three or four times the mean influent value (Yeoman *et al.*, 1988; Omoike and vanLoon, 1999).

Phosphate discharged into surface waters stimulates the growth of aquatic micro- and macroorganisms in nuisance quantities, which in excess can cause

eutrophication in stagnant water bodies. Therefore, waters containing phosphates must meet US discharge limits for phosphates of 0.5-1.0 mg/L P. In order to meet effluent quality standards, further treatment of secondary effluent is required (Yeoman *et al.*, 1988; Uğurlu and Salman, 1998).

The removal of phosphate from wastewaters has been conducted by chemical or advanced biological treatment. Various physical methods have been suggested including reverse osmosis, electrodialysis, contact filtration and adsorption (Yeoman *et al.*, 1988; Onar *et al.*, 1996; Clark *et al.*, 1997). Chemical treatment is widely used for the removal of phosphate. Lime, iron salts and aluminum sulfate (alum) are the common precipitants used for phosphate removal (Fytianos *et al.*, 1996, 1998; Clark *et al.*, 1997; Boisvert *et al.*, 1997). Although aluminum is the most expensive of these chemical coagulants, it is a very effective precipitant (Fytianos *et al.*, 1996; Clark *et al.*, 1997; Boisvert *et al.*, 1997; Zhang *et al.*, 2001).

Vegetable tannins may be found in almost any

part of a plant: bark, wood, leaves, fruit and root (Haslam, 1989). They are divided into two major groups-proanthocyanidins and polyesters based on gallic and/or hexahydroxydiphenic acid and their derivatives. The former category corresponds with condensed tannins and the latter with hydrolyzable tannins (Haslam, 1966; Zucker, 1983; Scalbert *et al.*, 1989; Lewis and Yamamoto, 1989; Özacar, 1997). They are water-soluble phenolic compounds having molecular weights between 500 and 3000, and, besides giving the usual phenolic reactions, they have special properties such as the ability to precipitate alkaloids, gelatin and other proteins (Zucker, 1983; Haslam, 1989).

Özacar and Şengil (2000, 2002) studied the use of tannin obtained from valonia as a coagulant and coagulant aid, and found that it could successfully remove suspended solids in water and the sludge could be filtered more easily when tannin was used as a coagulant aid compared to aluminum sulfate.

The purpose of this study is to investigate the effect of tannin on phosphorus removal from industrial wastewater that does not include organic matter during alum coagulation. Alum and synthetic anionic polyelectrolyte (AN913) were utilized as a coagulant and coagulant aid, respectively, and the results obtained with alum and AN913 are compared with those from tannin. The experiments were carried out at many different alum, phosphate and polymer concentrations. In additional experiments, the solid phase materials formed in the coagulation process were examined by Fourier transform infrared (FTIR) spectroscopy.

Materials and Methods

Material

The tannin used in this study was obtained from Sümer Holding A.Ş., Turkey. Tannin was extracted with hot water from valonia in the factory. The tannin content of valonia extracted in these studies was determined to be 53.50% as a hydrolyzable tannin according to the vanillin test (Broadhurst and Jones, 1978), the Prussian blue test (Price and Butler, 1977) and the 1,10-Phenanthroline test (Lau *et al.*, 1989; Özacar and Şengil, 1997).

Preparation of synthetic water

Synthetic water samples having different amounts of phosphate were prepared by adding certain quantities of NaH_2PO_4 to tap water. The mineral composition of the water used to simulate the raw water is presented in Table 1. The pH of the synthetic water samples was adjusted with 0.1 M HCl and 0.1 M NaOH.

Preparation of alum and polyelectrolytes solutions

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Merck) was dissolved in distilled water to obtain a final concentration of 1 mg Al^{3+} /mL. A tannin solution was prepared using distilled water to achieve a concentration of 1 mg tannin/mL. Other tannin solutions with concentrations of 0.01 and 0.1 mg/mL were daily prepared by dilution. Since tannin is a natural anionic polyelect-

Table 1. The mineral composition of the tap water used to simulate the raw water (Özacar and Şengil, 2000).

Cations	Concentrations (mg/L)	Anions	Concentrations (mg/L)
Ca^{2+}	41.6	HCO_3^-	125.73
Mg^{2+}	6.72	Cl^-	8.66
Fe^{2+}	0.097	SO_4^{2-}	3.45
NH_4^+	0.012	NO_3^-	0.946
Pb^{2+}	0.072	NO_2^-	< 0.05
Cu^{2+}	0.155	F^-	< 0.1
Ni^{2+}	0.128	CN^-	0.004
Zn^{2+}	0.865	PO_4^{3-}	0.015
Cd^{2+}	< 0.02	Phenol	0.525
Al^{3+}	-		
Total hardness: 132 mg/L CaCO_3		Total alkalinity: 101 mg/L CaCO_3	
pH: 7.3 ; Colour: - ; Turbidity: -			

rolyte, a synthetic anionic polyelectrolyte was chosen to compare with these tannin experiments. For this purpose, preliminary experiments were conducted using AN905, AN912, AN913, AN934 and AN945. The results showed that AN913 (SNF Floerger, France) was the best anionic polyelectrolyte as a coagulant aid among the polymers. Solutions of the AN913 were prepared with distilled water to achieve a concentration of 1.0 mg AN913/mL and then a solution with a concentration of 0.1 mg AN913/mL was prepared by dilution.

Jar test studies

A six beaker jar test apparatus was used with each beaker containing 1000 mL of solution. Polyelectrolytes were used as coagulant aids in conjunction with alum coagulant. Seven 1000 mL synthetic water samples were used. One of them was kept as a control to which no coagulant was added. In the remaining six beakers, a constant dose of alum was added to the liquid. The samples were mixed for 1 min at 200 rpm. Then various doses of polyelectrolytes were added using a micropipette. The samples were mixed at 45 rpm for 30 min. In all these experiments, the velocity gradient (G) value for flash mixing was 566 s^{-1} and for coagulation 60 s^{-1} . The solutions were allowed to settle for 15 min. Phosphorus analysis was carried out according to Standard Methods (APHA, 1985).

FTIR spectroscopy studies

FTIR spectra were recorded on a Mattson FTIR spectrophotometer. The samples were prepared after removing the supernatant, and a portion of the residue was filtered through $0.45 \mu\text{m}$ Millipore membrane filters. The remaining portion was dried at 378 K for 4 h. Potassium bromide pellets were prepared by mixing 1 mg of these samples with 200 mg of KBr (spectrometry grade) at $10,000 \text{ kg/cm}^2$ pressure for 30 min under vacuum. The spectra were acquired at 4 cm^{-1} resolution in the range of frequencies 4000 to 400 cm^{-1} , and 64 scans were averaged to reduce noise.

Results and Discussion

Effects of pH and alum doses on the removal of phosphate by alum

The results of the jar test experiments at different initial pH values using $10 \text{ mg Al}^{3+}/\text{L}$ in the syn-

thetic waters with $10 \text{ mg PO}_4^{3-}/\text{L}$ are presented in Figure 1. The optimum initial pH value to remove phosphate with $\text{Al}_2(\text{SO}_4)_3$ was 7.5. This value was found to be higher than those in the literature. The final pH was measured in the solution having an initial pH of 7.5 and $10 \text{ mg PO}_4^{3-}/\text{L}$, and the results are shown in Figure 2.

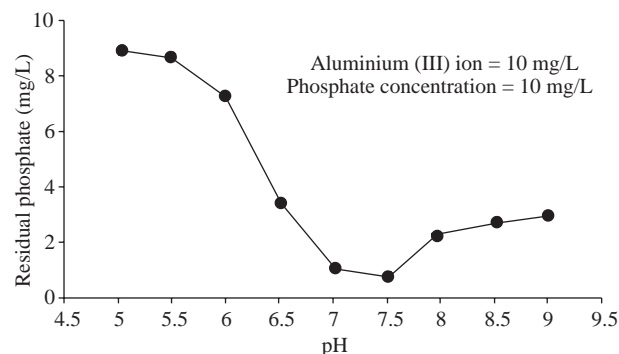


Figure 1. Effect of initial pH on the removal of phosphate with $\text{Al}_2(\text{SO}_4)_3$.

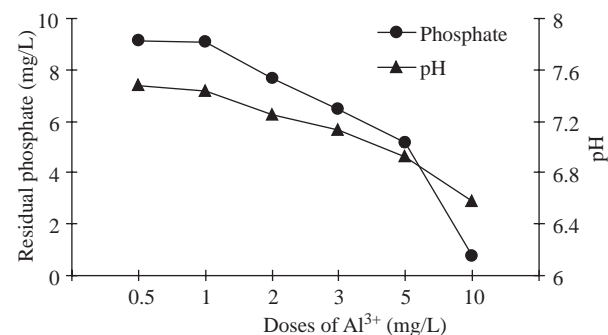


Figure 2. Effect of Al^{3+} dose on residual phosphate and final pH (initial pH 7.5).

The best phosphate removal was at a final pH of 6.5 (Figure 2). When $\text{Al}_2(\text{SO}_4)_3$ was added for removing phosphate, pH decreased from 7.5 to 6.5 and therefore phosphate removal occurred at pH 6.5. Thus, the result conformed with the optimum pH value of 5.5 to 6.5 for phosphate removal with $\text{Al}_2(\text{SO}_4)_3$ reported in the literature (US-EPA, 1976; Fytianos *et al.*, 1996; Boisvert *et al.*, 1997). The optimum pH for the removal of phosphate using aluminum coagulants probably lies in the range 5.5 to 6.5, although some removal occurs above pH 6.5 (US-EPA, 1976; Ferguson and King, 1977; Fytianos *et al.*, 1996). Ferguson and King (1977) presented a model by which the aluminum sulfate dosage to effect a given phosphate removal is obtained together

with acid or base requirements for pH adjustment. The model requires a knowledge of initial alkalinity and initial phosphate concentration. The addition of alum will lower the pH of wastewater because of the neutralization of alkalinity and a release of carbon dioxide. The extent of pH reduction will depend principally on the alkalinity of the wastewater. The higher the alkalinity, the smaller is the reduction in pH for a given alum dosage. Most wastewaters contain sufficient alkalinity so that even large alum dosages will not lower the pH below about 6.0 to 6.5.

The effect of $\text{Al}_2(\text{SO}_4)_3$ doses on phosphate removal by chemical precipitation from synthetic waters having an initial pH of 7.5 with 1, 3, 5, 10, 15 and 20 mg $\text{PO}_4^{3-}/\text{L}$ were studied and the results are given in Table 2.

The materials found practical for phosphorus precipitation include the ionic forms of aluminum, iron and calcium (US-EPA, 1976). There exists a stoichiometric relationship between the mass of aluminum added and the mass of phosphorus precip-

itated. In weight terms, the Al:P ratio has been reported to vary between 1.2, 1.5 and 2.0 for phosphorus reductions of 75, 85 and 95%, respectively (US-EPA, 1976; Baillod *et al.*, 1977; Brandes, 1977). Considering these ratios, Al^{3+} quantities theoretically required to precipitate 1-20 mg $\text{PO}_4^{3-}/\text{L}$ were calculated and they are given in Table 3. As can be seen from Tables 2 and 3, theoretically required Al^{3+} doses were used in our studies except at 20 mg $\text{PO}_4^{3-}/\text{L}$ for 95% removal. Assuming that each reported value corresponds to an optimum pH for phosphorus removal one can suggest that the differences in reported Al:P ratios are due to different wastewater constituents and/or different methods of solid liquid separation that may require different conditions of coagulant addition. In other words, with such applications it is perhaps not sufficient to form a (stoichiometric) aluminum-phosphorus precipitate. A settleable or filterable floc incorporating the precipitate is also required.

Table 2. Effect of Al^{3+} doses on phosphate removal from synthetic waters by chemical precipitation.

Initial phosphate (mg/L)	Residual phosphate (mg/L)					
	Al^{3+} doses (mg/L)					
	0.50	1.00	2.00	3.00	5.00	10.00
1.0	0.31	0.19	0.08	0.05	0.05	0.03
3.0	2.95	2.44	1.59	1.39	0.73	0.36
5.0	4.62	3.98	2.76	1.82	1.18	0.67
10.0	9.13	9.05	7.69	6.48	5.18	0.74
15.0	14.05	13.33	12.12	10.60	8.78	0.78
20.0	18.14	17.23	15.41	14.20	10.30	1.01

Table 3. Theoretical Al^{3+} quantities necessary to precipitate 1-20 mg/L PO_4^{3-} for the achievement of 75, 85 and 95% removal.

P reduction required	Al:P weight ratio	Initial phosphate quantity (mg/L)	1.00	3.00	5.00	10.00	15.00	20.00
		Initial P quantity (mg/L)	0.33	0.98	1.63	3.26	4.90	6.53
75%	1.2:1.0	Required Al^{3+} quantity (mg/L)	0.39	1.18	1.96	3.92	5.87	7.83
85%	1.5:1.0	Required Al^{3+} quantity (mg/L)	0.49	1.47	2.45	4.90	7.34	9.79
95%	2.0:1.0	Required Al^{3+} quantity (mg/L)	0.66	1.96	3.26	6.52	9.80	13.06

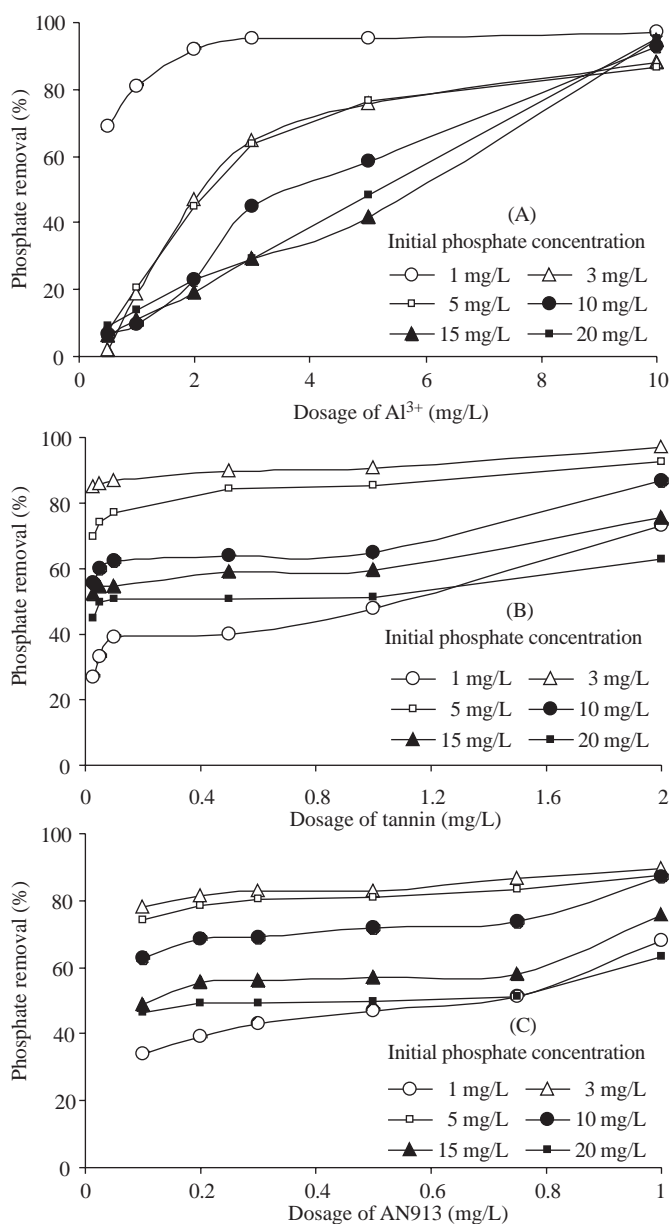


Figure 3. Comparison of alum and polyelectrolytes (tannin and AN913) in the removal of phosphate (Polyelectrolytes used with together alum; for (B) and (C) alum doses: 1.5, 5, 5, 5, 5 and 5 mg/L for 1, 3, 5, 10, 15 and 20 mg/L PO_4^{3-} , respectively).

Effects of tannin and AN913 on the removal of phosphate by alum

Firstly, the optimum doses of $Al_2(SO_4)_3$ were determined for different phosphate concentrations at optimum pH. Figure 3a shows the results of experimental runs with varying initial phosphate concentrations and Al^{3+} doses at an optimum pH value. Then half quantities of the optimum $Al_2(SO_4)_3$ doses

at optimum pH in these studies in which $Al_2(SO_4)_3$ was used alone, and certain quantities of tannin and AN913 as coagulant aids were used to determine the optimum coagulant aids doses. The results are shown in Figures 3b-c.

The residual phosphate concentrations for each initial phosphate concentration in the cases of added optimum doses of coagulant aids and alum used alone were determined. The results are shown in Table 4

so that the results in the Figure 3 can be compared better.

In the case of alum coagulation, alum dissolved rapidly when added to water. The aluminum cations produced will then hydrolyze to form complexes. These complexes will change the solution's ionic strength and adsorb onto colloidal particles, resulting in particle destabilization. Once particles have been destabilized, interparticle collisions will result in the formation of aggregates. At a specific pH and Al concentration, an amorphous, gelatinous precipitate of $\text{Al}(\text{OH})_3$ is formed. Once formed, precipitated amorphous $\text{Al}(\text{OH})_3$ will begin to undergo structural changes that may continue with age.

The binding of phosphate by $\text{Al}(\text{OH})_3$ has also received considerable attention in the literature. Boisvert *et al.* (1997) reported $\text{Al}(\text{OH})\text{HPO}_4$ to be the most significant aluminum-phosphate complex formed at neutral pH conditions. Although aluminum-phosphate complexes have been observed at relatively high concentrations in solution, the uptake of phosphate by $\text{Al}(\text{OH})_3$ in the solid phase appears to have the most significant impact on aqueous phosphate activity (Hsu, 1975; Boisvert *et al.*, 1997).

The precipitation of phosphate can neither be explained by the equilibrium model of a single chemical compound, such as AlPO_4 , nor as a co-precipitation of AlPO_4 and $\text{Al}(\text{OH})_3$. On the contrary, the phosphorus precipitation can be seen as a result of the competitive action of phosphates, hydroxyls and other ions to react with alum. Because hydroxyl ions are the strongest competitors, the addition of these to the coagulant reduces the phosphorus removal efficiency. Precipitation occurs when the complex species formed from the competitive action of the various ions is neutral (Diamadopoulos and Benedek, 1984). At low phosphate concentrations (1-5 mg/L), phosphate is removed largely by the adsorption of phosphate ions onto formed $\text{Al}(\text{OH})_3$ flocs (Goldshmid and Rubin, 1988; Boisvert *et al.*, 1997). This situation requires the use of much more alum or higher Al:P mole ratios to form sufficient $\text{Al}(\text{OH})_3$.

Table 4 shows that $\text{Al}_2(\text{SO}_4)_3$ is effective in removing 1-20 mg PO_4^{3-} /L. However, in the experiments using tannin and AN913 as coagulant aids, if the results are compared with the experiments using $\text{Al}_2(\text{SO}_4)_3$ alone it is seen that $\text{Al}_2(\text{SO}_4)_3$ -tannin and $\text{Al}_2(\text{SO}_4)_3$ -AN913 are more effective except at 1 mg PO_4^{3-} /L. As can be seen from Figure 3, 1.5 mg Al^{3+} and the coagulant aids used together for the removal of 1 mg/L PO_4^{3-} resulted in less phosphate removal compared with using $\text{Al}_2(\text{SO}_4)_3$ alone. Poly-

electrolytes are not effective in phosphate removal directly. They contribute to phosphate removal with $\text{Al}_2(\text{SO}_4)_3$ by bridging between $\text{Al}(\text{OH})_3$ (or AlPO_4) flocs. The coagulant aids were not effective at a concentration of 1 mg PO_4^{3-} /L because the amount of $\text{Al}(\text{OH})_3$ (or AlPO_4) flocs was not sufficient to be bridged by the polyelectrolytes. Therefore, polyelectrolytes lead to restabilization by the adsorbing of their free terminals on the same particle surface because polyelectrolytes have less particle to bridge (O'Melia, 1972).

Benedek and Bancsi (1977) applied a wide variety of polyelectrolytes when phosphate was precipitated from domestic wastewater using aluminum sulfate as a primary coagulant. Polyelectrolyte addition for phosphorus removal is generally used in conjunction with normal chemical precipitants, as they improve floc aggregation (Gray, 1982). Özacar (1997) found that the addition of tannin and AN913 as polyelectrolytes improved supernatant quality and marginally reduced the precipitant alum required.

It can be seen that tannin formed aluminum-tannate complex with Al^{3+} ion, and was more effective than AN913 in the range 1-5 mg PO_4^{3-} /L (Figures 3b-c and Table 4). The hydroxyl groups included in tannin offer special opportunities for the formation of metal complexes. Aluminum also can complex with carbonyl groups, so that effective cross-linking of tannin-aluminum occurs (Bliss, 1989). Therefore, the ability of tannins to form metal complexes has been utilized in water treatment (Hemingway, 1989; Özacar and Şengil, 2000; Özacar and Şengil, 2002).

The reactions involving hydroxyl ions, tannin and orthophosphates with aluminum ions are parallel and competitive. At low tannin concentrations (lower than 5 mg/L), the tannin and phosphates are incorporated into the network of the hydrous aluminum oxide floc. However, as the tannin concentration increases (higher than 10 mg/L), a higher concentration of soluble complexed aluminum species is formed and a higher concentration of residual aluminum remains unprecipitated (Omoike and vanLoon, 1999). The interaction of organics to form complexes with soluble metal species prior to precipitation has been suggested as the first step for the removal of organic matter from drinking water. 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). Reactions with dissolved NOM can be impor-

Table 4. Comparison of alum and polyelectrolytes (tannin and AN913) in the removal of phosphate.

Initial phosphate (mg/L)	Doses (mg/L)			Residual phosphate (mg/L)
	Al ³⁺	Tannin	AN913	
1.0	1.5	-	-	0.14
	1.5	2	-	0.27
	1.5	-	1	0.32
3.0	5	-	-	0.73
	5	2	-	0.09
	5	-	1	0.31
5.0	5	-	-	1.18
	5	2	-	0.37
	5	-	1	0.67
10.0	5	-	-	5.18
	5	2	-	1.31
	5	-	1	1.41
15.0	5	-	-	8.78
	5	2	-	3.67
	5	-	1	3.74
20.0	5	-	-	10.3
	5	2	-	7.46
	5	-	1	7.48

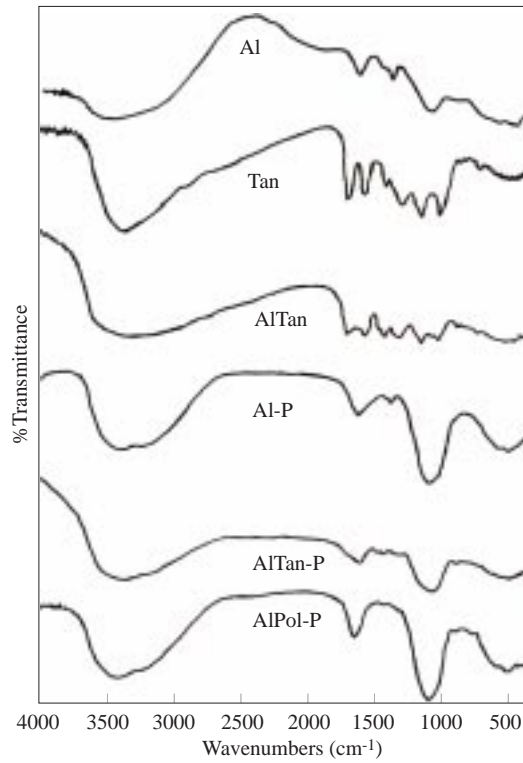


Figure 4. FTIR spectra of solid samples in the region 4000-400 cm^{-1} . Al: Simple aluminum hydrous oxide, Tan: Tannin, AlTan: Tannin that had been precipitated by alum, Al-P: Alum was added to the synthetic wastewater containing orthophosphate ions, AlTan-P: Both alum and tannin were added to the synthetic wastewater containing orthophosphate ions, AlPol-P: Both alum and AN913 were added to the synthetic wastewater containing orthophosphate ions.

tant in either the homogeneous or heterogeneous case, as these organic compounds can either form complexes with $\text{Al}(\text{OH})_3$ or with the surface groups on seed particles. Organic-Al complexation is favored at low Al concentrations and pH levels, whereas adsorption onto precipitate is favored at high Al concentrations and above pH 6 (Chowdhury *et al.*, 1991).

In the 1-5 mg PO_4^{3-} /L range, AN913 was less effective because of low particle concentrations in synthetic water. Organic polymers, whether cationic, anionic or nonionic, may not be effective coagulants or coagulant aids for waters containing low concentrations of colloidal particles. This is probably due to the low rate of interparticle contacts in such systems, although other phenomena may be involved (O'Melia, 1972).

In the 10-20 mg PO_4^{3-} /L range, tannin and AN913 provided approximately equal phosphate removal efficiencies (Figures 3b-c and Table 4). This result showed that AN913 formed bridges more easily among AlPO_4 because of increased AlPO_4 formation while the PO_4^{3-} concentration in the medium increased. Thus the efficiency of PO_4^{3-} removal by AN913 increased, reaching that of tannin.

FTIR Spectroscopy

The FTIR spectra of precipitated solids in the coagulation process are shown in Figure 4 so that interactions of phosphate with alum and polyelectrolytes can be understood better.

Generally, wide bands in the range 3550-3100 cm^{-1} correspond to OH bridging groups in all systems (Figure 4) and are attributed to the location of the hydrogen atom on different oxygen atoms in the framework (Temuujin *et al.*, 2001; Dimirkou *et al.*, 2002).

The band at 1639 cm^{-1} in the spectrum of $\text{Al}(\text{OH})_3$ (Al) arises from adsorbed water (Omoike and vanLoon, 1999; Temuujin *et al.*, 2001). The band at 1404 cm^{-1} shows the presence of carbonate as a unidentate complex with aluminum (Omoike and vanLoon, 1999). Bands about at 1110 cm^{-1} and between 620 and 483 cm^{-1} can be attributed to symmetric and asymmetric O-Al-O stretching vibrations in octahedral coordination (Omoike and vanLoon, 1999; Dimirkou *et al.*, 2002).

The band at 1738 cm^{-1} in the spectrum of tannin (Tan) belongs to carboxyl groups. The absorption bands between 1611 and 1503 cm^{-1} are related to aromatic $-\text{C}=\text{C}-$ bonds. The peaks between 1330

and 1037 cm^{-1} in the spectrum of tannin belong to phenol groups.

The band intensities belonging to tannin are reduced in the spectrum of the AlTan system. A reduction in the 1750-1000 cm^{-1} band indicates hydroxy-Al-tannate complex formation between Al and tannin (Omoike and vanLoon, 1999). A reduction in the intensity of the band belonging to the carboxylic acid group at 1738 cm^{-1} has been attributed to the dissociation of carboxylate groups to which Al ions were bonded via electrovalent linkages.

The FTIR spectrum of Al-P had an intense surface H-O-H bending vibration maximum at around 1639 cm^{-1} and a very strong broad absorption at 1110 cm^{-1} . The presence of a strong band between 1145 and 1040 cm^{-1} has been attributed to P-O vibrations in inorganic orthophosphates and the position of this band depends on the species of phosphate and associated ions (Omoike and vanLoon, 1999; Gong, 2001).

The FTIR spectra of AlTan-P have peaks that are characteristic of both aluminum tannate and aluminum phosphate linkages (Figure 4). The intensities of absorption bands at 1503, 1459, 1352 and 924 cm^{-1} in the AlTan system seem to be reduced in the case of AlTan-P. The cause of this reduction is that the amount of tannin was very low in the coagulation process while the amounts of Al and PO_4^{3-} were very high.

The FTIR spectrum of the AlPol-P system is essentially the same as that of the AlTan-P system. Tannin forms a structure similar to that of anionic polyelectrolyte (AN913) with respect to the FTIR spectra of AlTan-P and AlPol-P systems (Figure 4).

Economy

The cost of phosphate removal from a synthetic water having 10 mg/L PO_4^{3-} was calculated using the above data and the results are presented in Table 5.

Phosphate removal cost decreased when tannin and AN913 were used as coagulant aids while the alum dose was decreased to one half. The cost when tannin was used as a coagulant aid was \$11.1/1000 m^3 . As can be seen from Table 5, if tannin is used as a coagulant aid, the coagulation process will be cheaper than with alum and alum + AN913 by 41.6% and 8.3%, respectively. In addition, the sludges formed using tannin and AN913 as coagulant aids were less and could be filtered more easily than when using alum. Thus, a filtration process in which tannin and AN913 were used as coagulant aids would

Table 5. The price of phosphate removed from wastewater containing 10 mg/L PO_4^{3-} .

kg/1000 m ³ water			Price (\$)	PO_4^{3-} removal (%)
Alum	Tannin	AN913		
123.3	-	-	19.0	92.6
61.6	2	-	11.1	87.9
61.6	-	1	12.1	87.0
Alum: \$0.154/kg Tannin: \$0.795/kg AN913: \$2.553/kg				

be both easier and more economical than with alum. Özacar and Şengil (2000) reported that the formed

sludge could be filtered more easily when tannin was used as a coagulant aid.

Conclusions

In this study, the effect of tannin on the coagulation of aluminum sulfate was investigated for the removal of phosphate from synthetic water. The effect of initial pH on the $\text{Al}_2(\text{SO}_4)_3$ coagulation was investigated and it was found that the optimum initial pH value was 7.5. In the removal of phosphate from synthetic water, $\text{Al}_2(\text{SO}_4)_3$ was the most effective coagulant for all phosphate concentrations. However, both tannin and AN913 contributed to the removal

achieved with $\text{Al}_2(\text{SO}_4)_3$. While tannin and AN913 gave similar results in the high phosphate range of 10-20 mg/L PO_4^{3-} , tannin was more effective in the low phosphate range of 1-5 mg/L PO_4^{3-} . It was found that tannin indicated good flocculant characteristics. It was also found that a coagulation process with tannin would be cheaper than with an alum and alum + AN913 combination. Therefore, tannin can be used as a coagulant aid for the removal of phosphate in water treatment.

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