



Enhancing phosphate removal from wastewater by using polyelectrolytes and clay injection

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Abstract

Aluminum sulfate, alum, is a common chemical coagulant used for coagulation. Recently, polymers have been utilized in coagulation/flocculation processes for water purification. In this study, the ability of two organic polymers, tannin (natural polyelectrolyte) and AN913 (synthetic anionic polyelectrolyte), and clay to act as coagulant aids was tested, in the removal of phosphate from synthetic wastewater. Contaminants in synthetic waters were coagulated using alum, alum + clay, alum + tannin, alum + AN913, alum + tannin + clay and alum + AN913 + clay. Alum together with polymers as coagulant aids yielded a significant improvement in phosphate removal compared with alum alone, for initial phosphate concentrations of 5–15 mg/l PO_4^{3-} . The use of clay and polyelectrolytes improved the efficiency of phosphate removal and lowered the required alum dose. Fourier transform infrared (FTIR) spectroscopy was used for the identification and characterization of the aluminum species formed during dephosphorization of the synthetic wastewater with and without tannin, AN913 and clay. Evidence from FTIR spectroscopy showed the formation of aluminum hydroxyphosphate, hydroxy-Al-tannate and aluminum complexes containing phosphorus, tannin and AN913.

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1. Introduction

Phosphates in wastewaters are a growth-nutrient for microorganism in water bodies. As a result of increased phosphorus concentration, an excessive growth of photosynthetic aquatic micro- and macroorganisms occurs and ultimately becomes a major cause of eutrophication [1–3].

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Efforts to limit inputs of phosphorus to wastewaters have proved to be largely unsuccessful because of the wide variety of input sources. The alternative approach to reduction of source is effective wastewater treatment [4]. Phosphate removal from wastewater has received considerable attention since the late 1960s [5]. Phosphorus removal techniques fall into three main categories: physical, chemical and biological. Physical methods have proved to be either too expensive, as in the case of electro dialysis and reverse osmosis [6], or inefficient, removing only 10% of the total phosphorus [4]. Enhanced biological treatment can remove up to 97% of the total phosphorus, but this process can be highly variable due to operational difficulties [4]. Chemical removal techniques, using metal salts such as calcium, aluminum and iron, are reliable and well-established processes [3–10]. Calcium, which is supplied by lime, is less commonly employed because of handling difficulties and high sludge production. Its optimum dosing pH of 11 is also undesirable for use prior to or during biological treatment [4]. Iron salts are relatively inexpensive, but are less effective precipitants than aluminum [4,8,11,12]. Although aluminum is expensive, it is a very effective precipitant [4,7,9,12,13].

In conjunction with normal chemical precipitants, polyelectrolyte addition for phosphorus removal is usually used as it improves floc aggregation [14]. Özacar [13] found that the addition of natural polyelectrolyte (tannin) and synthetic polyelectrolyte (acrylamide/acrylic acid copolymer, AN913) improved supernatant quality and marginally reduced the precipitant alum required. Tannin was successfully used as a coagulant aid for clarifying water [15] and for sludge dewatering [16]. Clay can also serve as a flocculation aid. Clay particles serve as nuclei for flocculation, resulting in the formation of large, rapid-settling flocs [13]. Thus, clay serves as an aid in the settling of suspended solids. Phosphate can adsorb onto the large floc surfaces and settle with the flocs.

This study examined the effect of both clay and polyelectrolytes on phosphate removal by coagulation/flocculation/precipitation with alum. Phosphate removal with alum alone or in the presence of clay, tannin, AN913 or a mixture of clay and both polymers, at various alum, phosphate, clay, and polymer concentrations, was investigated. In addition, the solid phase materials were examined by Fourier transform infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Materials

Tannin used in this study was obtained from Sümer Holding A.Ş., Turkey. In this factory, tannin was extracted with hot water from valonea. The tannin content of the valonea (*Quercus aegilops*) extract was determined to be 53.50% as a hydrolysable tannin, according to the Vanilin test [17], the Prussian Blue test [18] and the 1,10-phenanthroline test [19,20]. Clay, the chemical composition of which is given in Table 1, was obtained from the Yarımca Ceramic Factory in Turkey.

2.2. Preparation of synthetic water

Synthetic water samples having different phosphate concentrations were prepared by adding selected quantities of NaH_2PO_4 to tap water. The mineral composition of the tap

Table 1
The chemical composition of the clay used in this research

Constituent	Composition (wt.%)
SiO ₂	55.38
Al ₂ O ₃	28.27
Fe ₂ O ₃	1.93
TiO ₂	0.88
CaO	0.35
MgO	0.23
K ₂ O	1.95
H ₂ O	10.08

water used to simulate the raw water is presented in Table 2. The initial pH of the synthetic water was adjusted to 7.5 without clay addition and 7.0 with clay addition, by addition of 0.1 M HCl or 0.1 M NaOH solutions.

2.3. Preparation of alum and polyelectrolytes solutions

Alum (Al₂(SO₄)₃·18H₂O, Merck) was dissolved in distilled water to obtain a final Al³⁺ concentration of 1 mg/ml. A tannin solution was prepared in distilled water, at a concentration of 1 mg tannin/ml. Other tannin solutions with concentrations of 0.01 and 0.1 mg/ml were prepared by dilution. The tannin solutions were prepared daily. Since tannin is a natural anionic polyelectrolyte, for comparative purposes experiments were also undertaken with a synthetic anionic polyelectrolyte. For this purpose, preliminary experiments were conducted using AN905, AN912, AN913, AN934 and AN945 polyelectrolytes. These polyelectrolytes are based on polyacrylamides by copolymerizing acrylamide with acrylic acid. The results showed that AN913 (SNF Floerger, France), a copolymer of acrylamide with acrylic acid and having molecular weight (1–2) × 10⁶ g/mol, was the best anionic polyelectrolyte for use as a coagulant aid. Moreover, this polymer is being used as a coagulant aid by ISKI (Istanbul Water and Sewerage Administration). AN913 solutions were prepared

Table 2
Mineral composition of the tap water used to simulate the raw water

Cation	Concentration (mg/l)	Anion	Concentration (mg/l)
Ca ²⁺	42.5	HCO ₃ ⁻	127.8
Mg ²⁺	6.75	Cl ⁻	8.45
Fe ²⁺	0.093	SO ₄ ²⁻	3.38
NH ₄ ⁺	0.01	NO ₃ ⁻	0.932
Pb ²⁺	0.07	NO ₂ ⁻	<0.05
Cu ²⁺	0.16	F ⁻	<0.1
Ni ²⁺	0.123	CN ⁻	0.003
Zn ²⁺	0.872	PO ₄ ³⁻	0.013
Cd ²⁺	<0.02	Phenol	0.517
Al ³⁺	–		

Total hardness, 134 mg/l CaCO₃; total alkalinity, 104 mg/l CaCO₃; pH 7.4.

at a concentration of 1 mg AN913/ml and then a solution with a concentration of 0.1 mg AN913/ml was prepared by dilution. The AN913 solutions were prepared daily.

2.4. Coagulation experiments

A conventional jar test procedure with a six-unit multiple stirrer system was employed. In all experiments, the velocity gradient, G , value for rapid mixing was 566 s^{-1} and for coagulation was 60 s^{-1} . Coagulant was added to samples of the synthetic water (1 l), and rapid mixing was performed at 200 rpm for 1 min. After the rapid mixing, a polymer or polymer–clay was added as a coagulant aid, followed by 30 min of flocculation at 45 rpm, and then 15 min of settling. Coagulation experiments were run in triplicate, and the results were highly reproducible.

2.5. Aluminum, phosphate and light scattering measurements

After settling, samples were taken at a 3 cm depth below the surface of the liquid, and analyzed for the residual aluminum concentrations by atomic absorption spectrophotometry, and phosphorus according to APHA Standard Methods [21]. Additionally, light scattering was used to detect the formation of a solid phase upon adding the aluminum to the synthetic water. Scattering intensities were measured with unfiltered light at 90° to the incident light with a nephelometer. The measurements are expressed as relative scattering units on a 0–100 scale. The solutions were placed in round 19 mm \times 105 mm cuvettes, which were previously matched to within 0.5 relative scattering units with distilled water. The nephelometer was calibrated with turbidity standards of relative scattering values ranging between 0 and 81.

2.6. Infrared spectroscopy

Following settling, the supernatant was removed, and a portion filtered through 0.45 μm Millipore membrane filters. The remaining portion was dried at 378 K. Potassium bromide pellets were prepared by mixing 1 mg of dried samples with 200 mg of KBr (spectrometry grade) at $10,000\text{ kg/cm}^2$ pressure for 30 min under vacuum. FTIR spectra were recorded from 2000 to 400 cm^{-1} (100 scans) on samples in KBr pellets using Mattson Infinity Series FTIR spectrophotometer.

3. Results and discussion

In this study, phosphate removal by coagulation/flocculation/precipitation with alum alone or in the presence of clay, tannin, AN913 or a mixture of clay and both polymers was investigated. Coagulation experiments were performed at a number of different alum, phosphate, clay, and polymer concentrations. The study covers the cases when clay only was used as a coagulant aid, and when both polymers or a mixture of clay, and both polymers were used as coagulant aids.

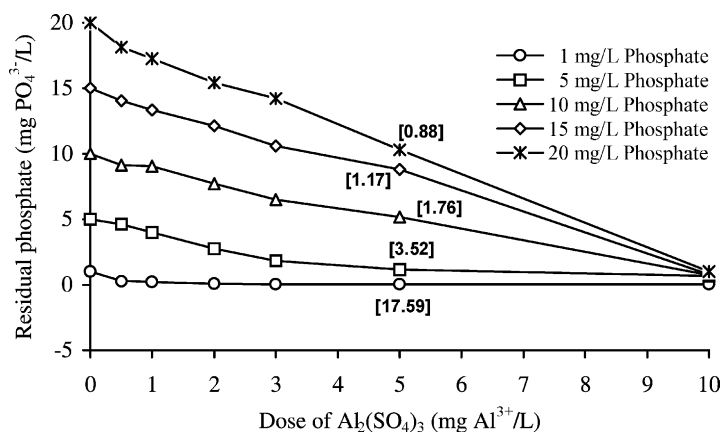


Fig. 1. Residual phosphate concentration as a function of $\text{Al}_2(\text{SO}_4)_3$ doses. The values given in square brackets denote Al/P molar ratio.

3.1. Removal of phosphate with alum and clay

The affect of $\text{Al}_2(\text{SO}_4)_3$ dose on phosphate removal by chemical precipitation from the synthetic waters having an initial pH of 7.5 with 1, 5, 10, 15 and 20 mg/l PO_4^{3-} was studied, and the results are shown in Fig. 1. In earlier studies, it was found that the optimum pH for phosphate removal by $\text{Al}_2(\text{SO}_4)_3$ was 7.5 without clay, and 7.0 with clay [13]. Therefore, the present experiments were carried out at pH 7.5 without clay addition, and at pH 7.0 with clay addition.

Fig. 1 shows the residual phosphate of the treated synthetic waters as a function of the dosage of alum without addition of clay. The optimal dosage, which is the minimum dosage corresponding to the lowest residual phosphate, varied between 3 and 10 mg/l Al^{3+} . The amount of the phosphate removed from the synthetic water increased when the Al/P molar ratio was decreased by increasing the initial phosphate concentration (Al/P molar ratios for a 5 mg/l Al^{3+} dose are shown as example values in Fig. 1). Dissolved concentration of precipitated aluminum phosphate increases at lower initial phosphate concentrations [7]. This observation agrees with the literature.

Similar studies were conducted with the synthetic waters including 20, 50, 150 and 300 mg clay; 1, 5, 10, 15 and 20 mg/l PO_4^{3-} for each clay quantity at pH 7.0. Phosphate removal efficiency obtained at the different Al^{3+} doses for all phosphate concentrations, with and without clay addition, are given in Table 3. Phosphate removal efficiencies for 1 and 20 mg/l PO_4^{3-} at the optimum alum doses (3 and 10 mg/l Al^{3+} , respectively), with and without clay (range of 20–300 mg/l), were found to be 95%. These results show that the clay is not effective for removal of 1 and 20 mg/l PO_4^{3-} . For 1 mg/l PO_4^{3-} , a coagulant aid is unnecessary since excess alum ($\text{Al}^{3+} = 3$ mg/l, or Al/P = 10.56) is used. It is known that in the case of excess alum used, the phosphate removal efficiency is high without any coagulant aid [7]. At such low phosphate concentrations, phosphate is removed largely by adsorption of phosphate ions onto formed $\text{Al}(\text{OH})_3$ flocs (presumably outer sphere complexation). To

Table 3
Effect of clay on phosphate removal by alum

Initial phosphate (mg/l)	Clay quantity (mg/l)	Phosphate removal efficiency (%)					
		0.5 ^a	1	2	3	5	10
1	0	69.0	81.0	92.0	95.0	95.0	97.0
	20	12.0	45.0	91.0	95.0	96.0	91.0
	50	14.0	53.0	85.0	92.0	93.0	96.0
	150	11.0	46.0	85.0	94.0	96.0	98.0
	300	6.0	46.0	88.0	95.0	98.0	98.0
5	0	7.6	20.4	44.8	63.6	76.4	86.6
	20	9.0	22.4	49.0	73.6	96.4	97.6
	50	10.0	21.4	49.2	73.4	94.2	97.8
	150	9.8	25.4	51.4	74.6	97.2	97.8
	300	5.2	18.6	47.6	69.4	94.0	98.0
10	0	8.7	9.5	23.1	35.2	49.7	92.6
	20	4.0	14.0	33.3	52.2	82.9	97.1
	50	5.9	14.3	33.8	48.2	79.7	99.4
	150	8.5	16.6	34.8	50.8	75.8	98.5
	300	5.1	16.3	33.0	51.5	75.9	99.3
15	0	6.3	11.1	19.2	29.3	43.2	94.8
	20	3.3	7.7	22.3	36.5	64.3	98.1
	50	6.1	11.0	26.3	40.0	63.5	98.2
	150	8.3	14.0	27.6	39.7	64.0	98.3
	300	8.1	14.7	27.6	40.7	63.2	98.6
20	0	9.3	13.8	22.9	29.0	48.9	95.0
	20	4.0	10.6	21.2	31.8	52.8	85.9
	50	2.9	10.3	22.3	32.5	55.6	79.2
	150	11.2	12.8	23.6	34.4	52.2	95.2
	300	8.6	13.8	24.6	34.0	53.8	96.3

^a Alum added (mg/l).

form sufficient $\text{Al}(\text{OH})_3$ flocs, excess alum at higher Al/P molar ratios is required: the higher the initial Al^{3+} concentration, the higher the concentration of colloidal $\text{Al}(\text{OH})_3$ particles, and the higher the rate of aggregation/sedimentation. On the other hand, at higher phosphate concentrations, such as 20 mg/l, tertiary salt (variscite, AlPO_4) mainly forms. Under these conditions, high efficiency in phosphate removal can be possible with lower alum quantity, even if no clay is added [22].

At 5–15 mg/l initial phosphate concentrations, clay addition significantly increases the phosphate removal efficiency. Under these conditions, adequate amounts of $\text{Al}(\text{OH})_3$ flocs do not form for adsorption of phosphate and adequate amounts of tertiary salt (AlPO_4) do not form also. To explain the affect of the clay, it can be hypothesized that the weakly positively charged amorphous $\text{Al}(\text{OH})_3$ colloidal particles electrostatically adsorb on the negatively charged surfaces of large clay platelets. Thereafter, the $\text{Al}(\text{OH})_3$ -coated clay particles flocculate and settle quickly. Phosphate is adsorbed and precipitates on these weakly positive particles and so settles with them. Thus, in the case of clay addition, much more and larger flocs form and thus adsorption of phosphate onto formed flocs increases.

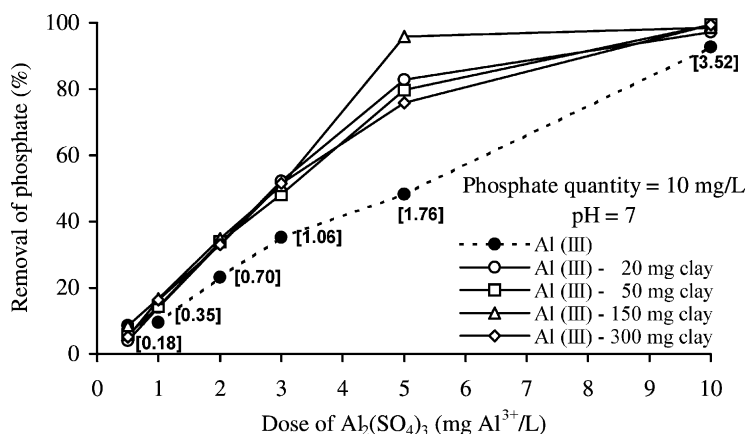


Fig. 2. Affect of clay on phosphate removal by $\text{Al}_2(\text{SO}_4)_3$. The values given in square brackets denote Al/P molar ratio.

To further illustrate the effect of clay addition, a typical result at 10 mg/l initial PO_4^{3-} concentration is shown in Fig. 2. At Al/P molar ratio of 3.52, phosphate removal was about 90% in the case where no clay is added, and about 98% where clay was added. This difference was more marked at Al/P molar ratio of 1.76; with no clay added, phosphate removal was about 50%, and with only 20 mg/l clay added, this increased to 83%.

In the phosphate removal studies, the FTIR spectra of precipitated solids in the coagulation process are presented in Fig. 3, so that interactions of phosphate with coagulant (alum) and coagulant aids (tannin, AN913 and clay) can be better understood.

The amorphous nature of the freshly precipitated aluminum hydrous oxide solid phases (Al) is indicated by broad, relatively featureless infrared absorption bands (not shown) in both the $-\text{OH}$ stretching and deformation regions. The absorption band at 1407 cm^{-1} shows the presence of carbonate as a unidentate complex with aluminum. The band at 1634 cm^{-1} is indicative of $\text{H}-\text{O}-\text{H}$ bending [10].

The infrared spectrum of aluminum phosphate (AIP) had an intense surface $\text{H}-\text{O}-\text{H}$ bending vibration maximum around 1634 cm^{-1} and a very strong broad absorption at 1110 cm^{-1} (Fig. 3). The presence of a strong band between 1145 and 1056 cm^{-1} has been attributed to $\text{P}-\text{O}$ vibrations in inorganic orthophosphate, and the position of this band depends on the species of phosphate and associated ions. The solid phase is a form of aluminum hydroxyphosphate combining both $\text{Al}-\text{OH}-\text{Al}$ and $\text{Al}-\text{PO}_4-\text{Al}$ linkages, rather than a mixed material containing aluminum hydroxide and aluminum phosphate individually [10,23].

When the optimum alum dose were decreased by one-half (Al/P = 1.76) and 150 mg/l clay were added to the medium, phosphate removal efficiency increased up to 95.8% (Fig. 2). This result clearly shows that the phosphate removal efficiency will increase if clay is used as a coagulant aid together with alum.

The band at 1634 cm^{-1} in the infrared spectra of clay and clay-phosphate (C and CP) is due to adsorbed water (Fig. 3). The band at 1120 cm^{-1} , together with the band at 1030 cm^{-1} , is due to a SiO stretching vibration. The band at 915 cm^{-1} arises from the stretching vibration

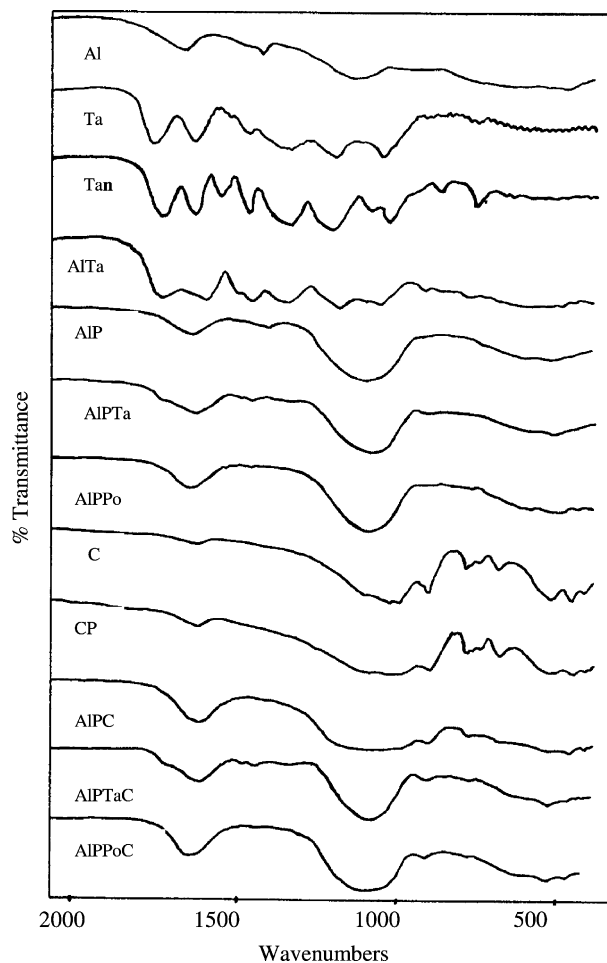


Fig. 3. FTIR spectra of solid samples in region 2000–400 cm^{-1} . Al: simple aluminum hydroxide; Ta: tannin; Tan: tannic acid; AlTa: tannin that had been precipitated by alum; AlP: alum was added to the synthetic wastewater containing orthophosphate ions; AlPTa: both alum and tannin were added to the synthetic wastewater containing orthophosphate ions; AlPPO: both alum and AN913 were added to the synthetic wastewater containing orthophosphate ions; C: clay; CP: clay was added to the synthetic wastewater containing orthophosphate ions; AlPC: both alum and clay were added to the synthetic wastewater containing orthophosphate ions; AlPTaC: alum, tannin and clay were added to the synthetic wastewater containing orthophosphate ions; AlPPOC: alum, AN913 and clay were added to the synthetic wastewater containing orthophosphate ions.

of a silanol group and that at 800 cm^{-1} is due to four-coordinated silica [24]. The absorption bands that can be attributed to Al–O vibrations of aluminum in the octahedral coordination in clay is seen in the region 750–400 cm^{-1} [10].

A comparison between the spectra of the species adsorbed on the clay surface from the phosphate solution and the spectra of the clay alone showed completely changed frequencies and intensity of bands. Thus, there must be some changes in the conformation after the

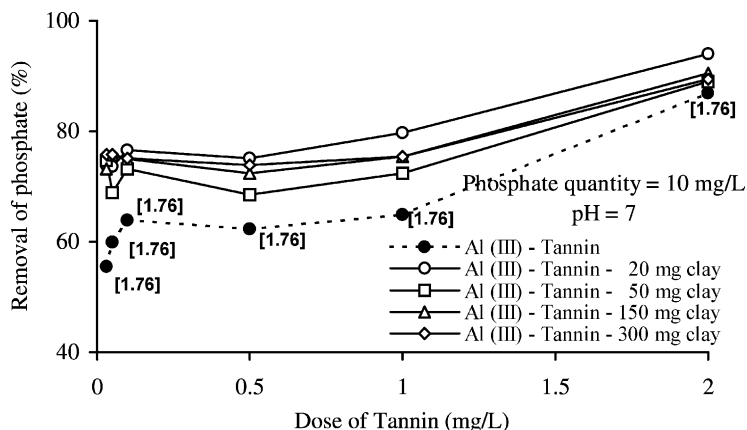


Fig. 4. Affect of tannin on phosphate removal efficiency by $\text{Al}_2(\text{SO}_4)_3$ with and without clay. The values given in square brackets denote Al/P molar ratio.

phosphate species transferred from the solution onto the clay surface. Some of the P–O may interact with the Si and Al species exposed on the clay surface. Bands at about 1120–990, 695 and 535–430 cm^{-1} showed significant changes.

As can be seen in Fig. 3, the H–O–H bending vibration at 1634 cm^{-1} in the spectrum of AIP did not change in the AIPC system. However, the presence of Si–O bonds in the clay expanded the band belonging to P–O vibration between 1226 and 950 cm^{-1} and reduced in intensity because of the excess amount of clay (150 mg/l) used in the AIPC system.

3.2. Effects of tannin, AN913 and clay on the removal of phosphate with alum

To examine the effects of tannin, AN913 and clay as coagulant aids to the removal of phosphate, studies were done with half quantities of the optimum doses of $\text{Al}_2(\text{SO}_4)_3$ obtained from the studies with alum only and selected quantities of tannin, AN913 and clay. As a typical result, for a solution containing initial phosphate concentration of 10 mg/l ($\text{Al/P} = 1.76$), the affect of added tannin and AN913 on the phosphate removal efficiencies are shown in Figs. 4 and 5, respectively.

The phosphate removal efficiency obtained was about 87% when 2 mg/l tannin was added together with alum (Fig. 4). However, when alum alone was used in the same experimental conditions, the phosphate removal efficiency was about 50% ($\text{Al/P} = 1.76$, Fig. 2). Thus, tannin addition increased the phosphate removal efficiency by about 37%. In the case of clay addition together with alum + tannin, the phosphate removal efficiency increased slightly. As can be seen from Fig. 4, increasing the clay quantity had little effect on phosphate removal efficiency (in fact, it decreased efficiency slightly); 20 mg/l clay was sufficient and the efficiency reached 94%. However, to obtain the same efficiency without using tannin in the medium it was found that the quantity of clay used with the alum must be 150 mg/l ($\text{Al/P} = 1.76$, Fig. 2). Thus, tannin addition significantly decreases the clay quantity that needs to be added.

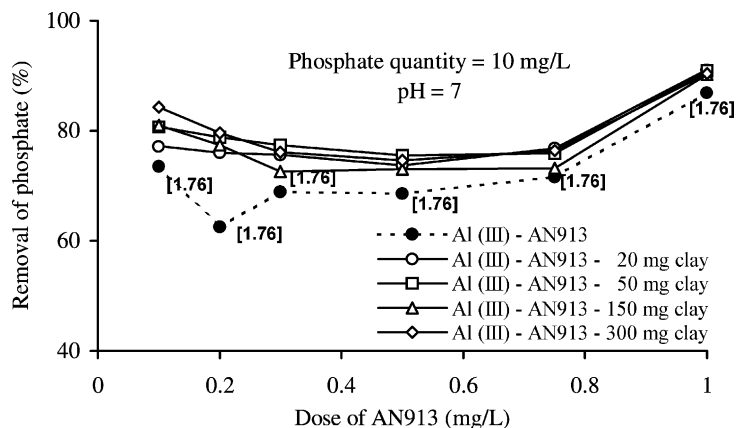


Fig. 5. Affect of AN913 on phosphate removal efficiency by $\text{Al}_2(\text{SO}_4)_3$ with and without clay. The values given in square brackets denote Al/P molar ratio.

From Fig. 3, it can be seen that the FTIR spectrums of tannic acid and tannin are largely similar. In the spectra of tannic acid and tannin, the bands at 1722 and 1741 cm^{-1} , respectively, are due to carboxyl groups (Fig. 3). The absorption bands between 1618 and 1450 cm^{-1} are related to aromatic $-\text{C}=\text{C}-$ bonds. The peaks at 1201 – 1031 cm^{-1} in the spectrum of tannic acid and at 1185 – 1043 cm^{-1} in the spectrum of tannin are due to phenol groups.

In the FTIR spectrum for the AlTa system, the band intensities for all the groups belonging to tannin are reduced between 1750 and 1000 cm^{-1} , which indicates hydroxy-Al-tannate complex formation between tannin and Al [10]. Reduction in the intensity of the band belonging to the carboxylic acid group at 1741 cm^{-1} has been attributed to its dissociation, and the new bands at about 1605 and 1352 cm^{-1} have been attributed to formation of carboxylate groups to which Al ions are bonded via electrovalent linkages.

The FTIR spectra of AlPTa has peaks that are characteristic of both aluminum tannate and aluminum phosphate linkages (Fig. 3). For AlPTa, the intensities of the absorption bands associated with the AlTa system at 1741 , 1459 , 1352 and 921 cm^{-1} seems to be reduced. The cause for this reduction is that the amount of tannin used in the coagulation process is very low and whereas the amounts of Al and PO_4^{3-} are very high. The intensity bands at 1634 and 1110 cm^{-1} are associated with the AlP system.

The FTIR spectrum of the AlPTaC system is near identical to that of the AlPTa system. Thus, clay had no effect on the bond structure of the AlPTaC system. The clay particles serve as nuclei for flocculation resulting in formation of large and rapid-settling flocs. The absorption peak at 1110 cm^{-1} is same as for AlPTa, because of the small amount of clay used in this system.

From Figs. 4 and 5, it is evident that tannin and AN913 show similar behaviors. For dosing with AN913 (Fig. 5), it can be seen that the phosphate removal efficiency obtained was about 87% when 1 mg/l AN913 was used together with alum. When clay was added, the efficiency increased to about 91%. It can also be seen that increasing the clay quantity had no effect on the efficiency.

Adding a polymer is an attempt to enhance the coagulation efficiency and economize the dosage of the primary coagulant. The coagulant aid polymer has functional groups capable of attracting suspended colloids and forming colloid–polymer complexes, i.e. particles linked together by a polymer which form a rather loose aggregate, resulting in flocculation. A polymer can be adsorbed onto the surface of a colloidal particle due to coulombic (charge–charge) interaction, dipole–dipole interaction, hydrogen bonding, or van der Waals interaction, or some combination of any or all of these forces. A balance must exist between the affinity of the polymer groups for the surface, and their interaction with water. The typical outcome is that the polymer adheres to certain points on the surface; however, for much of its length, it can extend into the aqueous solution. When two particles are brought together, the loops and tails of one polymer may attach themselves to bare patches on the approaching particle, to form bridges. This process is assisted if the adsorption density of the polymer is not too high. The optimum polymer concentration to achieve flocculation corresponds to roughly half the surface coverage of the polymer. The nature and concentration of the polymer can yield very effective aggregation of the colloid [25].

The FTIR spectrum of the AIPPo system is essentially same as the AlPTa system. Tannin forms a structure similar to that of the anionic polyelectrolyte (AN913) (Fig. 3). The AIPPoC system spectrum is also near identical to that of the AlPTaC system. Thus, clay did not cause any change in the bond structure.

The phosphate removal efficiencies obtained with and without using clay at the optimum doses where tannin and AN913 were used as coagulant aids together with alum are given in Table 4. To better illustrate this affect, the phosphate removal efficiency differences between the cases with and without added coagulant aids were calculated and the results are shown in Figs. 6–8.

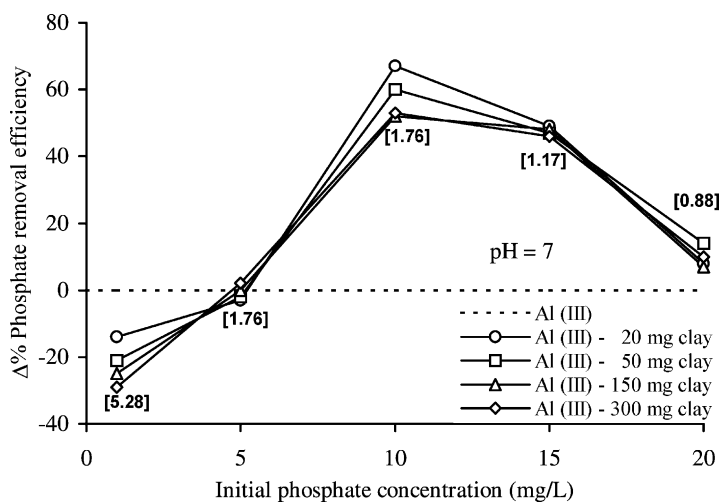


Fig. 6. Phosphate removal efficiency differences between clay added as a coagulant aid and alum used alone. The values given in square brackets denote Al/P molar ratio.

Table 4

Phosphate removal efficiencies at the optimum doses of coagulant aids

Clay quantity (mg/l)	Initial PO ₄ ³⁻ (mg/l)	Al/P molar ratio	Al ³⁺ dose (mg/l)	Coagulant aid dose (mg/l)		Phosphate removal efficiency (%)		
				Tannin	AN913	Al ³⁺	Al ³⁺ + tannin	Al ³⁺ + AN913
0	1	5.28	1.5	2.0	1.0	87.2	77.7	73.3
	5	3.52	5.0	2.0	1.0	76.4	92.8	83.0
	10	1.76	5.0	2.0	1.0	49.7	86.9	87.0
	15	1.17	5.0	2.0	1.0	43.2	75.9	75.7
	20	0.88	5.0	2.0	1.0	48.9	63.4	63.6
20	1	5.28	1.5	2.0	1.0	75.0	48.0	72.0
	5	1.76	2.5	2.0	1.0	60.0	84.2	77.4
	10	1.76	5.0	2.0	1.0	82.9	94.0	91.1
	15	1.17	5.0	2.0	1.0	64.3	76.5	72.2
	20	0.88	5.0	2.0	1.0	52.8	61.5	58.5
50	1	5.28	1.5	2.0	0.1	69.0	73.0	63.0
	5	1.76	2.5	2.0	1.0	61.0	78.8	79.2
	10	1.76	5.0	2.0	1.0	79.7	89.0	90.9
	15	1.17	5.0	2.0	1.0	63.5	72.9	75.1
	20	0.88	5.0	2.0	1.0	55.6	60.2	61.0
150	1	5.28	1.5	2.0	1.0	65.0	82.0	70.0
	5	1.76	2.5	2.0	1.0	62.0	81.0	78.8
	10	1.76	5.0	2.0	1.0	75.8	90.5	90.2
	15	1.17	5.0	2.0	1.0	64.0	74.1	71.9
	20	0.88	5.0	2.0	1.0	52.2	61.0	61.8
300	1	5.28	1.5	2.0	0.2	62.0	84.0	80.0
	5	1.76	2.5	2.0	0.1	63.0	87.0	87.0
	10	1.76	5.0	2.0	1.0	75.9	89.4	90.3
	15	1.17	5.0	2.0	1.0	63.2	73.5	74.8
	20	0.88	5.0	2.0	1.0	53.8	58.6	60.8

From Fig. 6, when the clay was added to the medium at the initial phosphate concentration of 1 mg/l, the phosphate removal efficiency decreased compared to when alum was used alone while the efficiency increased at the other initial phosphate concentrations. Phosphate adsorption and removal during water treatment by Al coagulants appear to be largely a result of a complexation driven by specific interactions. This complexation can lead to precipitation of the complex, or to its solubilization. Depending on the concentration of Al and PO₄³⁻, and on the pH, various precipitates of different Al/P molar ratio can be obtained [22].

From Fig. 6, it can be seen that clay addition did not have any effect at an initial phosphate concentration of 5 mg/l (Al/P molar ratio is 1.76). At initial phosphate concentration higher than 5 mg/l, clay addition increases phosphate removal efficiency.

As can be seen from Figs. 7 and 8, compared to alum addition alone, phosphate removal efficiency increased when alum + tannin, or alum + AN913 was used and increased further when used together with clay, except for 1 mg/l initial PO₄³⁻ concentration. Also, clay at 20 mg/l is sufficient and more clay is unnecessary.

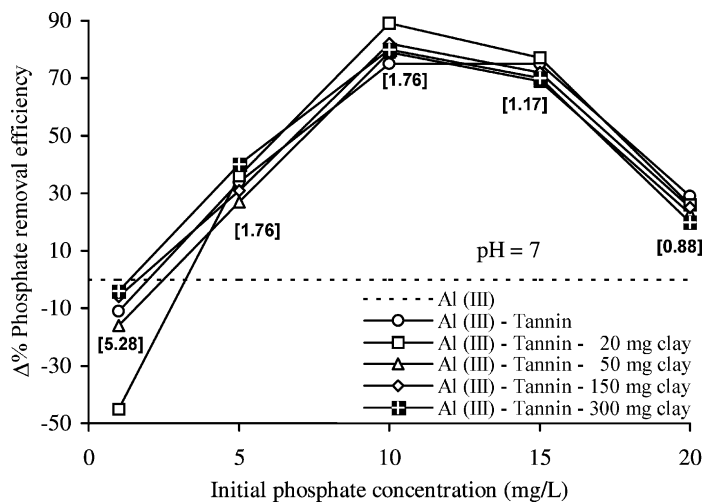


Fig. 7. Phosphate removal efficiency differences between tannin added as a coagulant aid and alum used alone for data with and without clay addition. The values given in square brackets denote Al/P molar ratio.

To illustrate, if Fig. 7 is examined, at 10 mg/l initial phosphate concentration (Al/P = 1.76), phosphate removal efficiency increases about 75% when alum was used together with tannin compared with when alum only was used. When 20 mg/l clay was added to the same medium, about a 90% phosphate removal efficiency increase was observed.

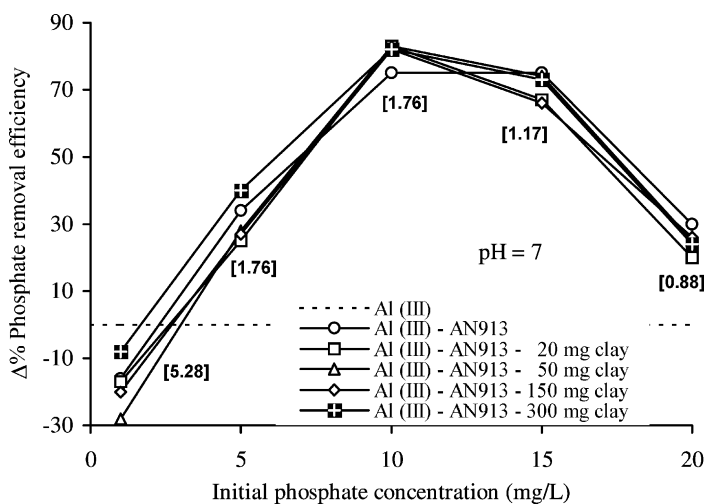


Fig. 8. Phosphate removal efficiency differences between AN913 added as a coagulant aid and alum used alone for data with and without clay addition. The values given in square brackets denote Al/P molar ratio.

Comparing Figs. 7 and 8, addition of tannin and AN913, respectively, show a similar increase in phosphate removal efficiency. From this result, it is clear that tannin can be used instead of AN913 as a coagulant aid.

As the initial phosphate concentration increases, the phosphate removal efficiency increases even if the solution has lower Al/P molar ratios. A possible reason for this result is that the particles concentration increases and more AlPO_4 (tertiary salt) forms. Consequently, the Al/P molar ratio at initial phosphate concentrations lower than 5 mg/l should be very high and coagulant aids are not needed. At initial phosphate concentrations greater than 5 mg/l, the Al/P molar ratio decreases while initial phosphate concentration increases. Thus, addition of coagulant aids significantly increases phosphate removal efficiency. Although the Al/P molar ratio decreases significantly, the coagulant aids increase phosphate removal efficiency by about 8–30%. When initial phosphate concentration increases to 20 mg/l in spite of the low Al/P molar ratio (Al/P = 0.88), phosphate can be removed at high efficiency by using only tannin (or AN913) without adding clay.

To better understand the effect of polyelectrolytes on phosphate removal, the amounts of residual Al and PO_4^{3-} , and their forms in the supernatant are useful. In the experiments in which half the optimum aluminum doses were used residual Al and PO_4^{3-} concentrations in the supernatants after settling were measured, and the results are shown in Fig. 9. Residual aluminum may be present as small $\text{Al}(\text{OH})_3$ colloids and/or soluble species. On the other hand, residual phosphate may be adsorbed on colloids and/or may be involved in soluble Al species and/or may be free in solution.

Polyelectrolyte addition to the coagulation process may have two affects. In the first situation (low initial phosphate concentration), when polyelectrolyte is added, small positively charged $\text{Al}(\text{OH})_3$ colloids with phosphate adsorbed on them form larger flocs by bridging flocculation. In the second situation (high initial phosphate concentrations), there are soluble Al-phosphate species in the supernatant. When the polyelectrolyte is added, soluble Al-phosphate species precipitate by bridging. Thus, in both situations the addition of large anionic polymers further increases the phosphate removal.

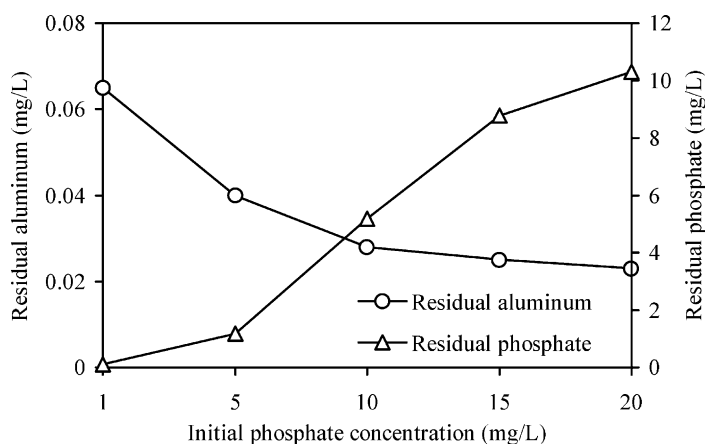


Fig. 9. Residual Al and PO_4^{3-} concentrations as a function of initial phosphate concentration.

Light scattering measurements were performed to detect whether aluminum in the supernatant is in the form of $\text{Al}(\text{OH})_3$ colloids or soluble Al-phosphate species. In the measurements, colloidal particles were not detected. It is concluded that residual aluminum in the supernatant is in the form of soluble Al-phosphate species.

4. Conclusions

Chemical phosphate removal during wastewater treatment is a complex process. However, the results of this comparative investigation on phosphate removal by coagulant and coagulant aids, namely alum and clay, tannin and AN913, support the following conclusions:

- In the removal of phosphate from synthetic water, alum was the most effective coagulant at all phosphate concentrations. At lower initial phosphate concentrations, phosphate was removed by adsorption of phosphate onto $\text{Al}(\text{OH})_3$ colloidal particles formed in the coagulation process. At higher initial phosphate concentrations, phosphate precipitated as AlPO_4 . Excess alum was required for complete removal of phosphate by alum alone, especially at lower phosphate concentrations.
- Adding coagulant aids (clay, tannin and AN913 studied) significantly increase phosphorus removal efficiency, by enhancing coagulation efficiency. In the coagulation process, the polymers attach themselves to $\text{Al}(\text{OH})_3$ flocs or to $\text{Al}(\text{OH})_3$ -coated clay particles. For the former, inter-floc bridges are formed which increase floc size and aid settling. For the latter, clay–polymer complexes are formed. In both cases, the flocs/complexes have an affinity for phosphate. The phosphate in aqueous solution is adsorbed onto the $\text{Al}(\text{OH})_3$ or clay–polymer complex and settles along with the flocs/complexes.
- Addition of coagulant aids decreases significantly the required alum dose.

Therefore, it can be concluded that the polyelectrolytes examined can be successfully used as a coagulant aid for removal of phosphate in wastewater treatment.

References

- [1] D.S. Bhargava, S.B. Sheldarkar, *Water Res.* 27 (2) (1993) 303.
- [2] K.C. Cheung, T.H. Venkitachalam, *Chemosphere* 41 (2000) 243.
- [3] A. Uğurlu, B. Salman, *Environ. Int.* 24 (8) (1998) 911.
- [4] T. Clark, T. Stephenson, P.A. Pearce, *Water Res.* 31 (10) (1997) 2557.
- [5] A.N. Onar, N. Balkaya, T. Akyüz, *Environ. Technol.* 17 (2) (1996) 207.
- [6] S. Yeoman, T. Stephenson, J.N. Lester, R. Perry, *Environ. Pollut.* 49 (1988) 183.
- [7] K. Fytianos, E. Voudrias, N. Raikos, *J. Environ. Sci. Health A31* (1996) 2621.
- [8] K. Faytianos, E. Voudrias, N. Raikos, *Environ. Pollut.* 101 (1998) 123.
- [9] J.P. Boisvert, T.C. To, A. Berrak, C. Jolicoeur, *Water Res.* 31 (8) (1997) 1939.
- [10] A.I. Omoike, G.W. vanLoon, *Water Res.* 33 (17) (1999) 3617.
- [11] M.A. Butkus, D.S. Grasso, P. Cristian, *J. Environ. Qual.* 27 (5) (1998) 1055.
- [12] M. Zhang, A.K. Alva, Y.C. Li, *Soil Sci.* 166 (12) (2001) 940.
- [13] M. Özacar, A study on the use of tannins, obtained from oak acorns (valonea), as natural polyelectrolyte in water treatment, Ph.D. thesis, Science Technology Institute, Sakarya University, Sakarya, Turkey, 1997.
- [14] A.V. Gray, *Effl. Water Treat. J.* 22 (1982) 68.
- [15] M. Özacar, İ.A. Şengil, *Turkish J. Eng. Environ. Sci.* 26 (3) (2002) 255.

- [16] M. Özacar, İ.A. Şengil, *Water Res.* 34 (4) (2000) 1407.
- [17] R.B. Broadhurst, W.T. Jones, *J. Sci. Food Agric.* 29 (1978) 788.
- [18] M.L. Price, L.G. Butler, *J. Agric. Food Chem.* 25 (6) (1977) 1268.
- [19] O.W. Lau, S.F. Luk, H.L. Huang, *Analyst* 114 (1989) 631.
- [20] M. Özacar, İ.A. Şengil, in: H. Ceylan, O.Y. Ataman (Eds.), *Spectrophotometric Methods for the Estimation of Tannins in Plant Tissues*, Proceedings of the 11th National Chemistry Congress, Van, Turkey, 1997, p. 502.
- [21] American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater*, 16th ed., New York, 1985.
- [22] T. Goldshmid, A.J. Rubin, *Sep. Sci. Technol.* 23 (14–15) (1988) 2269.
- [23] S.J. Duffy, G.W. vanLoon, *Environ. Sci. Technol.* 28 (11) (1994) 1950.
- [24] J. Temuujin, G. Burmaa, J. Amgalan, K. Okada, T.S. Jadambaa, K.J.D. MacKenzie, *J. Porous Mater.* 8 (2001) 233.
- [25] J.F. Lee, P.M. Liao, D.H. Tseng, P.T. Wen, *Chemosphere* 37 (6) (1998) 1045.