Turkish J. Eng. Env. Sci.
26 (2002) , 255 – 263.

The Use of Tannins from Turkish Acorns (Valonia) in Water Treatment as a Coagulant and Coagulant Aid

Mahmut ÖZACAR and İ. Ayhan ŞENGİL
Sakarya University, Science & Arts Faculty, Department of Chemistry,
54100 Sakarya-TURKEY
e-mail: mozacar@hotmail.com

Received 27.02.2001

Abstract

Coagulants play an important role in the treatment of water and wastewater and in the treatment and disposal of sludge. Aluminum sulfate, alum, is the common chemical coagulant used in the coagulation process. Recently polymers have been utilized in coagulation/flocculation processes for water purification. In this study, a natural indigenous coagulant is suggested as a substitute for alum or as an aid for alum. The coagulant characteristics of the tannins obtained from valonia were examined and whether or not tannins could be used as a primary coagulant and a coagulant aid was determined. Jar tests were done with a synthetic water prepared with varying pH and turbidity. It was found that the best slow stirring velocity and flocculation time were 45 rpm and 30 min, respectively. It was also found that tannins operated much better as a coagulant aid than as a primary coagulant. Tannin as a coagulant aid was more effective than synthetic anionic polyelectrolyte (AN913). At the optimum conditions with tannin, the turbidity decreased from 10 and 20 to <0.02 and 0.9 FTU (formazin turbidity units), respectively.

Key words: Tannins, Turkish acorn, Coagulant, Coagulant aid, Synthetic anionic polyelectrolyte.

Introduction

Tannins are high molecular weight polycyclic aromatic compounds widely distributed through the plant kingdom. Tannins can be classified into two groups (Haslam, 1989), the proanthocyanidins (or condensed tannins) and the polyesters of gallic acid and (or) hexahydroxydiphenic acid (hydrolyzable tannins, respectively, gallo- and ellagitannins). The co-occurrence of both kinds of tannins in the same plant or plant tissue is often observed. Tannins are found in the leaves, fruits, barks, roots and wood of trees (Scalbert *et al.*, 1989).

They are particularly important as raw material to tan hides, in oil-well drilling, production of adhesives (Aydın *et al.*, 1990), dyeing, pharmaceutical industries, corrosion inhibitors (Gust and Wawer, 1992), and for several other industrial uses.

Polymers have been utilized in coagulation/flocculation processes for water purification for more than three decades. Organic polymers may be used as primary coagulants as well as in the more traditional flocculation step of binding already formed small flocs into larger particles in drinking water treatment. Coagulation with organic polymers followed by sedimentation can clean up industrial effluent when the flocs formed are dense enough. A major use of organic polymers in water treatment is as a coagulant aid to bridge the coagulated particles formed when aluminum or iron salts have been used as the primary coagulant. The large aggregates formed then settle more rapidly (Bolto, 1995).

The main advantages of natural polyelectrolytes are ready acceptance on health grounds and ease of biodegradation. Tannins have already received attention. Of historical interest is the purification of drinking water with macerated seeds from the horseradish tree, while recently the enhanced extraction of algae from ponds with crushed red sorella seeds has been reported (Bolto, 1995).

Complex polysaccharide tannin derivatives have been used extensively in potable water, wastewater and industrial effluent treatment applications (Bratby, 1980). The reaction of tannin with formaldehyde and aminoethanol produces a weakly, basic polymer that is more effective than alum in removing turbidity and especially color from river water (Bolto, 1995). In addition tannin helps the filtration process. Özacar and Şengil (2000) studied the effect of tannin on filterability of sludge formed in the coagulation process and showed that the formed sludge could be filtered more easily when tannin was used as a coagulant aid. The various studies that have been conducted on water treatment using the tannins as a coagulant have revealed that the effectiveness of tannins depends mainly on the chemical structure of tannins that have been extracted from thet plant and the degree of tannin modification (Steiner, 1989; Pulkkinen and Mikkohen, 1992 (a) and (b); Özacar, 1997).

In this study, the use of tannin as primary coagulant and coagulant aid in water treatment has been investigated. The results are compared to alum and a synthetic anionic polyelectrolyte (AN913). The natural coagulant (tannin) was extracted from acorns (valonia).

Materials and Methods

Valonia is obtained from the corn cup of the oak which grows in Asia Minor. The tannin content of valonia is about 35%. Turkish oak is a source of valonia which grows in 260,000 hectare areas in Turkey, where there are two factories having extraction units producing tannin from valonia. Their capacities are about 5000 tons/year (Aydın *et al.*, 1990).

Tannin used in this study was obtained from Sümer Holding A.Ş. – Türkiye. In this factor tannins extracted from valonia using hot water. The tannin content of valonia extracted in this study was determined to be 53.50% hydrolyzable tannins according to the Vanilin-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).

Tannin solutions were prepared with a concentration of 1 mg tannin/mL and then solutions with a concentration of 0.01 and 0.1 mg tannin/mL were prepared by dilution with distilled water. The solutions were prepared daily. Since tannin is a natural anionic polyelectrolyte, a synthetic anionic polyelectrolyte was chosen to compare with the results obtained from the experiments with tannin. For this purpose, pre-experiments were done using AN905, AN912, AN913, AN934 and AN945. These showed that (AN913) (SNF Floerger, France) was the best anionic polyelectrolyte as a coagulant aid. AN913 solutions were prepared with a concentration of 1.0 mg AN913/mL and then solutions with a concentration of 0.1 mg AN913/mL were prepared by dilution with distilled water.

The jar tests were conducted in a system containing six paddles. In all these experiments before the best slow stirring velocity and time were determined, the velocity gradient, G, value for flash mixing was 566 s^{-1} and for coagulation 12 s^{-1}. The experiments were run by using synthetic water having different pH and turbidity values. The mineral composition of the water used to simulate the raw water is presented in Table 1. Turbidity values were adjusted with clay and pH was adjusted with 0.1 M HCl and 0.1 M NaOH. $Al_2(SO_4)_3.18H_2O$ (Merck) solution with a concentration of 1 mg Al^{3+}/mL was used in the jar test.

After the coagulants were added to the jars, rapid mixing was done for 1 min at 200 rpm and slow stirring for 15 min at 15 rpm. Fifteen minutes were allowed for the settling of the flocs. The turbidity of the supernatant, sampled from a 3 cm depth, was measured by using a Turbidimeter. The sensitivity of the instrument permits the detection of turbidity as low as 0.02 FTU (formazin turbidity units).

Results and Discussion

Tannin as a primary coagulant

The jar test experiments with $Al_2(SO_4)_3$, tannin and AN913, using synthetic water with turbidities of 10, 20, 50, 100, 200 and 300 FTU, and for each turbidity value with pH values of 6, 7, 8, 9, 10 and 11 respectively, were run. The results obtained are shown in Figures 1 and 2. It is seen from Figure 1 that the optimum pH is 7 for 10-100 FTU turbidities and it is 8 for 200 and 300 FTU turbidities. It was found that the optimum Al^{3+} doses at the optimum pH were 2, 2 and 3 mg Al^{3+}/L for 10, 20 and 50 FTU turbidities respectively, and it was 5 mg Al^{3+}/L for 100, 200 and 300 FTU turbidities (Figure 2). The efficiencies of the turbidity removal with $Al_2(SO_4)_3$ were found to be 96%, 97%, 98%, 98.5%, 99% and 98.3% for 10, 20, 50, 100, 200 and 300 FTU turbidities, respectively.

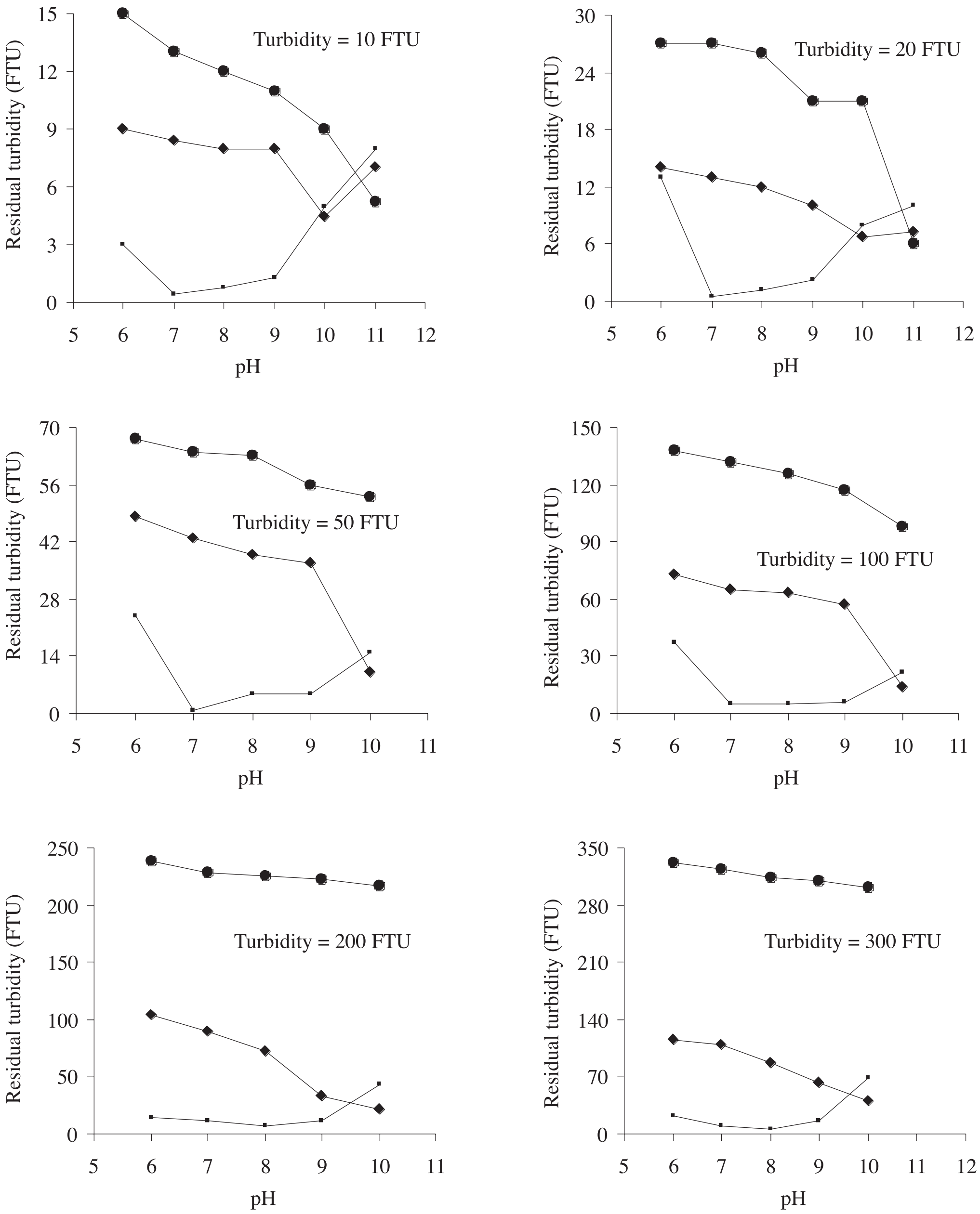

Figure 1. Effect of pH on turbidity removal ■ Al^{3+} (dose: 3 mg/L), • Tannin (dose: 0.1 mg/L), ♦ AN913 (dose: 0.1 mg/L)

As can be seen from Figure 1, tannin is only effective at pH 11. At this pH value, it is only possible to prepare synthetic water which 10 and 20 FTU turbidities. At pH 11, higher turbidities were not experimented on because of the difficulty of preparing stable suspensions. This is in agreement with the findings of Nozaki *et al.* (1993), who used the cactus as a natural polyelectrolyte in the cleaning of tannery waste. Finally, it is interesting to note that at low pH values (below pH 11), with tannin as a primary coagulant, the phenomenon of restabilization was clearly observed from Figure 1. It was found in the studies on the removal of turbidity using tannin, that the optimum tannin dose was 0.03 mg tannin/L, in which the optimum pH was 11 for 10 and 20 FTU turbidities (Figure 2). It was also found that the efficiencies of turbidity removal using tannin at the optimum conditions were 63% and 80.5% for

Table 1. The mineral composition of the tap water used to simulate raw water

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 : -			

10 and 20 FTU turbidities, respectively. Since both the optimum pH is as high as 11 and the efficiencies are lower than when alum is used in the turbidity removal from synthetic water, the use of tannin in water treatment as a primary coagulant is hardly ever preferred.

Examining Figure 1, it is seen that AN913 is effective at pH 10 only. The turbidity removal efficiencies with AN913 as a primary coagulant were 55%, 66%, 80%, 86% 91.5% and 86.7% for 10, 20, 50, 100, 200 and 300 FTU turbidities, respectively (Figure 2). It can be seen from Figure 2 that the coagulation power of AN913 is somewhat lower than that of alum for the two turbidity values of 10 and 20 FTU. AN913 could not be more effective at 10 and 20 FTU turbidities. This is in agreement with the literature. Synthetic organic polymers, whether cationic, anionic, or nonionic may not be effective coagulants for low turbidity waters, that is, 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). It can be concluded that AN913 performed better as a primary coagulant at turbidity levels about or higher than 50 FTU. However, the turbidity removal efficiencies of AN913 were found to be lower than those with alum.

Effect of mixing velocity on residual turbidity

The growth of floc is accomplished by gentle stirring. For this purpose, jar test experiments, with different mixing velocities during the flocculation process, were done at 10 and 20 FTU turbidities, at the effective pH values and the optimum doses of $Al_2(SO_4)_3$, tannin and AN913. The mixing velocity was varied from 15 to 90 rpm to obtain its optimum value where the residual turbidity was at a minimum. The results obtained are shown in Figure 3.

As can be seen from Figure 3, the optimum mixing velocity for the three coagulants is 45 rpm, which is equivalent to a G value of 60 s^{-1}. This result is comparable with the recommended G values in the literature, which are 20-70 s^{-1} for low-turbidity and 50-150 s^{-1} for high-turbidity (Cornwell and Bishop, 1981). The results in Figure 3 show an optimum flocculation intensity of 45 rpm, above which floc break up was observed for alum and tannin. The break up of flocs at higher rpm may be due to the surface erosion of flocs by turbulent drag or by bulgy deformation and floc splitting.

Effect of flocculation time on residual turbidity

The effect of flocculation time on residual turbidity was studied by varying the flocculation time from 10 to 60 min, at optimum pH, does and mixing velocity, for 10 and 20 FTU turbidities. The results obtained are shown in Figure 4.

As can be seen from Figure 4, the optimum mixing time for the three coagulants is 30 min. The figure shows an increase in residual turbidity with flocculation times. This could be due to the redispersion and restabilization of flocs at higher flocculation time. The results found are in agreement with the literature where Nozaki *et al.* (1993) and Şengil (1995) had shown that better results are obtained at a 30-min mixing time.

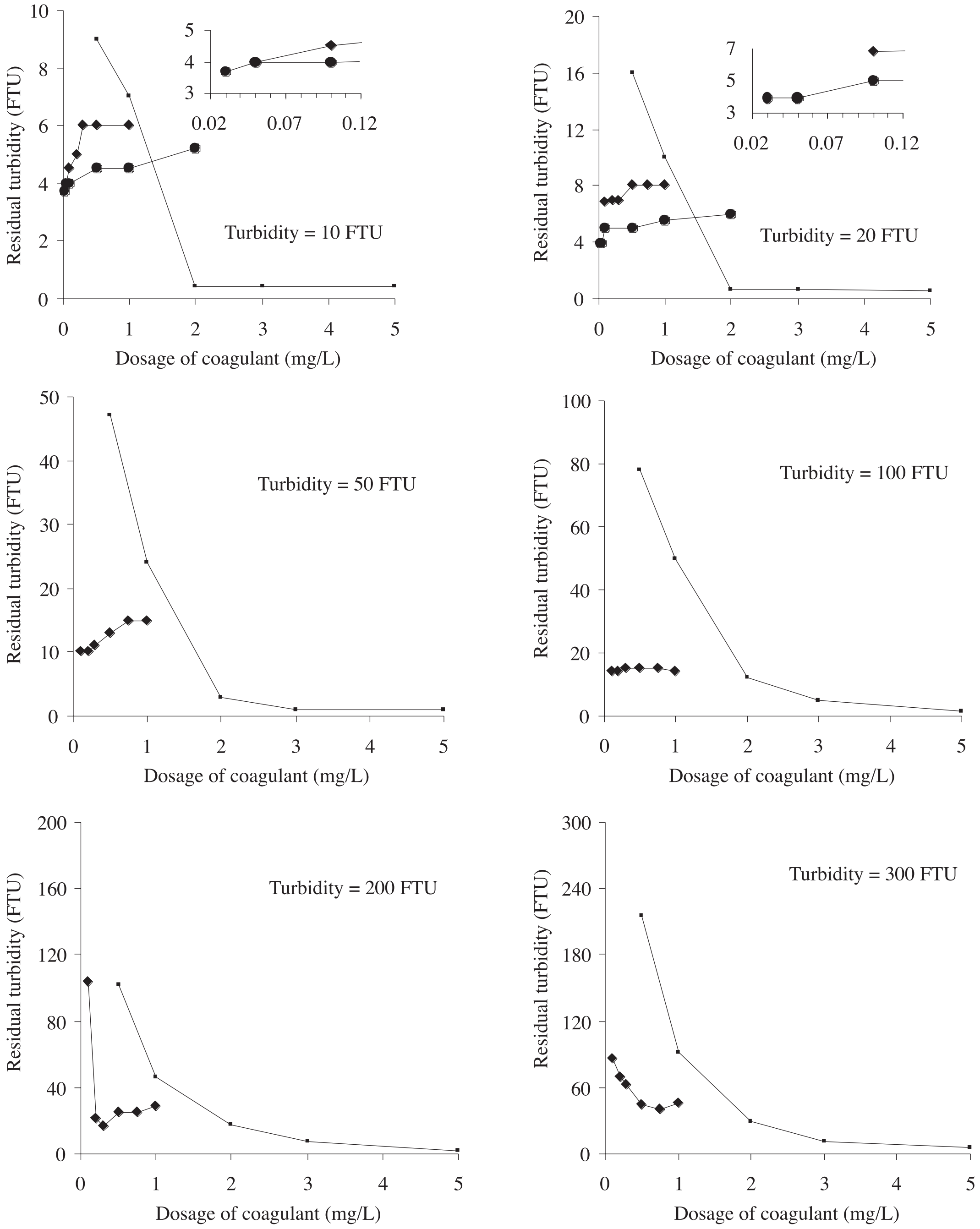

Figure 2. The comparison of three coagulants in removing turbidity ■ Al^{3+}(pH = 7 for 10-100 FTU and 8 for 200-300 FTU), ● Tannin (pH = 11), ♦ AN913 (pH = 10)

Tannin as a coagulant aid

After the $Al_2(SO_4)_3$ was added to the jars, a rapid mix was done for 1 min at 200 rpm, and coagulant aids (tannin and AN913) were added to the jars, and then slow stirring for 30 min at 45 rpm was performed. Half of the doses of the optimum $Al_2(SO_4)_3$ concentrations at optimum pH value in these studies in which $Al_2(SO_4)_3$ was used alone, and certain quantities of tannin as a coagulant aid were used to determine the optimum coagulant aid doses. The results obtained for the optimum doses of $Al_2(SO_4)_3$ and coagulant aid (tannin) are given in Table 2.

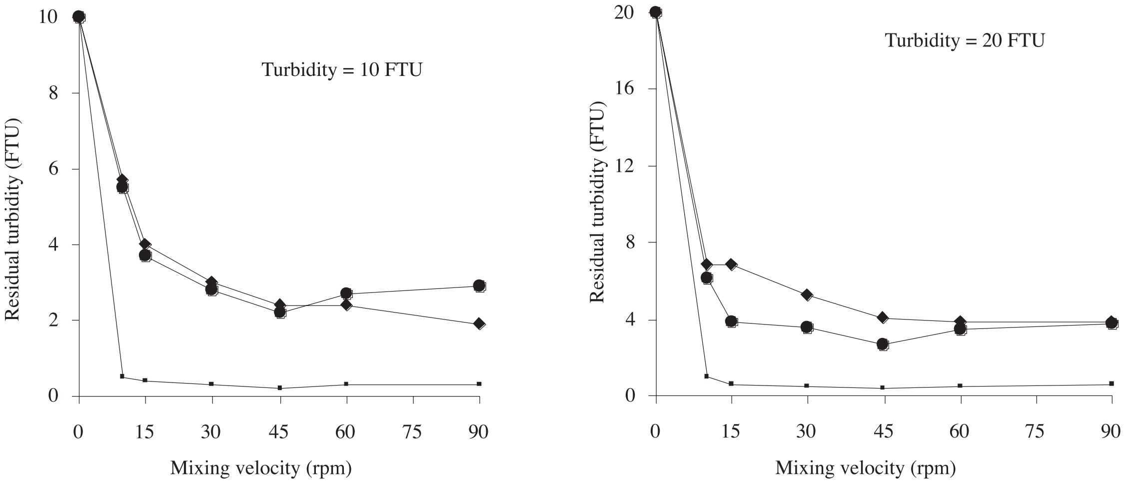

Figure 3. The effect of mixing velocity on turbidity removal ■ Al^{3+}, • Tannin, ♦ AN913

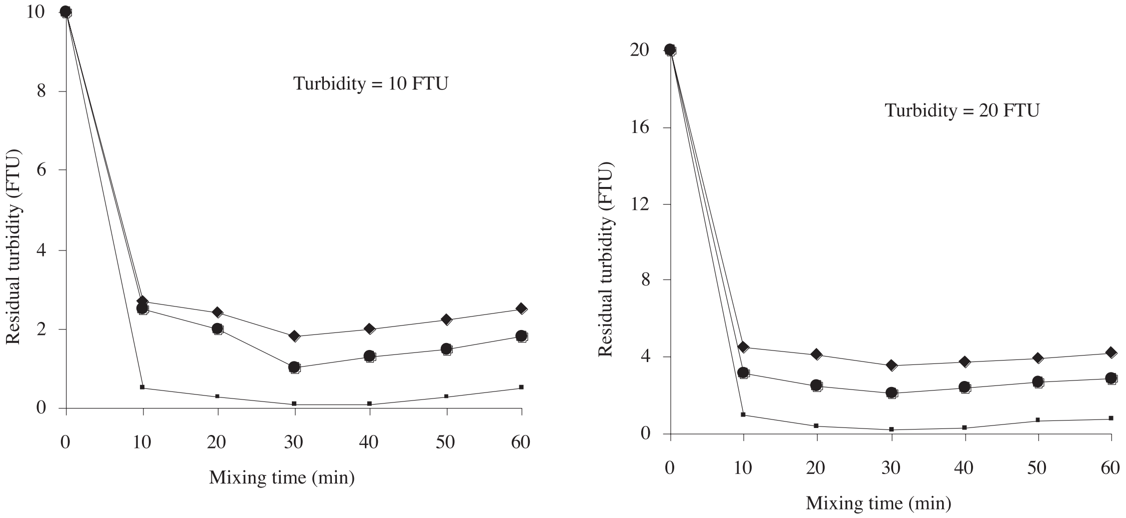

Figure 4. The effect of flocculation time on turbidity removal ■ Al^{3+}, • Tannin, ♦ AN913

The same experiments were rerun with AN913 as a coagulant aid to compare with the results obtained from experiments done with tannin as the aid. The results obtained are given in Table 2.

As can be seen from Table 2, the best results in terms of residual turbidity were obtained from the experiment using tannin as a coagulant aid. When tannin and AN913 are compared with respect to residual turbidity, it is seen that although AN913 precipitates, through forming dense flocs while stirring, the supernatant has a high residual turbidity. This situation occurs because the flocs formed by AN913 precipitate in a short time and the AN913 contact time in the dispersed medium is not long enough resulting in more residual turbidity. In the experiments with tannin, the turbidity decreased from 10 and 20 to <0.02 and 0.9 FTU, respectively, while in the experiments with AN913 it decreased from 10 and 20 to 2.4 and 10.3 FTU, respectively, at their optimum doses.

The effectiveness of tannin for removal of turbidity is due to the aluminum-tannin-clay particle complexes formed. At the pH of flocculation, complexing occurs between the soluble aluminum ions and the acidic functional groups of the tannin (predominantly carboxyl, but also some phenolic) that link it together. The reaction of tannin with a monomeric or polymeric Al(III) hydroxo species is kinetically faster than the precipitation of aluminum hydroxide (Rebhun and Lurie, 1993). Cationic aluminum interacts electrostatically with anionic tannin to form insoluble charge-neutral products (Gregor *et al.*, 1997).

Table 2. The effect of Tannin and AN913 as coagulant aids on turbidity removal

Initial turbidity (FTU)	pH	$Al_2\ (SO_4)_3$ as (mg Al^{3+}/L)	Residual turbidity (FTU)					
			Tannin added (mg/L)					
			0.03	0.05	0.10	0.50	1.00	2.00
10	7.0	1.0	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
20	7.0	1.0	0.9	0.9	0.9	0.3	0.3	<0.02
			Residual turbidity (FTU)					
			AN913 added (mg/L)					
			0.05	0.10	0.20	0.30	0.50	0.75
10	7.0	1.0	2.4	2.4	2.9	3.8	5.3	2.1
20	7.0	1.0	10.3	11.8	10.6	9.7	9.7	9.7
			Residual turbidity (FTU)					
			$Al_2(SO4)_3$ added (mg/L)					
			0.50	1.00	2.00	3.00	5.00	10.00
10	7.0		9.0	7.0	0.4	0.4	0.4	0.4
20	7.0		16.0	10.0	0.6	0.6	0.5	0.5

Table 3. The economic comparison of the $Al_2(SO_4)_3$ and coagulant aids

Optimum dose (g/1000m^3)			Price of coagulation (\$/1000m^3)
$Al_2(SO_4)_3$	Tannin	AN913	
2000			0.308
1000	30		0.178
1000		50	0.282
$Al_2(SO_4)_3$: 0.154 \$/Kg Tannin: 0.795 \$/Kg AN913: 2.553 \$/Kg			

There is a competition in the reaction with the coagulant between the soluble organic natural anionic macromolecule (tannin) and the mineral clay particles in suspension. The cationic coagulant reacts preferentially with the tannin (Narkis and Rebhun, 1997). The aluminum-tannin complex formation proceeds first, and the resulting products serve as bridging precipitates for the agglomeration of clay particles with the effect of charge neutralization of the clay (Tambo and Kamei, 1998).

Table 2 shows the remarkable effectiveness of using tannin as a coagulant aid in reducing the doses of the primary coagulant. This is in line with reported literature on coagulant aids whose main function is to reduce the doses of the primary coagulant (Al-Samawi and Shokralla, 1996). Tannin as a coagulant aid is quite efficient in reducing turbidity from raw waters, and also in sludge conditioning (Özacar and Şengil, 2000).

A cost analysis of $Al_2(SO_4)_3$, $Al_2(SO_4)_3$ + tannin and $Al_2(SO_4)_3$ + AN913 for a coagulation process are given in Table 3. As can be seen from Table 3, if tannin is used as a coagulant aid, the coagulation process will be cheaper than $Al_2(SO_4)_3$ by 42% and $Al_2(SO_4)_3$ + AN913 by 37%. If AN913 is used as a coagulant aid, it will be cheaper than $Al_2(SO_4)_3$ by 8.5%. So tannin usage in a coagulation process has an economic advantage.

Coagulation-flocculation followed by sedimentation, filtration and disinfection, often with chlorine is used worldwide in the water treatment industry before the distribution of treated water to consumers. Aluminum salts are by far the most widely used coagulants in water and wastewater treatment (Bratby, 1980). However, recent studies have pointed out several serious drawbacks of using aluminum salts, such as Alzheimer's disease and similar health related problems associated with residual aluminum in treated waters (Ndabigengesere and Narasiah, 1998).

Ferric salts and synthetic polymers have also been used as coagulants but with limited success, because of the same disadvantages as in the case of aluminum salts (Bratby, 1980). Therefore, it is desirable that other cost effective and more environmentally acceptable alternative coagulants be developed to supplement if not replace alum, ferric salts, and synthetic polymers (Ndabigengesere and Narasiah, 1998).

Trihalomethanes (THMs) may have carcinogenic and mutagenic properties, and concerns over human exposure prompted the US Environmental Protection Acency (USEPA) to place an upper limit of 0.1 mg/L on the mean of four quarterly measurements for total THM levels in finished drinking water. In the studies using tannin as a coagulant aid, the optimum tannin dose was found to be 0.03 mg/L. On the basis of the complex formation model between natural organic matter (NOM) and Al^{3+} ions which was suggested by Gregor *et al.* (1997), during the complex formation between tannin and Al^{3+} ions, three tannin molecules bind to each Al^{3+} ion. Initial tannin dose (0.03 mg/L) used in the experiments is almost used up or decreases below the 0.1 mg/L limit value, because of its complex forming with Al^{3+}. Thus, the tannin doses used do not lead to concentrations exceeding the limit set for THMs.

Conclusions

The following conclusions concerning the use of tannins as a primary coagulant and coagulant aid in water treatment were drawn:

1. The use of tannins as a primary coagulant could be a beneficial substitute for alum at high pH values, such as 11.

2. Required dose of tannin for the 10 and 20 FTU turbidity values were found to be generally much lower than those of alum and AN913.

3. Restabilization phenomenon was observed for all turbidity levels and pH values below pH=11 for tannins as a primary coagulant.

4. The use of AN913 as a primary coagulant could be at high turbidity levels (especially at a turbidity level of 50 FTU and above).

5. The optimum mixing velocity and flocculation time were found to be 45 rpm and 30 min, respectively.

6. The effectiveness of tannin as a coagulant aid was demonstrated by its power in reducing turbidity levels down to <0.02 FTU.

7. Comparing results obtained with tannins as a coagulant and as a coagulant aid, it was clear that tannins operated much better as a coagulant aid than as a primary coagulant. Furthermore it reduced the amount of required alum significantly. It was found that tannin could be used as a coagulant aid in water treatment.

References

Al-Samawi, A.A., and Shokralla, E.M., "An Investigation into an Indigenous Natural Coagulant", J. Environ. Sci. Health, A31(8), 1881-1897, 1996.

Aydın, K., Öztürk, T., Yorgun, S., and Gülbaran-Tülbentçi, H.S., "The Extraction of Tannin from Valonia with a New Extractor", JALCA, 85, 1-5, 1990.

Bolto, B.A., "Soluble Polimers in Water Purification", Prog. Polym. Sci., 20, 987-1041, 1995.

Bratby, J., Coagulation and Flocculation, Uplands Press, England, 1980.

Broadhurst, R.B., and Jones, W.T., "Analysis of Condensed Tannins Using Acidified Vanilin", J. Sci. Food Agric., 29, 788-794, 1978.

Cornwell, D.A., and Bishop, M.M., "Determining Velocity Gradients", AWWA Seminar on Coagulation and Filtration Back to the Basics, (ed., Tate, C.H.), Missouri, 103-123, 1981.

Gregor, J.E., Nokes, C.J., and Fenton, E., "Optimising Natural Organic Matter Removal from Low Turbidity Waters by Controlled pH Adjustment of Aluminum Coagulation", Wat. Res., 31(12), 2949-2958, 1997.

Gust, J., and Wawer, I., "The Studies of Relationship Between Structure and Anticorrosion Properties of Gallotannins. Part I", Polish J. Chem., 66, 733-741, 1992.

Haslam, E., Plant Polyphenols, Vegetable Tannins Revisited, Cambridge Univ. Press, U.K., 1989.

Lau, O.W., Luk, S.F., and Huang, H.L., "Spectrophotometric Determination of Tannins in Tea and Beer Samples with Iron (III) and 1,10-Phenanthroline as Reagents", Analyst, 114, 631-633, 1989.

Narkis, N., and Rebhun, M., "Flocculation in Presence of Organic Macromolecules of Natural Water and Secondary Effluents", Wat. Sci. Tech., 36(4), 85-91, 1997.

Ndabigengesere, A., and Narasiah, K.S., "Quality of Water Treated by Coagulation Using Moringa Oleifera Seeds", Wat. Res., 32(3), 781-791, 1998.

Nozaki, J., Messerschmidt, I., and Rodriguez, D.G., "Tannery Wastes Cleaning with Natural Polyelectrolytes. Chemical Speciation Studies of Chromium", Arq. Biol. Tecnol., 36(4), 761-770, 1993.

O'Melia, C.R., "Coagulation and Flocculation", Physicochemical Process for Water Quality Control, (ed., Weber W.J.), Wiley Interscience, New York, 61-109, 1972.

Özacar, M., "A Study on the Use of Tannins, Obtained from Oak Acorns (Valonia), as Natural Polyelectrolyte in Water Treatment", PhD. Thesis, Sakarya University, Science Technology Institute, Sakarya, 1997.

Özacar, M., and Şengil, İ.A., Spectrophotometric Methods for the Estimation of Tannins in Plant Tissues, Proceeding of XI. National Chemistry Congress, Van, 502, 1997.

Özacar, M., and Şengil, İ.A., "Effectiveness of Tannins Obtained from Valonia as a Coagulant Aid for Dewatering of Sludge", Wat. Res., 34(4), 1407-1412, 2000.

Price, M.L., and Butler, L.G., "Rapid Visual Estimation and Spectrophotometric Determination of Tannin Content of Sorghum Grain", J. Agr. Food Chem., 25(6), 1268-1273, 1977.

Pulkkinen, E., and Mikkohen H., Preparation and Performance of Tannin-Based Flocculants, In: Plant Polyphenols, (eds., Hemingway R.W. and Laks P.E.), Plenum Press, New York, 953-966, 1992a.

Pulkkinen E., and Mikkohen H., Cationic Tannins from Conifer Bark Extracts for Use in Wastewater Flocculation., Patent, Ger. Offen. DE 4, 219,343, 24 Dec 1992b.

Rebhun M., and Lurie M., "Control of Organic Matter by Coagulation and Floc Separation", Wat. Sci. Tech., 27(11), 1-20, 1993.

Scalbert, A., Monties, B., and Janin, G., "Tanins in Wood: Composition of Different Estimation Methods", J. Agr. Food Chem., 37(5), 1324-1329, 1989.

Steiner, P.R., Tannins as Specialty Chemicals: An Overview, In: Chemistry and Significance of Condensed Tannins, (eds., Hemingway R.W. and Karchesy J.J.), Plenum Press, New York, 517-523, 1989.

Şengil, İ.A., "The Utilization of Alunite Ore as a Coagulant Aid", Wat. Res., 29(8), 1988-1992, 1995.

Tambo, N., and Kamei, Y., "Coagulation and Flocculation on Water Quality Matrix", Wat. Sci. Tech., 37(10), 31-41, 1998.

USEPA, "Is Your Drinking Water Safe ?" Office of Water (WH-550), EPA 570/9-91-005. Washington DC, 1991.