

Evaluation of a tannin-based cationic polymer as a coagulant for coloured humic water

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ABSTRACT

The performance of a new commercial tannin-based cationic polymer (TBP) has been investigated at bench-scale in terms of its capability to coagulate colour and humic material. The TBP is characterised as a moderate-to-high molecular weight polymer ($\sim 600,000 \text{ g mol}^{-1}$) with a cationic charge ($\sim 3 \text{ meq g}^{-1}$) arising from a single tertiary amine group per monomer. The TBP is substantially affected by hydrolysis/hydration processes which lead to changes in its charge density and solubility with solution time and pH. Laboratory experiments were carried out to evaluate the optimal dose, pH and treatment performance of TBP with simulated and real coloured waters. With simulated water TBP was able to achieve a high dissolved organic carbon (DOC) reduction over a wide pH range (4–9), but the optimal dose increased with pH as a consequence of the loss of cationic charge and solubility. At pH 7, the coagulation performance of TBP was comparable to that of alum and polyDADMAC at optimum coagulant doses. With real coloured water, jar and flotation tests showed that the TBP was able to match the performance of a polymeric iron sulphate in terms of treated water colour and turbidity, but residual DOC was significantly higher with TBP.

Key words | cationic, coagulation, colour, humic, polymer, tannin

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INTRODUCTION

In water and wastewater treatment, coagulation/flocculation is most commonly achieved with inorganic metal salts, e.g. aluminium/ferric sulphate or polyaluminium chloride (PACl), owing to their proven performance, acceptable cost and relative ease of handling. However, in recent years there has been an increasing interest in the use of cationic polymers to partially or completely replace metal salts. The perceived advantages of such polymers, e.g. polyDADMAC (poly-diallyldimethyl ammonium chloride) and polyamines, include the reduced generation of voluminous sludge, the lower sensitivity to pH, the formation of strong and large flocs and the improvement of finished water quality. Various studies have considered the use of cationic polymers, either alone or in combination with inorganic metal salts, to treat surface waters. Several studies, for example [Lindqvist *et al.* \(2004\)](#), have observed that the

performance of cationic polyelectrolytes as primary coagulants is not as effective as inorganic metal salts in the removal of dissolved organic matter ($\sim 30\%$ reduction of UV_{254} with polyDADMAC, versus $\sim 70\%$ with ferric chloride). In contrast, [Bolto *et al.* \(1999\)](#) reported that organic polymers (e.g. polyDADMAC) were almost as effective as aluminium sulphate in the removal of dissolved organic matter ($\sim 85\%$ of the UV_{254} removal by aluminium sulphate). In practice, cationic polymers have been used successfully for many years in the direct filtration of coloured, upland waters ([Bolto & Gregory 2007](#)).

The treatment of coloured, low pH humic waters is particularly suitable for coagulation by cationic polymers owing to the predominance of a charge neutralisation mechanism under conditions where the electronegativity of the humic substances is low and the polymer cationic

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repeating units, and a reasonably narrow molecular weight distribution. The cationic nature of the polymer is believed to be a single tertiary amine group per monomer, giving a fully protonated charge density of approximately 3 meq g^{-1} at pH 4. In solution, the TBP is substantially affected by hydrolysis/hydration processes which lead to changes in its charge density and solubility with storage time and pH. Thus, the charge density (meq g^{-1}) reduces with pH to: 2.66 at pH 5, 2.05 at pH 6, 0.67 at pH 7, and 0.20 at pH 9. The aqueous solubility of the TBP at room temperature was found to be very high at $\text{pH} < 6$, but decreased sharply at pH 6–7. Thus, at a nominal concentration of 40 mg l^{-1} the degree of insolubility was determined as: 28% at pH 6; 40–48% at pH 7, 8 and 9. To avoid ageing effects, all TBP solutions were made freshly and used within several hours. Stock solutions of TBP were prepared either in de-ionised water at 3 g l^{-1} (simulated water tests), or in distilled water at 5 g l^{-1} (real water tests).

A commercial cationic polyelectrolyte, poly-diallyl-dimethyl-ammonium chloride (polyDADMAC), was provided by SNF Ltd, UK (Flobeads DB 45 SH). The polymer has a molecular weight and a charge density of approximately $1 \times 10^6 \text{ g mol}^{-1}$ and 6 meq g^{-1} , respectively. The product was supplied in solid form and diluted to give a stock solution of 2 g l^{-1} . Aluminium sulphate hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), 'alum', was obtained from Sigma-Aldrich Company Ltd, UK, and Feripol XL, a polymeric iron sulphate (13.75% w/w Fe), was provided by EA West, UK. Stock solutions of alum and Feripol were prepared weekly at concentrations of 5.4 g Al l^{-1} and 1 g Fe l^{-1} , respectively, and kept at 4°C .

Test solutions

Coagulation experiments were conducted in simulated and real coloured waters. The simulated water was prepared using commercial reagent grade humic acid, HA (Sigma-Aldrich Company Ltd, UK), and 5 g HA l^{-1} stock solutions were made from the humic acid product and de-ionised water (Millipore Q, $18.2 \text{ m}\Omega$). Working solutions at concentrations of $10\text{--}30 \text{ mg HA l}^{-1}$ were prepared from the stock solution with de-ionised water and pH was adjusted using 0.1 M NaHCO_3 , NaOH or HCl solutions. The overall water quality for the 30 mg HA l^{-1} solution is shown in Table 1.

Table 1 | Summary of simulated and real water quality

Parameter	Real water ^a	Simulated water ^b
pH	7.0	8.6
Total alkalinity ($\text{mgCaCO}_3 \text{ l}^{-1}$)	10	
Conductivity ($\mu\text{S cm}^{-1}$)	82	
Turbidity (NTU)	2.1	~0
Colour	76.4 ($^\circ\text{Hazen}$)	22.7 ($\text{abs}_{400} \text{ m}^{-1}$)
UV ₂₅₄ absorbance (abs m^{-1})	35.3	74.8
DOC (mgCl^{-1})	5.3	9.9
SUVA ^c	6.7	7.5
Aluminium ($\mu\text{g l}^{-1}$)	106	
Iron ($\mu\text{g l}^{-1}$)	192	
Manganese ($\mu\text{g l}^{-1}$)	3.7	
Ammonia (mgN l^{-1})	< 0.05	
Nitrate (mgN l^{-1})	0.4	
Total nitrogen (mgN l^{-1})	1.1	

^aBamford WTW.

^b 30 mg HA l^{-1} .

^cUV₂₅₄/DOC.

The samples of real water used in this study were obtained from an operational treatment works located in the north of England that employs Feripol XL as coagulant. The raw water is supplied from an upland reservoir and the water quality at the time of sampling is summarised in Table 1. It can be seen that the reservoir water has high colour and SUVA (specific ultraviolet absorbance) values, which indicate a highly aromatic, humic type organic content. The SUVA values for the real and simulated waters are similar which allowed the treatment performance of the two waters to be compared, as described subsequently.

Coagulation tests

The coagulation tests with simulated water were evaluated by use of a photometric dispersion analyser (PDA 2000, Rank Brothers, UK) in a modified jar test procedure. The PDA is an instrument for observing rapidly changing particle suspensions via an optical technique that analyses the light transmitted through a flowing suspension; the instrument measures the average transmitted light intensity (dc value) and the root-mean-square (rms) value of the fluctuating component. The output, either the rms or

rms/dc ratio, is qualitative in nature and serves as a relative measure of the change in particle size and density distributions (Gregory & Nelson 1986); it is referred to as the flocculation index (FI). Tests were carried out by connecting the PDA to a stirred 2 litre acrylic reactor ('Gator jar') where the coagulant was added to the humic solutions under defined mixing conditions. The Gator jar was equipped with an overhead, variable speed stirrer and constructed to a standard design (AWWA 2000) with a paddle speed-velocity gradient calibration that could be applied directly.

The optimum dosage of coagulant was determined at each pH value in the range of 4–9 and the experiments were performed under ambient conditions in an environmentally controlled laboratory (room temperature was $21 \pm 1^\circ\text{C}$). The dynamic coagulation tests were carried out under standard conditions which involved: the rapid addition of the coagulant to the suspension followed by paddle stirring at 200 rpm (350 s^{-1}) for 30 s; the stirring speed was then reduced to 50 rpm (48 s^{-1}) and held at this value for the required time (10–60 min). Coagulation/flocculation of the humic solution was indicated by a sharp rise in the FI and the maximum steady value of FI was taken for comparison between tests in order to identify the optimum polymer dosage and conditions (Gregory & Nelson 1986). A subsequent 30 min period of quiescent settlement was allowed after the stirring phase, and samples of the solution supernatant were taken for the measurement of colour (by Lovibond Nessleriser or UV absorbance at 400 nm) and dissolved organic carbon (DOC) (by TOC analyser: Shimadzu Ltd, Japan).

The coagulation tests with real water were evaluated by a standard jar test procedure involving 1 min of rapid stirring following coagulant addition, 15 min of 'slow' stirring to flocculate the water, and filtration by Whatman No. 50 filter paper ($2.7 \mu\text{m}$ nominal pore size); the resultant quality from these tests has been shown to be a good indicator of actual treated water. The water was first tested with a relatively wide range of TBP dose and without pH adjustment to determine the minimum dose required to provide an acceptable treated water quality. Subsequently, three doses were selected to evaluate the impact of both coagulant dose and pH value; the pH was adjusted using either H_2SO_4 or $\text{Ca}(\text{OH})_2$.

The dissolved air flotation process is widely used in the UK for the treatment of coloured humic waters and therefore the flotation performance of TBP with the real water was compared with that of Feripol XL using a laboratory flotation jar tester (Aztec, UK). For the flotation tests, one litre samples of the raw water were treated with TBP and Feripol XL at the optimum conditions of dose and pH previously determined for these coagulants. The coagulated, flocculated water was then dosed with 60, 80 and 100 ml of air saturated water (4.4 bar, $10\text{--}12^\circ\text{C}$) using a laboratory flotation jar tester. After flotation the clear water under the layer of floated contaminants was sampled. The quality of the clarified water from each of the samples (60 and 80 ml recycle) was analysed in detail; the samples dosed with 100 ml recycle were only analysed for turbidity, colour and UV absorbance as there appeared to be no further improvement in the samples receiving a greater dose of air.

RESULTS AND DISCUSSION

Simulated water tests

A series of coagulation tests was carried out with the simulated water at different pH values, beginning with low pH values which represent the most favourable and realistic conditions for destabilising humic substances. The results of the coagulation tests with 30 mg HA l^{-1} and TBP at pH 4, in terms of FI response, are shown in Figure 2. The optimal TBP dose was taken to correspond to the maximum steady value of FI response, and the changes in the solution DOC and UV-visible light absorbance. Since the addition of TBP itself gives rise to DOC and UV-visible light absorbance in the solution, the change in these parameters by coagulation was based on assuming that a unit dose of TBP corresponds to a given quantity of DOC and UV-visible light absorbance (previously determined). At pH 4 where the TBP has its greatest charge ($\sim 3 \text{ meq g}^{-1}$), the coagulation performance was relatively high (see Table 2) and a clear optimum dose stoichiometry of 1 g TBP: 1 g HA was observed; this is equivalent to 3 g TBP: 1 g DOC. Since humic acid and humic substances have been reported to have charge densities in the range $5\text{--}10 \text{ meq g}^{-1}$ DOC (e.g. Kam & Gregory 2001), and the corresponding optimal cationic dose

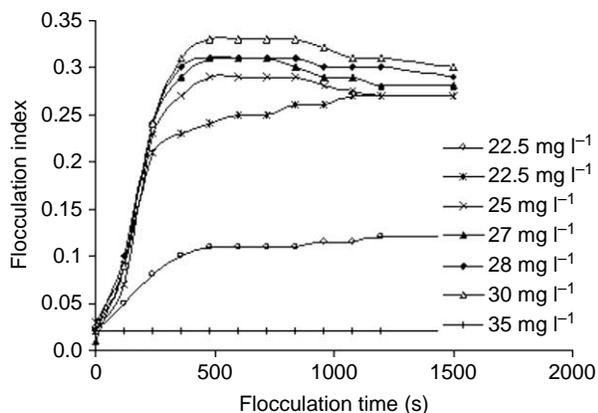


Figure 2 | Flocculation index response with TBP dose at pH 4 (30 mg l⁻¹ HA).

of TBP was 9 meq g⁻¹ DOC, the results broadly showed a charge equivalence at pH 4, and therefore confirmed a charge neutralisation mechanism.

A distinct dose stoichiometry was also observed at pH 7 where the TBP cationic charge is relatively weak (~0.7 meq g⁻¹), but the stoichiometric ratio was correspondingly higher at 2 g TBP: 1 g HA (Table 3). This ratio was surprisingly low, given that the polymer charge density was relatively weak and a much greater ratio would have been expected from the corresponding results at pH 4 based on charge neutralisation. However, the study of Kam & Gregory (2001) also reported that the optimum flocculation of humics occurred with less cationic charge in the case of low-charge polyelectrolytes than those with higher charge density. The specific reason for this is unclear and remains to be investigated.

In the alkaline range, where the polymer has very little cationic nature, there was no evidence of a close dose stoichiometry, as expected, and the optimal dose was comparatively high (6 g TBP: 1 g HA, at 10 mg HA l⁻¹ and pH 9). Nevertheless, the coagulation performance of

Table 2 | Coagulation performance of TBP with simulated water at pH 4

HA concentration (mg l ⁻¹)	Optimum TBP dose mg l ⁻¹ (TBP:HA)	FI	DOC reduction (%)	Colour * reduction (%)	
15	15	1	0.10	68.6	96.80
30	30	1	0.33	83.5	97.02
50	50	1	0.24	89.9	97.14

*Absorbance @ 400 nm.

Table 3 | Variation in optimum TBP dose with pH with simulated water

pH	Charge density (meq g ⁻¹)	Optimum TBP dose (mg l ⁻¹) (TBP:HA)	FI	DOC reduction (%)	DOC residual (mg l ⁻¹)	
4	3.07	30	1	0.33	83.50	4.353
7	0.67	58	2	0.35	83.26	6.854
9	0.20	60*	6*	0.25	80.61	6.804

*10 mg l⁻¹ HA.

Table 4 | Comparison of optimum coagulant doses with simulated water

pH	Optimum coagulant dose TBP (g/g DOC)	Alum (g Al/g DOC)	polyDADMAC (g/g DOC)
4	3.0		1.0
6	4.5	0.41	
7	5.8	0.68	1.4

the TBP in basic conditions was surprisingly strong with a TOC reduction of ~80% achieved (Table 3). In the absence of charge neutralisation in these conditions it is believed that TBP causes coagulation/flocculation of humic substances by mechanisms of polymer bridging and adsorption/enmeshment by solid phase TBP hydrolysis products.

Similar tests were conducted with the simulated water using alum and polyDADMAC as the coagulant, and the optimum dose at certain pH values for the three coagulants are compared in Table 4; the optimum dose was based on the maximum FI value from the PDA and the maximum DOC removal after the coagulation process. At pH 4, alum

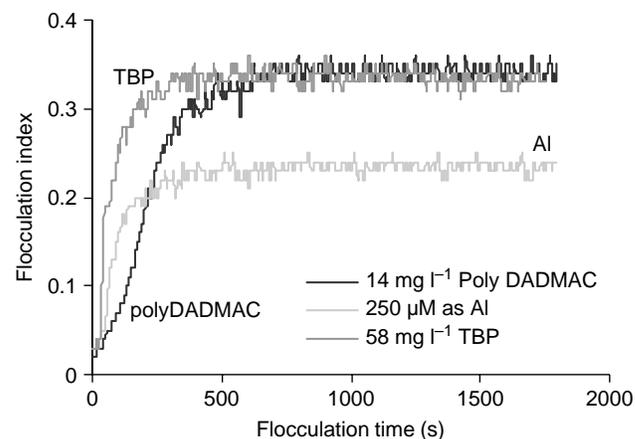


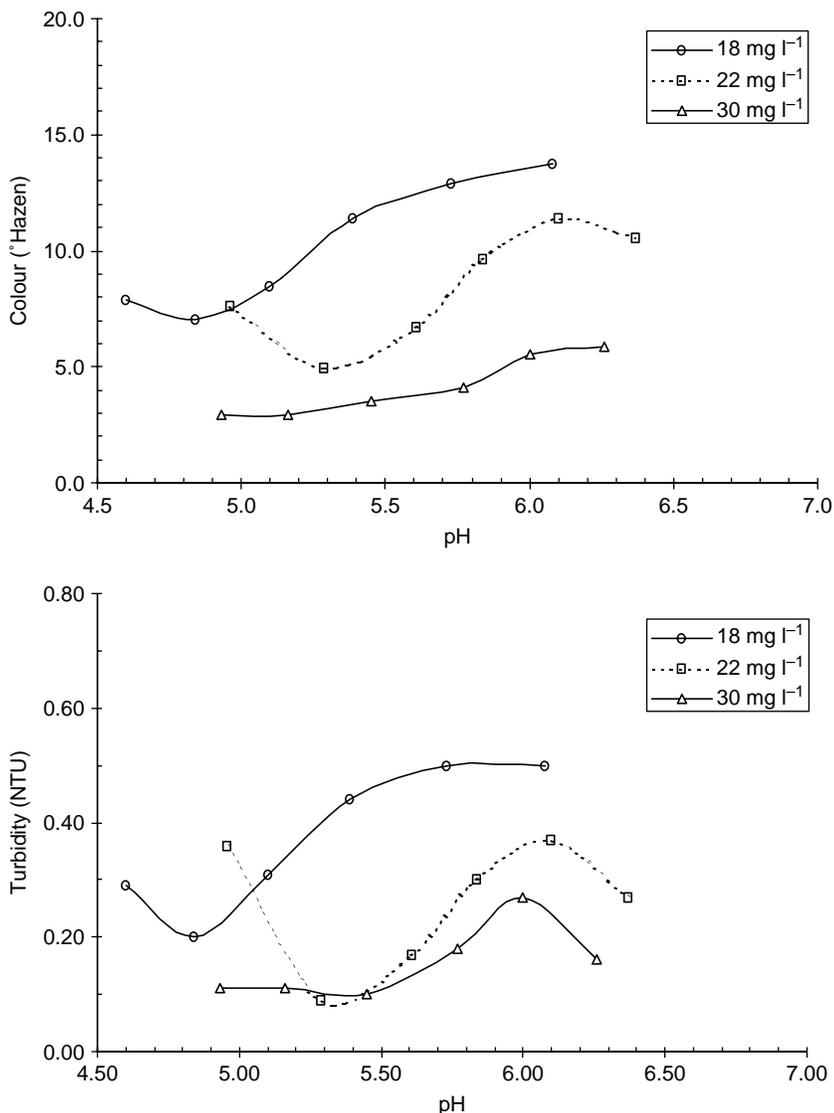
Figure 3 | Flocculation index response with different coagulants (at pH 7, and optimum dose).

Table 5 | Coagulation performance of coagulants with simulated water at pH 7

Coagulant	Optimum dose		FI	DOC reduction (%)	DOC residual (mg l ⁻¹)
	mg/l	(g/g DOC)*			
Alum (as Al)	6.8	0.68	0.24	88.11	1.19
PolyDADMAC	14	1.4	0.35	63.26	5.10
TBP	58	5.8	0.35	83.26	6.85

*30 mg HA l⁻¹ (DOC = 9.9 mg Cl⁻¹).

is not likely to be effective and coagulation tests were not carried out at this pH. The greater optimum dose for alum at pH 7 than at pH 6 was consistent with a greater HA electronegativity and the lower cationic charge nature of the Al hydrolysis species at pH 7. For polyDADMAC, the quaternary ammonium cationic charge is largely insensitive to pH, and thus the performance of the polymer reflects the change in HA electronegativity and the polymer

**Figure 4** | Coagulation of real water: effect of TBP dose and pH on residual colour and turbidity.

configuration and bridging mechanism with pH. These phenomena should cause a greater coagulation effect and a reduced optimal polymer dose at lower pH and this was found to be the case (Table 4).

Figure 3 and Table 5 summarise the coagulation performance at pH 7 for the different coagulants at their optimum doses. The results indicated clearly that in mass dose terms, the TBP was the least effective coagulant since its optimal dose was substantially greater than the other chemicals. However, it can be seen from Figure 3 that both cationic polymers promoted a much greater degree of coagulation/flocculation (possibly significantly larger flocs) than alum, with the maximum FI values (~ 0.35) about 1.5 times higher than that with alum (0.24). Also, the rate of coagulation with TBP appeared to be noticeably greater than for polyDADMAC. In terms of the overall removal of DOC, both TBP and alum achieved over 80% removal, and clearly out-performed polyDADMAC. However, it is noted that this removal degree includes the DOC added to the solution directly by the organic polymer itself, and a more valid comparison is given by the residual DOC in the filtered water. On this basis the TBP did not perform as well as the other coagulants (Table 5) and in general both polymers left significant quantities of DOC remaining in solution, which is undesirable in terms of final water quality.

Real water tests

A series of jar and flotation tests were undertaken with the samples of real water (Table 1) using both TBP and Feripol XL as coagulants. Based on some preliminary tests, TBP doses of 18, 22 and 30 mg l⁻¹ were selected to demonstrate the influence of dose and pH on treatment performance. Figure 4 shows the effect of dose and pH on the filtered water colour and turbidity. The results indicate that the pH range over which acceptable colour removal occurs broadens with increasing dose, and that colour removal deteriorates at higher pH. Based on this, it is suggested that for this water TBP would be used at a dose of 30 mg l⁻¹ and a pH of approximately 5.0. This dose is equivalent to 5.7 g/g DOC which is somewhat higher than the optimal dose found for the simulated water (3.0–4.5 g/g DOC) at a similar coagulation pH (Table 4). Three samples of treated/filtered water were taken for more detailed analysis (Table 6) and these are discussed below.

Initial coagulation tests with Feripol XL over a dose range of 5–8 mg Fe l⁻¹ and resultant pH range of 4.9–3.9 (no pH adjustment), gave filtered water colour values in the range 4.7–2.6°H. Based on these results, Feripol XL doses of 4, 5 and 6 mg Fe l⁻¹ were selected to demonstrate the influence of dose and pH on coagulation performance. Figure 5 shows the effect of Feripol dose and pH on filtered

Table 6 | Quality of real water and samples treated with TBP and Feripol XL

Dose*	pH	Filtered organic carbon (mgCl ⁻¹)	Filtered colour (°H)	Filtered UV ₂₅₄ (abs m ⁻¹)	Filtered turbidity (NTU)	Metals (µg l ⁻¹)		
						Al	Fe	Mn
Raw water								
–	7.0	5.3 [†]	79	37	1.08	106	192	3.7
Samples treated with TBP								
18	4.8	4.1	7.0	9.1	0.20	20	<10	15
22	5.3	4.2	5.0	7.4	0.09	2	<10	14
30	5.2	4.1	2.9	5.0	0.11	12	<10	14
Samples treated with Feripol XL								
4	4.2	1.9	3.2	4.1	0.08	36	107	41
5	4.5	1.9	2.6	3.4	0.09	42	74	52
6	4.2	1.4	1.5	2.6	0.06	48	74	54

*mg l⁻¹ as either TBP or Fe.

[†]Dissolved organic carbon.

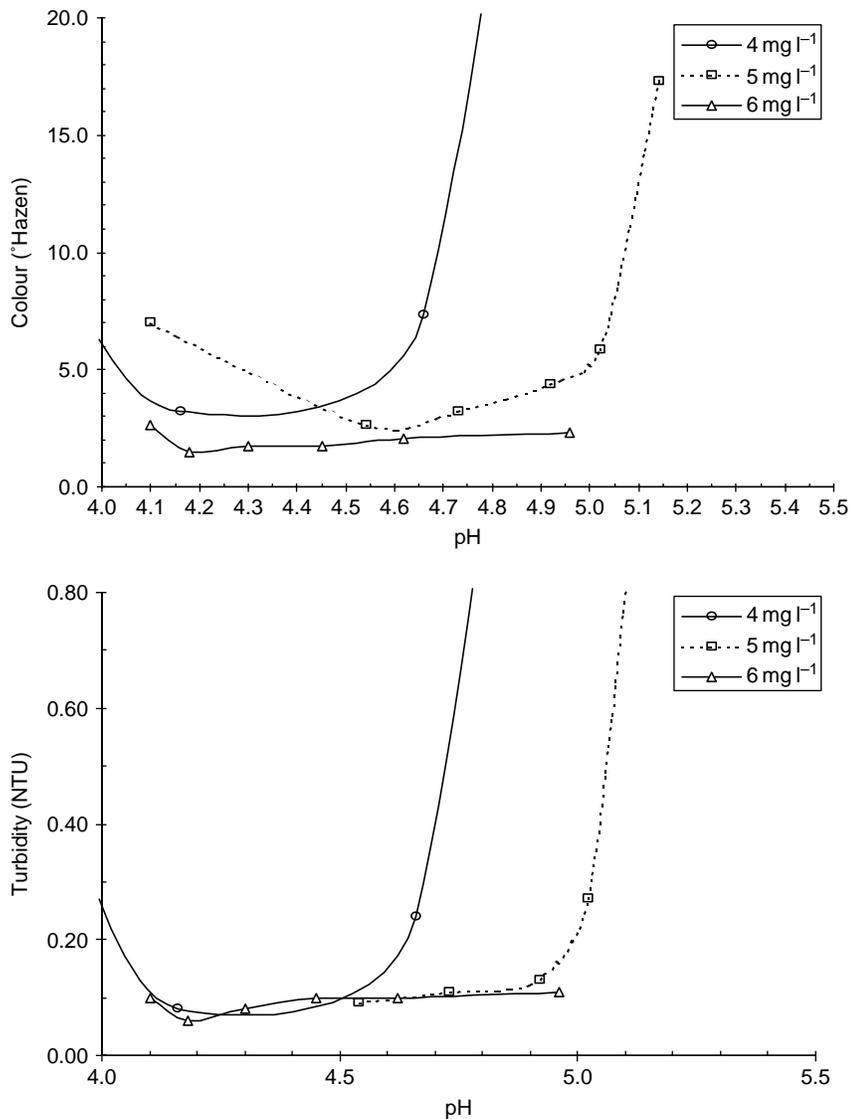


Figure 5 | Coagulation of real water: effect of Feripol XL dose and pH on residual colour and turbidity.

water colour and turbidity. The results show a typical pattern of broadening of the pH range, with dose, over which acceptable colour removal occurs, and a sharp deterioration at higher pH values. Based on these results the optimal dose and pH value were the same as used at the treatment works where the raw water samples were taken from, specifically 5 mg Fe l⁻¹ and 4.6, respectively. Again, three samples of treated/filtered water were taken for more detailed analysis (Table 6).

The quality of the three samples of treated/filtered water selected from the tests with TBP and Feripol XL are shown

in Table 6 and at optimal conditions of coagulation the following conclusions can be drawn:

- The colour and turbidity values for both coagulants were very similar.
- The TOC for the TBP treatment (~4.1 mg C l⁻¹) was more than double the Feripol treated samples (~1.7 mg C l⁻¹). This is consistent with the results from the simulated water tests comparing the performance between TBP and alum. It was noted that for the TBP treatment the TOC concentrations remain unchanged despite marked changes in filtered colour and UV absorbance, indicating

Table 7 | Quality of post-flotation samples treated with TBP and Feripol XL

	TBP: 30 mg l ⁻¹ , pH 4.9			Feripol XL: 5 mgFe l ⁻¹ , pH 4.6				
Volume of recycle (ml)	60	80	100	100	60	80	100	100
Turbidity (NTU)	0.6	0.4	0.6	0.5	1.0	0.9	0.9	1.0
Colour (°H)	10.0	8.5	9.1	8.8	19.3	17.9	18.2	18.5
UV ₂₅₄ Abs (m ⁻¹)	9.2	8.3	9.0	8.6	9.4	8.9	9.1	9.4
Total Al (µg l ⁻¹)	7.9	15.2	n/a	n/a	51.8	33.2	n/a	n/a
Total Fe (µg l ⁻¹)	< 10	< 10	n/a	n/a	280	260	n/a	n/a
Total Mn (µg l ⁻¹)	17.6	17.1	n/a	n/a	47.8	50.1	n/a	n/a
TOC (mgC l ⁻¹)	3.6	3.9	n/a	n/a	1.3	1.5	n/a	n/a

n/a = not analysed.

that either very fine particulate or soluble organic matter was passing into the filtrate.

- Feripol XL gave significantly higher background metals concentrations relative to TBP. This was believed to be due to the iron and manganese contributed by the Feripol; the greater aluminium concentration is because the Feripol coagulation was undertaken at a relatively acidic pH value of 4.2 where aluminium is more likely to be in dissolved form.

The results of the flotation tests are shown in Table 7. The pattern of results reflected those obtained from the jar testing whereby the metals concentrations were lower for the TBP treated water, but the TOC concentration was greater. The turbidity was significantly greater for the Feripol test relative to the TBP test possibly indicating that the residual flocs are smaller/more dispersed; this also explains why the colour and UV absorbance were greater for Feripol XL relative to TBP. The results may indicate that TBP produced a stronger floc than Feripol XL.

CONCLUSIONS

The application of natural polymers as primary coagulants in water treatment is of increasing interest and the tannin-based polymer described in this study is a commercially available product with interesting properties. At low pH (<6) the TBP behaves as a soluble cationic polyelectrolyte with a significant charge density (~3 meq g⁻¹), but it substantially loses its charge and solubility at neutral and

higher pH values. This sensitivity to hydrolysis/hydration processes makes the behaviour of TBP similar to that of conventional metal salt coagulants. Although the treatment performance of the TBP at elevated pH (pH 9) was surprisingly effective, presumably through mechanisms of polymer bridging and precipitation enmeshment ('sweep' type coagulation), the TBP dose required was significantly high (~18 g/g DOC) and this would be undesirable in practice from economic and residual polymer considerations.

The most effective approach to treating coloured, humic waters is under low-to-neutral pH conditions, usually at their natural pH, which can range between pH 4 and 7. Under these conditions in our study the TBP was able to achieve destabilisation and removal of humic substances by charge neutralisation with a dose stoichiometry in the range of 3–6 g/g DOC. This range of stoichiometric ratio was greater than was found in our tests with the polyDADMAC (1–1.4 g/g DOC), which can be attributed to the greater charge density and molecular weight of polyDADMAC compared with TBP. A recent study of the treatment of humic substances by the natural polymer chitosan indicated an optimal dose of 1–2.4 g/g DOC for the pH range 5–7 (Vogelsang *et al.* 2004), suggesting a superior effectiveness, in terms of optimal dose, compared with TBP. However, although the molecular weight of chitosan was believed to be greater than TBP, no information on its charge density was cited in the reported study with which to compare it with TBP and polyDADMAC.

Comparison of the coagulation performance of TBP with alternative organic and inorganic coagulants, in terms

of the removal of organic colour/humic substances, is difficult since the presence of organic polyelectrolytes (i.e. TBP and polyDADMAC) contribute themselves to the pool of organic material in solution. Thus, measurements of changes in DOC or UV absorbance cannot clearly distinguish between the background organic substrate and the polymer. Notwithstanding these difficulties, the results in this study indicate that TBP as a primary coagulant was capable of achieving a treated water quality almost equivalent to that of the polymeric iron salt under conditions identical to those at full scale. Although the residual organic content of the water treated by TBP was clearly greater than was found with Feripol in the jar and flotation tests, and with alum in the simulated water jar tests, the much lower metal ion residuals with the use of TBP, evident from both the jar and flotation tests, may be a particular advantage in practice. An optimal arrangement to achieve both low residual organics and metal ions may be the combination of TBP with a metal-ion coagulant and this will be evaluated subsequently.

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