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Surface water and wastewater treatment using a new tannin-based coagulant. Pilot plant trials

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ABSTRACT

A new tannin-based coagulant-flocculant (*Tanfloc*) was tested for water treatment at a pilot plant level. Four types of water sample were treated: surface water (collected from a river), and municipal, textile industry (simulated by a 100 mg L^{-1} aqueous solution of an acid dye), and laundry (simulated by a 50 mg L^{-1} aqueous solution of an anionic surfactant) wastewaters. The pilot plant process consisted of coagulation, sedimentation, and filtration. The experiments were carried out with an average coagulant dosage of 92.2 mg L^{-1} (except in the case of the surface water for which the dosage was 2 mg L^{-1}). The efficacy of the water purification was notable in every case: total turbidity removal in the surface water and municipal wastewater, about 95% dye removal in the case of the textile industry wastewater, and about 80% surfactant removal in the laundry wastewater. Filtration improved the removal of suspended solids, both flocs and turbidity, and slightly improved the process as a whole. The efficiency of *Tanfloc* in these pilot studies was similar to or even better than that obtained in batch trials.

1. Introduction

Given the need to implement water treatment technologies that are appropriate for specific wastewater effluents, and adapted to the constraints of developing countries, the potential of natural coagulants as sustainable and readily available options is increasingly being recognized and studied at a laboratory level (Beltrán-Heredia and Sánchez-Martín, 2008a,b, 2009b). These agents are typically easy for unskilled personnel to handle and maintain. Examples of such natural coagulants are *Moringa oleifera* (Fuglie, 2001) and *Opuntia ficus* (Young et al., 2005).

Studies of plant products as potential water treatment agents have a long history. In particular, wood derivatives are considered to be highly effective adsorbents (Geay et al., 2000). The original natural material is usually modified by a thermal process that leads to the development of a microporous structure. The actual chemical modifications are incompletely understood (Kawamoto et al., 1990) due to the complex nature of wood as a raw material.

The term tannins covers many families of chemical compounds. Traditionally they have been used for tanning animal skins, hence their name, but one also finds several of them used as flocculants. Their natural origin is as secondary metabolites of plants (Schofield et al., 2001), occurring in the bark, fruit, leaves, etc. While *Acacia* and *Schinopsis* bark constitute the principal source of tannins for the leather industry, the bark of other non-tropical trees such as *Quercus ilex*, *Quercus suber*, *Quercus robur*, *Castanea*, and *Pinus* can also be tannin rich.

The product *Tanfloc* is a trademark of the TANAC company (Brazil). It is a tannin-based product, modified by a physicochemical process, with a high flocculant power. It is obtained from *Acacia mearnsii* de Wild. bark. The tree is very common in Brazil and has a high concentration of tannins. The industrial production process of *Tanfloc* is protected by intellectual patents – the US patent number is 6,478,986 B1 – but similar procedures are referred to as Mannich-based reactions (Tramontini and Angiolini, 1994). It involves tannin polymerization through the addition of formaldehyde (37%), ammonium chloride, and commercial hydrochloric acid. The resulting product, obtained under specific temperature conditions, has a viscous appearance, and contains 36% active material. There have been earlier studies of *Tanfloc's* coagulant activity (Graham et al., 2008; Beltrán-Heredia and Sánchez-Martín, 2008c; Beltrán-Heredia et al., 2009b).

The objective of the present work was to characterize the coagulant and flocculant's activity of Tanfloc as a wastewater treatment agent implemented in a pilot plant. In this plant, the coagulation and flocculation stages are followed by slow sand filtration, so that the treatment can be scaled up in future studies.

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2. Materials and methods

2.1. Buffered solution

The trials with added dye (textile wastewater simulation) and surfactant (laundry water simulation) were performed with pH-stable media. To this end, a pH-7 buffer solution was prepared of 24 g of NaH_2PO_4 and 17.60 g of Na_2HPO_4 in 20 L of water. The pH was then adjusted to 7 with HCl 1M or NaOH 1M. All reagents were analytical grade from PANREAC.

2.2. Coagulant solution and wastewater samples

Three types of wastewater and surface water were studied:

- Textile industry effluent wastewater was simulated with an aqueous solution of a dye. In particular, a stock solution of ca. 100 mg L^{-1} of Alizarin Violet 3R (Aldrich) was prepared by mixing appropriate amounts of this dye into the buffered solution. This intense violet dye is a synthetic anthraquinonic characterized by high chemical and biological oxygen demand (Zollinger, 1987). These characteristics make industrial effluents containing this dye highly toxic and extremely injurious to both aquatic and terrestrial life forms (Cabaço et al., 2008). The difficulty of removing or degrading this dye is well documented (Robinson et al., 2001). It is mainly caused by the five aromatic rings and the two sulfonated groups (Fig. 1) that give it its persistent character. It belongs to the acid family of dyes, which are extensively used to dye wool, silk, and synthetic polyamide fibers in bright shades (Schoenauer et al., 1977).
- Laundry wastewater was simulated by a surfactant solution. In particular, a stock solution of ca. 50 mg L^{-1} of sodium dodecylbenzene sulfonate (SDBS, Chem. Service Inc.) was prepared by dissolving the corresponding amount of this surfactant in the buffered solution. This compound belongs to the linear alkylbenzene sulfonate family (Fig. 2), and is commonly used as a detergent and dispersant. Wastewater containing surfactants (from detergent manufacturers or from laundries) usually presents a high COD (up to 50 g L^{-1}) (Patterson et al., 2006) which is a cause of problems in normal water treatment plants. Surfactants greatly affect food chains due to their harmful and noxious character for aquatic animal and plant life. The main routes by which surfactants can alter environmental equilibrium are contamination of groundwater and lakes (Cserháti et al., 2002), association with pharmaceuticals (thereby considerably enhancing their contaminating potential), biopersistence, and toxicity for animals including humans (Clara et al., 2007).
- Real municipal wastewater, collected from a sewage treatment plant. This effluent is considered to be a hazardous product (Otterpohl et al., 1997) since it normally contains contaminants from industrial and residential zones. It needs to be suitably treated in order to avoid environmental (Koivunen et al., 2003) and health problems (Cabaço et al., 2008; Sherwin, 2000). Our samples were taken from the sewage treatment plant of La Albuera, a small town near the city of Badajoz (south-west Spain). This sewage treatment plant was constructed about 5 years ago. It receives municipal wastewater from approximately 4000 people. The sources of contamination are household effluent and some agricultural waste and slurry. The effluent has a moderately low COD. The average incoming flow rate is 41 m^3 h^{-1}, with the maximum permissible being 125 m^3 h^{-1}. The water sample was collected after the removal of large solids, but before the separation of oil and sand. Its main physicochemical properties are given in Table 1, and are within the range reported by the plant's management (JOCA, 2006). Compared with the literature data for other sewage wastewaters (Arslan-Alaton et al., 2007; Gómez-Cerezo et al., 2001), this water has a lower pollutant load. This is probably due to the nature of the waste, especially its domestic origin, as is appropriate for testing *Tanfloc* as a technology of potential use for small communities (Dorf, 2001).
- Surface water was collected from the River Guadiana, in Badajoz (south-west Spain, Extremadura Community). This choice of studying an actual surface water avoided the need to simulate turbidity with different physicochemical procedures such as kaolin addition (Ghebremichael, 2004). This water was treated on the day of its collection. Its main characteristics are also given in Table 1.

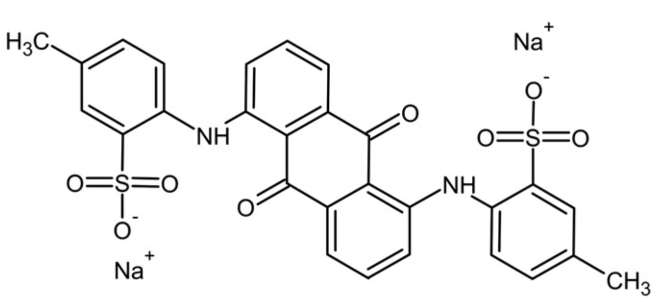

Fig. 1. Chemical structure of Alizarin Violet 3R.

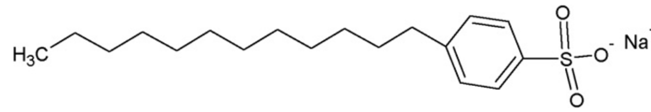

Fig. 2. Chemical structure of sodium dodecylbenzene sulfonate (SDBS).

Tanfloc stock solution, 1000 mg L^{-1}, was prepared by dissolving appropriate amounts of coagulant in distilled water. Although the production process of *Tanfloc* is patented, the product seems to be an aqueous extract of plant tannin, consisting mainly of flavonoid

Table 1
Municipal wastewater and surface water characterization data.

Parameter	Municipal wastewater	Surface water	Units
pH	8.2	7.5	
Conductivity	1006	400	$\mu S\ cm^{-1}$
Suspended solids	100	15	mg L^{-1}
Total solids	650	452	mg L^{-1}
Turbidity	82.5	123.3	NTU
Chloride	21.3	40.4	Cl^- mg L^{-1}
Calcium	94.6	37.7	Ca^{2+} mg L^{-1}
Hardness	444	152	$CaCO_3$ mg L^{-1}
Ammonium	2.1	1.81	N mg L^{-1}
Nitrate	22.5	5.3	NO_3^- mg·L^{-1}
Nitrite	0.04	0.033	N mg L^{-1}
Phosphate	7.3	0.044	P mg L^{-1}
Total phosphorus	11.9	0.064	P mg L^{-1}
Chemical oxygen demand	320	N/A[a]	O_2 mg L^{-1}
Biological oxygen demand	262	N/A[a]	O_2 mg L^{-1}
$KMnO_4$ oxidability	65.6	19.3	O_2 mg L^{-1}
Polyphenols	6.4	N/A[a]	Tannic acid equivalent mg L^{-1-1}
Anionic surfactants	19.6	N/A[a]	mg L^{-1}
Total coliforms	N/A[a]	800	Colonies/100 mL
Faecal coliforms	N/A[a]	400	Colonies/100 mL
Faecal streptococcus	N/A[a]	140	Colonies/100 mL

[a] Not appropriate.

structures with an average molecular weight of 1.7 kDa. It is presented in powder form. Other groups, such as hydrocolloid gums and soluble salts, are also present (Fig. 3 shows a probable approximation). The industrial production of *Tanfloc* involves the reaction between formalin, ammonium chloride, and commercial hydrochloric acid. The mixture is stirred and heated, and the tannin extract is added. The reaction is maintained for several hours until a viscous mixture with 40% of solid content is achieved. *Tanfloc* in its powder form is obtained by allowing this mixture to evaporate (Lamb and Decusati, 2002). Toxicological information on *Tanfloc* is given by TANAC (TANAC, 2009). There are no indications of health risk at operational dosages, since the 50% lethal dose (LD_{50}) for mice is 9241 mg kg^{-1}. This compares with the case of alum, for example, for which another supplier (Comercial Godó, Spain) gives an LD_{50} of 1735 mg kg^{-1} (GODÓ, 2004).

2.3. Analytical procedures

All analytical determinations were performed in accordance with American Public Health Association standard methods (APHA, 1998).

Dye concentration was determined by photometric analysis in a 1-cm glass cell. The maximum absorbance wavelength was 549 nm and a linear relationship of absorbance versus dye concentration was deduced at this wavelength.

The anionic surfactant concentration was determined by a method based on its association with methylene blue (Tôei and Fujii, 1977). The final surfactant concentration was determined by visible spectrophotometry at 652 nm, with zero being set using pure trichloromethane. The spectrophotometer used was a HEL-λIOS (Unicam, England) UV-Vis.

The COD was determined using a Selecta mod. Tembloc oven, a PF-10 Macherey–Nagel photometer, and pre-prepared test cuvettes for the desired measurement range (50–1000 mg $O_2 \cdot L^{-1}$). This corresponds to the APHA-AWWA-WPCF standard method 5220-D (APHA, 1998) of closed reflux with colorimetric measurement. The COD value was determined colorimetrically by the absorbance at 600 nm. The BOD_5 was determined using an electronic pressure sensor in an OxiTop-C system (WTW) with biosystem seeds (Cole–Parmer).

Turbidity was measured using an HI93703 turbidimeter (Hanna instruments).

2.4. The pilot plant

The pilot plant consists of coagulation/flocculation, sedimentation, and slow sand filtration sections. Table 2 lists the design parameters, and Fig. 4 is a schematic diagram of the installation. The water inflow was 77 mL min^{-1}. A period of 20 min was fixed for coagulation and mixing, followed by 1 h for sedimentation of the flocs. These experimental conditions were set by taking into account the results of the published preliminary studies (Sánchez-Martín et al., 2009; Beltrán-Heredia et al., 2009a,b; Beltrán-Heredia and Sánchez-Martín, 2009a). Two peristaltic pumps with their corresponding flow regulators completed the installation – one for the raw water (DINKO 25-V, Dinter) and another for the *Tanfloc* solution (MASTERFLEX DV, Cole–Parmer). The operating conditions are listed in Table 2, and the specific data of the sand filter in Table 3.

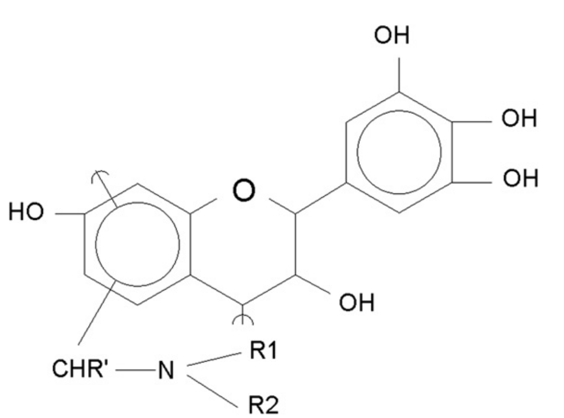

Fig. 3. Probable chemical structure of *Tanfloc*.

2.5. Jar-test

In order to compare the efficiency of *Tanfloc* in the pilot plant and in batch trials, normalized jar tests were carried out for each water treated. To aliquots of 1 L of raw water in a beaker, the equivalent dose of coagulant was added for each case (see Table 2), followed by stirring at 30 rpm for 1 h. After a further 1 h to allow the flocs to settle, a sample was taken at 3 cm below the surface in the center of the beaker, and centrifuged if required (for the dye and surfactant determinations).

3. Results and discussion

The efficacy of each process needs to be compared with the corresponding batch trial results. To this end, one must first define an objective measure of the efficiency of the removal of the specific contaminant relative to the amount of coagulant. The parameter extensively used in adsorption processes is the coagulation capacity, *q*. Our working hypothesis was that contaminant removal by coagulation and flocculation occurs in two stages. First, there is destabilization of colloids which may be governed by chemical interactions between molecules of the coagulant (cationic, positively charged) and of the contaminant (anionic, negatively charged). Then, once the coagulant–contaminant complex has been formed, flocs begin to grow by sorption mechanisms. This should be the controlling stage, so that the entire process can be simulated as an adsorption phenomenon. Previous studies have found the coagulation capacity *q* to be a suitable evaluation parameter (Beltrán-Heredia et al., 2009b). It can be calculated according to equation (1):

$$q = \frac{Q_0 \cdot C_0 - Q \cdot C_f}{Q_c \cdot C_c} \tag{1}$$

where Q_0 is the water inflow (L min^{-1}); C_0 is the initial contaminant concentration (mg L^{-1}); Q is the total inflow (L min^{-1}); C_f is the final contaminant concentration (mg L^{-1}); Q_c is the coagulant solution inflow (L min^{-1}); and C_c is the coagulant concentration (mg L^{-1}).

Table 2
Operation conditions in pilot plant trials.

Parameter	Value
Experimental temperature	20 °C
Experimental pH[a]	7
Coagulant dosage[b]	92.2 mg L^{-1}
Residence time in slow mixer	20 min
Residence time in sedimenter	60 min
Raw water flow	77.1 mL min^{-1}

[a] For municipal wastewater, no pH adjustment.
[b] For surface water clarification, 2 mg L^{-1}.

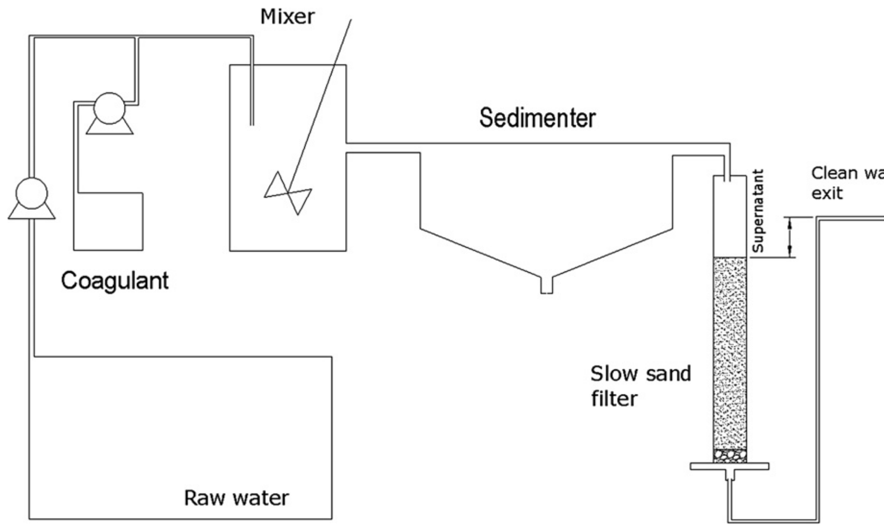

Fig. 4. Pilot plant installation.

For each contaminant, q can be compared between the present pilot plant trials and the batch trials, so that the variation of efficiency due to scaling up to the pilot plant can be appreciated.

3.1. Dye removal

Dyes in aqueos solutions are present in the form of colloids. Their stability as a suspension is due to their polar molecular character, which makes them to keep an electrical equilibrium. The sulfonate groups attached to the first and last aromatic rings, the oxygen atoms in the middle, and the two N–H bonds provide the whole molecule with sufficient polarity. Anionic dyes, negatively charged, can then react with the coagulant's positively-charged nitrogen atom (Fig. 3) to form a more complex molecule, and subsequently the dye becomes unstable and begins to settle (Kim, 1995). Following this initial stage of floc formation, free active centers on the floc surface can appear because of the large structure of the coagulant. The adsorption process occurs via electrostatic attraction between suspended dye colloids and the floc surface. The flocs begin to grow, and dye removal increases (Bulatovic, 2007). *Tanfloc's* action leads to the formation of flocs, so that these two effects – coagulation and adsorption onto flocs – work synergistically (Beltrán-Heredia et al., 2009a).

Fig. 5 shows the removal of color from the simulated textile industry wastewater. The steady state was reached almost at once, and the percentage removal was high at the end of the process (after the sand filtration). However, the filtration stage only reduces the dye concentration by about 10 mg L^{-1} from the value at the outlet of the sedimenter. That may be due to the removal of fine flocs (sand entrapment) and to the partial adsorption of dye onto sand grains (Marmagne et al., 1996). From equation (1), the value of q is 435 mg of dye per g of coagulant. Under the same conditions, the batch trials gave a q value of 490 mg (Beltrán-Heredia et al. (2009a)), so that the efficiency of the process is very similar in the two cases.

Table 3
Characteristic sand-bed data.

Dimension	Value	Units
Average particle diameter	0.75	mm
Sphericity factor φ	0.95	
Corrector factor F_{Re}	45	
Bed porosity	0.4	
Particle specific surface	8421	m^{-1}

3.2. Surfactant removal

The interaction between surfactants and natural polymers (such as that produced by the coagulation of *Tanfloc*) has long been studied because of its importance to successful production in many areas (pharmaceuticals, cosmetics, food processing, etc.). Although the basic mechanisms of surfactant-polymer interaction are reasonably well understood, there is still disagreement about the process at the molecular level. It is generally accepted that the interaction may occur between individual surfactant molecules and the polymer chain, or in the form of surfactant-polymer complexes (micellar or hemimicellar interactions). In the current case of SDBS removal from aqueous solution, the structure of the surfactant molecule suggests that electrostatic bonds may arise between the positively-charged nitrogen atoms of *Tanfloc* and the negatively-charged polar end of the sulfonate (Fig. 2).

Fig. 6 shows the removal of SDBS from a simulated laundry wastewater. One observes that the steady-state regime is reached quickly, with the removal efficiency remaining almost constant at about 80%. The initial surfactant concentration (ca. 50 mg L^{-1})

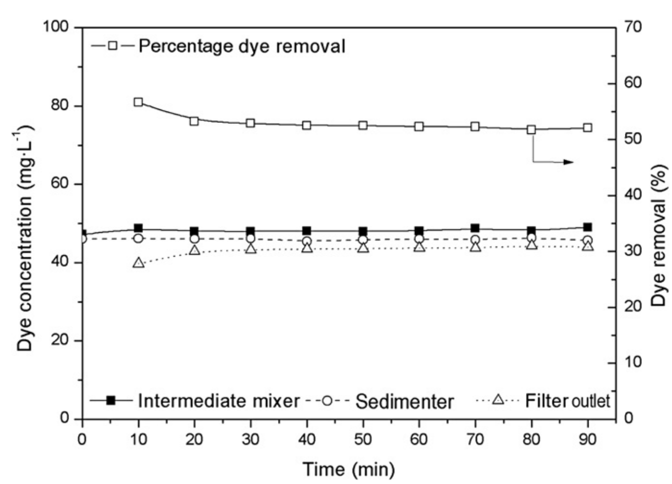

Fig. 5. Dye removal in simulated textile industry wastewater treatment.

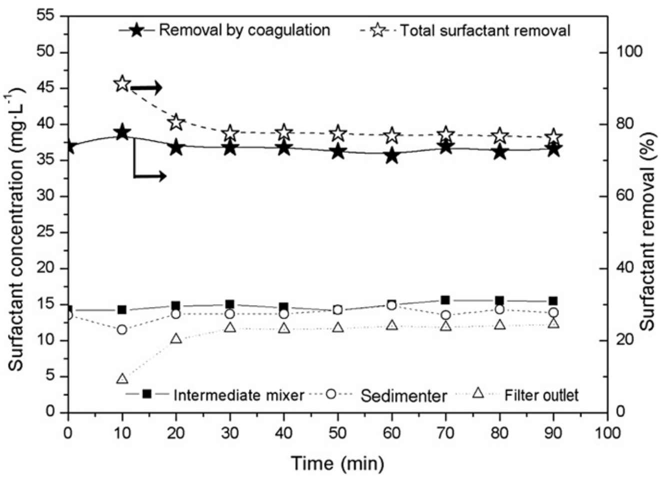

Fig. 6. Surfactant removal in simulated laundry wastewater treatment.

undergoes a decrease to around 15 mg L^{-1}. The total surfactant removal is greater than that only by coagulation. This can be attributed to the slow sand filtration operating in two forms – by adsorption onto sand grains (Lukacs, 2001) and by the total removal of fine flocs (Huisman and Wood, 1974). While one observes small differences in SDBS concentrations between the three sections of the plant, the most effective surfactant removal occurs in the coagulation stage.

Equation (1) yields an average q value of 359 mg of surfactant per g of coagulant. This datum is coherent with previous studies, and is similar to the efficiency that was achieved in batch trials (ca. 300 mg of surfactant per g of coagulant) (Beltrán-Heredia et al., 2009b).

3.3. Surface water clarification

The results of the surface water treatment are shown in Fig. 7. In the same way as the previous cases, the steady-state regime is reached quickly. The turbidity removal remains in the range 50–60%, and the residual turbidity is below 50 NTU throughout the trial. Higher doses of coagulant could yield greater turbidity removal, but a low coagulant dosage (ca. 2 mg L^{-1}) had been selected in order to evaluate the stability and relative effectiveness of the process. Data at the filter outlet are not shown, as no turbidity was detected after this section.

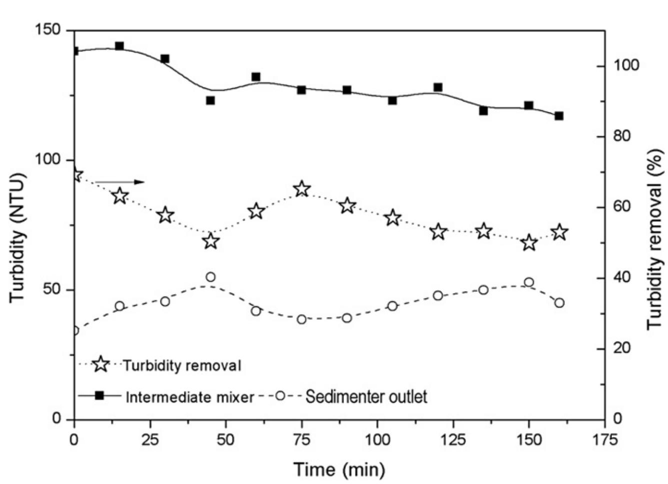

Fig. 7. Turbidity removal in surface water treatment.

Fig. 7 also shows the increase in turbidity in the intermediate mixer. This may be due to the coagulation process, as the flocculation adds turbidity to the sample.

The effectiveness of the pilot plant process was lower than that of the batch trials – 49.3 versus 118 NTU per mg of coagulant (Sánchez-Martín et al., 2009). In the latter, with similar operating parameters, the average turbidity removal was 80%, with the remnant turbidity being 20 NTU. This may be attributed to the lightness of the flocs, since even the slightest flow will lead to floc movement in the sedimenter, whereas a total lack of flow will benefit separation.

The present results are coherent with those of previous work on surface water clarification. Although Graham et al. (2008) present their conclusions in the form of a Flocculation Index (rather than NTU removal), in their evaluation of the clarification capacity of *Tanfloc* they report an optimal dosage of 14 mg L^{-1}, with a similar NTU removal.

Our own previous study (Sánchez-Martín et al., 2009) presented the optimization of the dosage using statistical procedures that took the energy balance into account. Therefore, compared with those results, the performance of the pilot plant is only around 10% poorer, and this small difference is due to the hydrodynamic conditions (Bratby, 2006).

3.4. Municipal sewage remediation

Municipal sewage presents high values of turbidity, COD, and BOD_5. If it is released untreated into the environment, surfactant concentrations can also be significant (Mungray and Kumar, 2008). These four parameters were therefore taken into account in evaluating the efficiency of *Tanfloc* in the treatment of this kind of wastewater.

Özacar and Sengil (2000, 2003a, b) investigated the capacity of tannin-based coagulants like *Tanfloc*. Their work focused on municipal wastewater, although they studied not condensed tannins, but hydrolyzable tannins from *Valonia*. Consequently, their results showed much lower effectiveness in water clarification, and they therefore concluded that these products are unsuitable for use alone, and must be used as support coagulants together with alum.

Fig. 8 shows the reduction of these parameters by the coagulation, flocculation, and filtration processes. One observes that the efficiencies of the filtration and sedimentation are indistinguishable with respect to BOD_5, COD, and surfactant removal, so it is probable that the main reduction of these three parameters takes place in the coagulation stage. However, the implementation of the sand filter is clearly interesting for turbidity reduction.

3.5. System stability

In order to evaluate the stability of the system, even though only small deviations were observed in the steady-state regime (almost from the beginning of effluent from the filter), Fig. 9 shows a box-and whisker-plot of the statistics of the results. One observes that the most stable processes are those involving dye and surfactant removal, as their error bars are fairly narrow. The surface water treatment is slightly more variable (the error bars cover from 50% to 70% of turbidity removal), which surely reflects fluctuations in the influent and the colloidal nature of the suspended organic matter.

Fig. 9 also shows a summary of the reduction of turbidity, COD, BOD_5, and surfactant (measured as SDBS equivalent). This

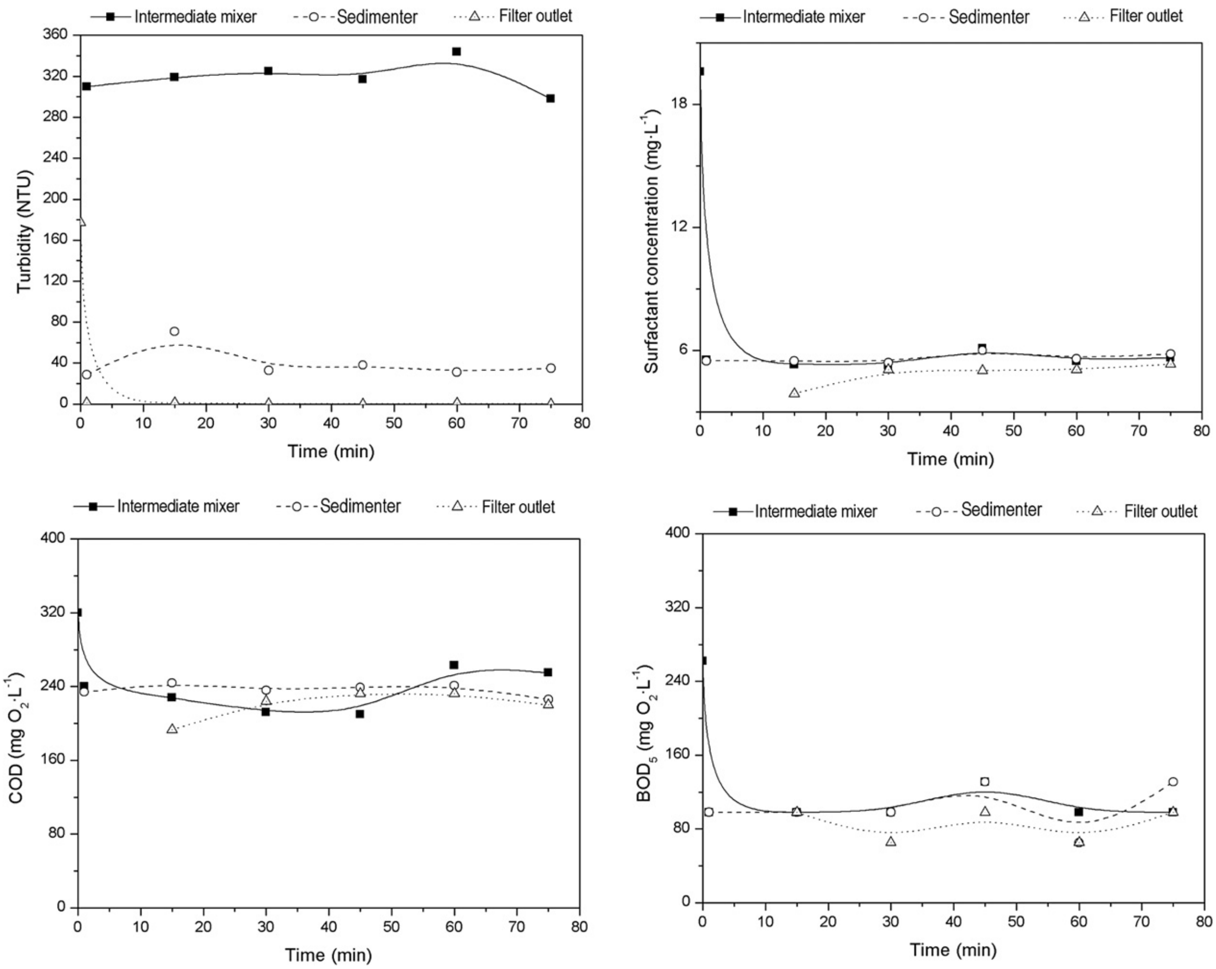

Fig. 8. Municipal wastewater treatment.

last reduction is particularly high (around 75%), while the BOD_5 and COD reductions are around 69% and 28%, respectively.

The mean values of q and the efficiency (%) are given in Table 4. In most cases, the pilot plant's effectiveness would seem to be greater. Only in the case of the surface water did the coagulation and sedimentation stages lead to lower turbidity removal than obtained with the jar test procedure. However, the implementation of the slow sand filter yielded the total removal of suspended solids, as was to be expected.

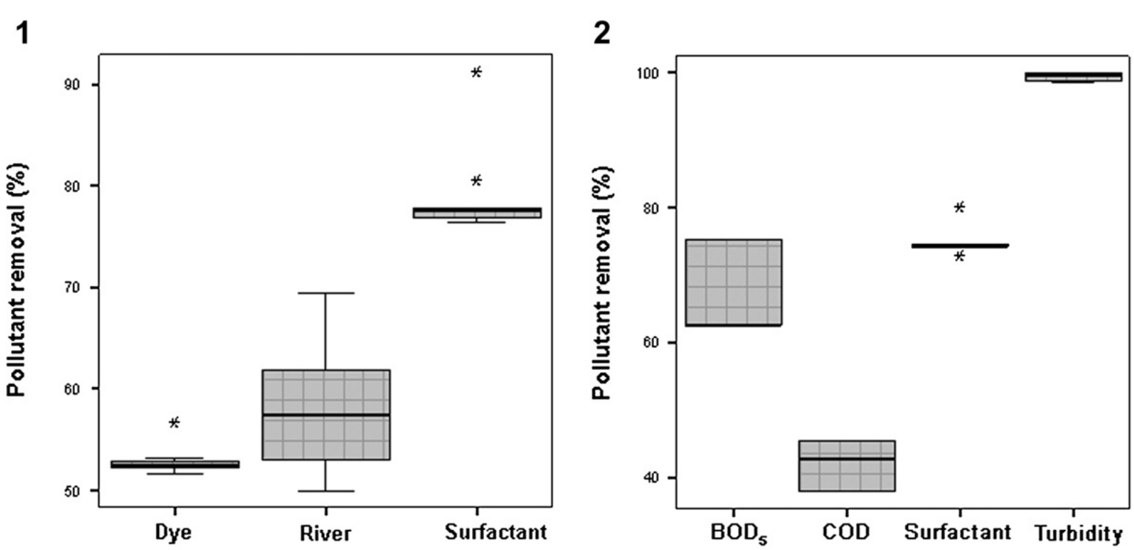

Fig. 9. Box-and whisker-plot for steady state. (1) Surface water, dye and laundry wastewater samples. (2) Municipal sewage wastewater.

Table 4
Mean values in steady-state regime.

Water type	q (mg· (g of coagulant)$^{-1}$)	Average efficiency (%)	Reference for batch-scale trials
Textile industry (dye)	434	38	Beltrán-Heredia et al., 2009a
Laundry	359	79	Beltrán-Heredia et al., 2009b
Municipal wastewater[a]	1970	68	Beltrán-Heredia and Sánchez-Martín, 2009a
Surface water	49.3[b]	58	Sánchez-Martín et al., 2009

[a] q Values referred to BOD_5 removal.
[b] NTU (mg of coagulant)$^{-1}$.

4. Conclusions

The following conclusions can be drawn from the present results:

- *Tanfloc* is a highly effective treatment agent for the three types of wastewater and the raw surface water tested. The pilot plant trials gave a very significant improvement in water quality, especially respecting contaminant removal and the classical quality parameters of turbidity and BOD_5.
- In spite of the continuous flow, the pilot plant studies showed an increase in the quality of the treatment for color reduction (up to 50%), surfactant removal (up to 75%), and organic matter (COD and BOD_5) removal (40% and 60%, respectively). Compared with jar-test results, the efficiency of turbidity removal was less.
- The implementation of slow sand filtration after the sedimentation stage enhances turbidity removal, and achieves almost 100% removal of suspended solids. It also enhances other parameters.
- *Tanfloc* and presumably other tannin-derived flocculants are consequently recommendable agents for treating surface water, and industrial or municipal wastewater.

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