Short communication

Removing heavy metals from polluted surface water with a tannin-based flocculant agent

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ABSTRACT

Many environmental and health problems come from the presence of metals in surface water. Effectiveness of a new commercial tannin-based flocculant has been tested in order to remove Zn^{2+}, Ni^{2+} and Cu^{2+} by coagulation–flocculation process. pH has been adjusted in order to evaluate the real heavy metal removal due just to flocculant effect and not to hydroxide precipitation. At least a 75% of metal removal has been reported in every case, depending on pH value. Flocculant doses have been reported to be about 100–150 ppm.

1. Introduction

This paper aims to study water treatment agents that may differ from industrial and commercial ones. Implementation of an adequate technology for water treatment, above all in developing countries, is the scope of this and other works. Sustainable and available technologies that fit to poverty situation may be characterized and researched at laboratory scale. In this sense, natural coagulants/flocculants are wide-spread, easy-handling resources and its installations are not difficult to maintain by non-qualified personal. There are some examples of these agents, such as *Moringa oleifera* [1] or *Opuntia ficus* sp. [2].

Under *tannins* denomination there are lots of chemical families. Tannins have been used traditionally for animal skins process, but it is possible to find several products that are distributed as flocculant. Tannins come from vegetal secondary metabolytes [3]: bark, fruits, leaves and others like bark from *Acacia*, *Castanea* and *Schinopsis*. However, it is not needed to search for tropical species: *Quercus ilex*, *suber* or *robur* have also tannin-rich bark.

As tannins are widely spread, they can be an effective agent in water treatment in developing countries. Their usage presents several advantages versus traditional flocculant and coagulant agents:

- Technologically, using tannins modified extracts is much easier than the traditional coagulation and flocculation process. From unpublished investigations (Beltrán-Heredia and Sánchez-Martín, 2008) we know that using modified tannins in turbidity removal requires low dosages (between 1 and 10 ppm), pH adjustment is not needed (as it is in coagulation/flocculation processes involving alum or ferric salts) and further flocculant agents are not needed (as it occurs again with alum or ferric salts).
- Environmentally, the origin of tannins is completely natural, so several disadvantages linked to $Al_2(SO_4)_3$ usage are avoided, particularly those that have to do with the aluminium intake [4].
- Tannins are available and easy to storage. It can be a social-change factor, as it allows water treatment without coagulants and flocculants exterior dependence [5], just with a simple chemical modification.

Many few authors have investigated about tannins water treatment capacity. Some of them have researched about tannin plus alum coagulant effect [6,7], others about tannin gelification and heavy metal removal [8–10].

The present paper wants to explore the capacity of Tanfloc to remove heavy metals (Ni^{2+}, Cu^{2+} and Zn^{2+}) from surface water that has been polluted due to industrial activity.

Tanfloc flocculant product is a trademark that belongs to TANAC (Brazil). It is a tannin-based product, which is modified by a physico-chemical process, and has a high flocculant power. It is obtained from *Acacia mearnsii* bark. This tree is very common in Brazil and it has a high concentration of tannins.

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According to TANAC specification, Tanfloc is a vegetal water-extract tannin, mainly constituted of flavonoid structures with an average molecular weight of 1.7 kDa. More groups as hydrocolloid gums and other soluble salts are included in Tanfloc structure. Chemical modification includes a quaternary nitrogen that gives Tanfloc cationic character.

Several references have been found regarding this kind of chemical processes [11–13]. Most of them are patents, including the specific process for Tanfloc, which is reported [14]. The scientific literature refers a reaction mechanism that involves three reagents: a tannin mixture, mainly polyphenol tannins whose structure may be similar to flavonoid structures such as resorcinol A and pyrogallol B rings; an aldehyde such as formaldehyde and an amino compound, such as ammonia or a primary or secondary amine or amide compound [12]. The three reagents, under certain conditions of pH (under 7) and temperature (80 °C), may produced the mentioned flocculant agents.

Toxicological information referring Tanfloc is given by TANAC. There are not indicated health risks at the working dosages, as semilethal dosage in mice was determined to be in 9241 mg/kg. In the case of alum, for example, another supplier (GODÓ Chemistry, Spain) gives a semilethal dosage of 1735 mg/kg.

2. Materials and methods

Raw surface water was obtained from Guadiana river, in Badajoz (Southwest of Spain) and was enriched with different metal solutions. It is pretended with this decision to study the problem from a real point of view. River water was treated the same day it was collected. Table 1 shows the main chemical characteristics of this water. Analytical techniques were standard methods [15].

Treatment was the following: 1 L of surface turbidity-known water was put into a beaker. Around 20 ppm of metal was added, and pH of the experiment was fixed by using HCl 1 M solution and saturated Ca(OH)$_2$ solution. Jar-test procedure was carried out (VELP-Scientifica JLT4 apparatus), without flocculant adding (100 rpm for 2 min time, and 30 rpm for 20 min time). Metal-enriched water was kept 1 h for settling and metal concentration was determined. By this procedure, it is possible to determine the real initial metal concentration, excluding that amount of metal that has been removed just by pH adjustment from the final metal balance. Then, a certain dose of flocculant was added, pH was fixed again and Jar-test proceeding was repeated in the same way. After 1 h of settling, metal concentration loss was determined.

Metal concentration analysis was carried out by a spectrophotometric method [16]. 1 mL of sample was put into a 25-mL flask.

Table 1
Raw water characterisation data.

| Parameter	Value	Units
Conductivity	400	µS/cm
Suspended solids	15	ppm
Total solids	452	ppm
Turbidity	123	NTU
Calcium	37.7	Ca^{2+} ppm
Hardness	152	CaCO$_3$ ppm
Ammonium	1.81	N ppm
Nitrate	5.3	NO$_3^-$ ppm
Nitrite	0.033	N ppm
Chloride	40.4	Cl$^-$ ppm
KMnO$_4$ oxidability	34.6	O$_2$ ppm
Phosphate	0.044	P ppm
Total phosphorus	0.064	P ppm
Total coliforms	800	Colonies per 100 mL
Fecal coliforms	400	Colonies per 100 mL
Fecal streptococcus	140	Colonies per 100 mL

5 mL of borate buffer (sodium borate and sodium carbonate in equal quantities, pH 10) and 2 mL of 4-(2-pyridyl-azo)-resorcinol (PAR) were added, and mixture were diluted to the mark with water. Then the solution was mixed and after 20 min absorbance at 505 nm in a 1-cm optical glass cell was measured. Calibration was prepared with appropriate standards.

3. Results and discussion

3.1. pH influence

As pH is an important factor to metal hydroxide precipitation, it is needed to adjust pH in order to avoid this effect and evaluate metal removal caused just by coagulation and flocculation process. An orientative pH working value for each metal is given by the solubility product constant values at each pH, which shows an idea of what quantity of metal is dissolved and what quantity is under solid form. Solubility product constants of Ni^{2+}, Zn^{2+} and Cu^{2+} hydroxides are well known and its values are 5.54×10^{-16}, 1.2×10^{-17} and 1.6×10^{-19}, respectively [17]. It should be difficult to calculate the solubility of these species exactly, as the working water is not distilled, but river water. The large amount of impurities, such as organic matter, turbidity, hardness, etc. makes the solubility of the metals become higher, due to the interactions between organic matter and metal, above all. This fact makes difficult to apply exactly the equilibrium equations by means of solubility products K_{sp}, but these values give an idea of how Cu^{2+} will be insoluble at lower pH than Ni^{2+} and Zn^{2+}.

In fact, pH precipitation is a commonly method for metal removal. Contaminated water is pH-adjusted till a basic value (pH 10–11). At this pH, metal ions become into a hydroxide form according to the following equation:

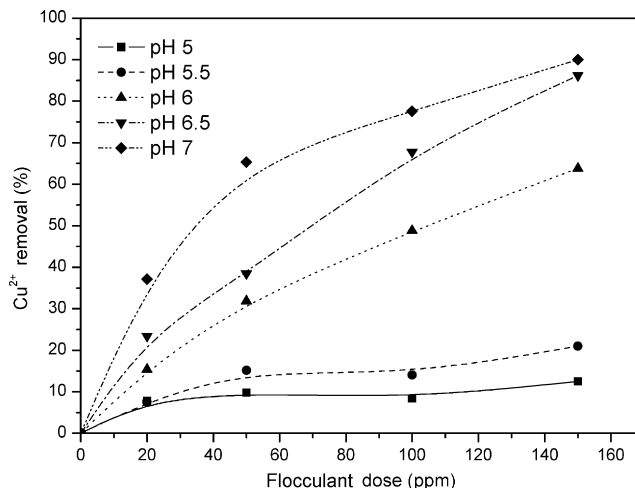$$M^{2+} + 2(OH)^- \rightarrow M(OH)_2 \downarrow \tag{1}$$
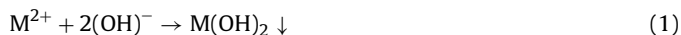
As pH is supposed to be favorable to metal removal, it is very important to adjust its value and evaluate the amount of metal is removed by Tanfloc effect and the metal ion loss due to natural precipitation. Natural removal by hydroxide precipitation is excluded from metal removal results in this paper, as the initial metal concentration was considered after the first Jar-test assay, in which no flocculant was added (see Section 2).

An initial metal dose of 20 ppm approximately was used. Four flocculant dosages were used: 20, 50, 100 and 150 ppm. As it is shown in Figs. 1–3, and having in mind that metal removal is

Fig. 1. Influence of flocculant dose on Cu^{2+} removal.

Fig. 2. Influence of flocculant dose on Zn^{2+} removal.

Fig. 4. Metal removal at optimum pH.

referred to initial metal concentration after first Jar-test flocculant-free, the higher flocculant dosage the higher metal removal is achieved.

3.2. Metal removal

Different assays on Cu^{2+} removal were carried out. pH was varied between 5 and 7. Higher pH dosages were avoided because, as it has been referred previously [18], they provoke natural Cu^{2+} removal in the form of $Cu(OH)_2$ through chemical precipitation. Under 5, pH values carry a lack of flocculant activity, so metal remains dissolved.

Fig. 1 shows Cu^{2+} removal with flocculant doses variation. As it can be appreciated, higher pH values and flocculant doses enhances metal removal. It is not due to hydroxide precipitation, as this effect is avoided by Jar-test procedure (see Section 2).

Other data have been taken from Ref. [19] and it is observed dosages of polyferric sulphate (around 25 mg/L) for a similar metal removal. pH is also much more basic (around 11), so it is difficult to discriminate what amount of Cu^{2+} is removed by coagulation and what because of the pH precipitation. With Tanfloc treatment this aspect is well isolated.

In order to achieve higher metal removal levels, there have been several studies. Normal enhancing procedures, as flocculation by using sodium diethyl-dithiocarbamate (DDTC) as a trapping agent
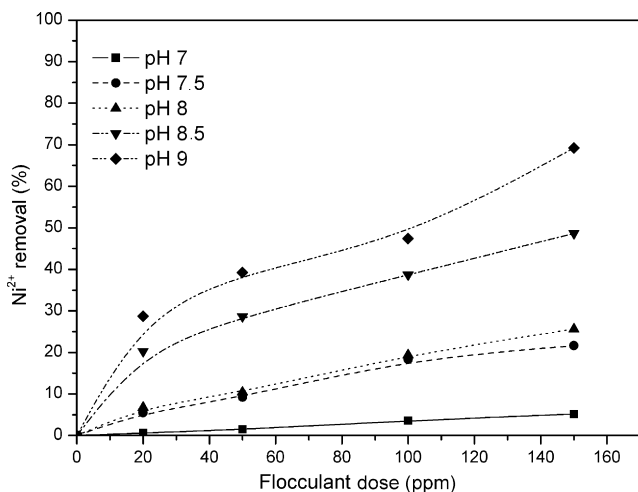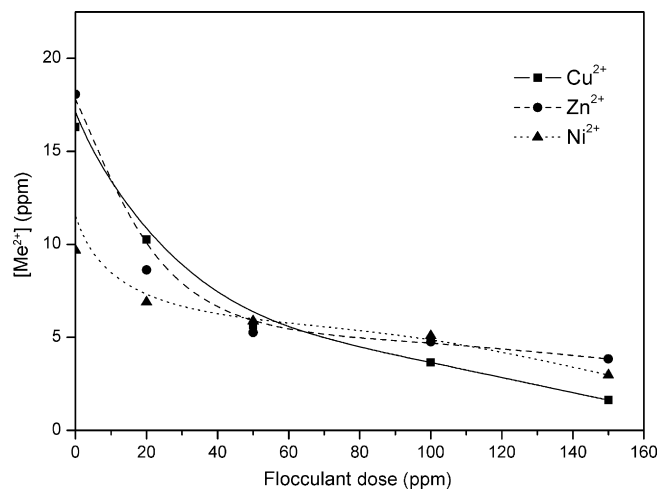

Fig. 3. Influence of flocculant dose on Ni^{2+} removal.

and both polyferric sulphate and polyacrylamide as the floccu-lants [20] involves another reagent and a rather close operational control.

In the same way, different assays with Zn^{2+} were done. pH val-ues were varied between 6 and 8. pH range is set out according to different Zn^{2+} behaviour. As solubility product constant indicates, Zn^{2+} presents hydroxide form at more basic pH values than Cu^{2+}.

In Fig. 2 it is shown Zn^{2+} removal as a function of pH and floc-culant dosage. As it can be seen, Zn^{2+} behaviour is the same as observed in Ni^{2+} and Cu^{2+}, but with different pH range.

Previous studies [21] achieved a final Zn^{2+} concentration of 5 mg/L, but optimum pH was determined in 11. The flocculant agent was determined to be Na_2S. Referring to this study, Tanfloc has a better behaviour, in the sense that no pH effect has been considered and it is quite more affordable product, either available.

Assays with Ni^{2+} were done, varying pH values between 7 and 9. Again, pH range is modified for Ni^{2+} working and it is moved to higher levels. Fig. 3 shows Ni^{2+} removal with this dosage variation and through pH range. It is appreciated that Ni^{2+} removal increases as pH values and flocculant doses increase, although metal removed by chemical precipitation is not considered.

Some investigations about Ni^{2+} have been developed previously [22] and chemical precipitation is the usual method to remove this metal. Similar removal levels have been achieved (almost 71% and 85%). All of them precise pH adjustment between 7 and 10.5, so ranges of removal obtained with Tanfloc are rather higher than those due just to chemical precipitation.

Contact time is higher as well. With Tanfloc treatment, Jar-test duration was fixed to 22 min (2 min in fast stirring plus 20 min in slow stirring, see Section 2). Instead, 1 h contact time has been referred in chemical precipitation procedure [19].

3.3. Equilibrium metal concentration at optimum pH

Experiments lead to see an equilibrium metal concentration, even with different pH values, very similar in every case. This aspect is graphically shown in Fig. 4, which represents Cu^{2+}, Zn^{2+} and Ni^{2+} at optimum pH values of 7, 8 and 9, respectively. As it can be seen, metal loss in the three cases is very close one to other.

A large series of metal ions removal with tannins have been stud-ied [23], but no data of Ni^{2+} or Zn^{2+} removal through tannins have been referred. Palma et al. [23] recommended metal removal to be done through modified bark adsorption, as modified tannin proce-dure was not enough effective. In the present research, it can be

seen in Figs. 2 and 3, this particular tannin-based flocculant is quite effective.

4. Conclusions

This investigation has revealed the following conclusions:

Tanfloc has been observed as a quite effective flocculant agent for heavy metal removal in surface water treatment.

Cu^{2+} concentrations were found to be reduced up to 90% at optimal pH and flocculant conditions; Zn^{2+} and Ni^{2+} concentrations were reduced up to a 75% and 70%, respectively. In all cases, higher pH values and higher flocculant dosage improved metal removal process.

pH were found to be a very important variable which has an optimum value in 6, 7 and 8 for Cu^{2+}, Zn^{2+} and Ni^{2+} removal, respectively. It is not considered metal removal through chemical precipitation in any case, but it is also observed a metal loss due to pH adjustment.

Tanfloc presents several advantages versus chemical precipitation and traditional coagulation–flocculation process. Some of them are its natural origin, its quite easy production through chemical modification of tannins and the fact that pH adjustment needed is rather easier than the one needed for aluminium and iron salts.

Further investigations may take out different data about other metals, above all those which should have a difficult removal with traditional methods.

Acknowledgments

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