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RESEARCH ARTICLE

TANNERY LIMING DRUM WASTEWATER TREATMENT BY NATURAL COAGULANTS FROM *C. SPINOSA, P. GRANATUM, EUCALYPTUS SPP.* AND *V. VINIFERA*

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ABSTRACT

The tannery industry worldwide not only represents economic growth, but is also a source of contaminants that are polluting rivers and groundwaters. Highly turbid and foul-smelling wastewaters are commonly discharged from this industry and their treatment by physical or chemical means is usually expensive. The goal of this study was to treat highly contaminated tannery wastewaters using plant extracts. Polyaluminum chloride and natural coagulants from *Caesalpinia spinosa, Punica granatum, Eucalyptus spp.* and *Vitis vinifera* were examined in their effectiveness of turbidity removal of tannery liming drum wastewater. The addition of these coagulants decreased turbidity to 99.5% using polyaluminum chloride and up to 99.1% using natural coagulants. Among these plant extracts, *P. granatum* had the highest phenol index (20 mg.L^{-1}) and its extract removed turbidity between 97 and 99% by applying doses among 7.0 - 11.7 g.L^{-1}peelextracts and 0.001- 0.03 g.L^{-1} polyacrylamide into 500 mL of tannery liming drum wastewater. Final clarification was obtained with a hydrogen peroxide 5% solutionwhich oxidized color residuals from treated water.The present eco-friendly remediation process enabled a remotion of chemical oxygen demand by 99.8%. Alum treatment of tannery liming drum wastewater could be replaced by an efficient remediation process with plant extracts and hydrogen peroxide in benefit of the environment.

INTRODUCTION

In developing countries, 70% of industrial wastes (globally, two millions tons of sewage, industrial and agricultural waste) are discharged untreated into waterways, being tannery industry one of the major source of pollution (Corcoran *et al.*, 2010; Mwinyihija, 2010; UNWATER, 2014).The tanning process, which turns raw hides and skins into finished leather products, include a complexity of pollutants like chromium and chlorinated phenols even certain streams are hypersaline (Lefebvre and Moletta, 2006; Harris and McCartor, 2011). The tanning process involves liming which is the use of alkalis to condition raw hides and skins: the aim is to remove the hair, flesh and splitting up of the fiber bundles by adding sodium sulfide (Mwinyihija, 2010). One ton of raw skin generally leads to the production of 20 to 80 m^3 of foul-smelling tannery liming drum wastewater including chromium, sulfide, surfactants, lime, high levels of fat, scraps, skins and alkaline pH (El-Bestawy, Al- Fassi, Amer, and Aburokba, 2013). Many conventional processes are used to treat tannery wastewater including coagulation-flocculation using aluminium sulphate, ferric chloride and ferric sulphate(Song, Williams, and Edyvean, 2004; Banuraman and Meikandaan, 2013), electro-oxidation (Naumczyk and Kucharska, 2011), and aerobic-anaerobicprocesses (El-Bestawy *et al.*, 2013). Lately, plant extracts as natural coagulantshave been used to treat industrial wastewater and in some cases, they have replaced the currently expensive methods of wastewater treatment. For example, *M. oleifera* powder seeds are used as a powerful absorbent and antimicrobial agent (Yarahmadi *et al.*, 2009; Yongabi, 2010; Alo *et al.*, 2012; Mangale Sapana, Chonde Sonal, and Raut, 2012; Pallavi and Mahesh, 2013). Natural coagulants like *Moringa stenopetala* (Seifu, 2015), *Caesalpinia spinosa* (Sánchez-Martín, Beltrán-Heredia, and Gragera-Carvajal, 2011), *Cicer arietinum* (Kazi and Virupakshi, 2013), *Cactus opuntia* (ficus-indica) (Vishali and Karthikeyan, 2014) have been investigated as well. In the present work, plant extracts from *Caesalpiniaspinosa* (tara), *Eucalyptus spp., Punica granatum* (pomegranate) and *Vitis vinifera*are used as natural coagulantsto evaluate their efficiency for treating tannery liming drum wastewater.

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MATERIALS AND METHODS

Natural coagulants by solvent extraction

The coagulant stock solutions were prepared by dissolving *Caesalpinia spinosa*, *Eucalyptus spp., Punica granatum* and *Vitis vinifera* dried powders in nail varnish remover (approx. 60% acetone). *C. spinosa* powder was obtained from pods, *Eucalyptus spp.* from barks, *P. granatum* from peels and

V. vinifera from seeds. Each suspension was shaken for 30 min at 40ºC and 100 rpm with nail varnish remover (1 g powder per mL of solvent). To this suspension, pure methanol (99.8%) was added at 40ºC for 10 min (0.3 mL pure methanol per mL suspension). A brine solution (3.5% NaCl) at 4ºC was then added to obtain two phases. The upper milky phase was removed by a pipette and dried at room temperature by 24 hours. Dried crystals were formed and resuspended in sodium bisulfate 5% solution. Best results were obtained using commercial nail varnish remover instead of dichloromethane (99.8%). To characterize the phenolic content of plant extracts, a phenol index (PI) was determined. It was measured by photometry at 470 nm using the reaction with antipyrine, peroxydisulfate and ammonia (M-N Ref. 985 074, Germany). PI determines the concentration in $mg.L^{-1}$ of phenols that react with 4-aminoantipyrine. All chemicals were purchased from Sigma-Aldrich.

Remediation studies of tannery liming drum wastewater

The remediation process consisted of four steps: filtration, coagulation-flocculation, sedimentation and oxidation. They were carried out in a jar test equipment (Selecta, Spain) using 500 mL of tannery liming drum wastewater at pH 12.5. The wastewater was first filtered using a screen filter (1.0 mm) to remove hair, flesh and fiber bundles. Coagulation was done in 10 min and flocculation in 5 min using polyacrylamide (PA). Sedimentation occurred after 15 min and then compact and stable sludge was formed. Chemical oxidation using a hydrogen peroxide 5%solution removed yellowish color from treated water. The turbidity removal efficiencywas used to compare the performance of polyaluminum chloride (PAC) with natural coagulants. To compare the performance of coagulants, a 2^2 full factorial design at two levels was applied (Tables 1 and 2). The statistical analysis was performed using RSM package in R-project (R Core Team, 2014; Russell, 2014) and JMP (SAS Institute, Inc. version 9.0). The efficiency of turbidity removal ($\%T_R$) was calculated by Equation 1:

$$\% T_R = \frac{T_o - T_f}{T_o} \qquad ------ \text{(Eq. 1)}$$

where T_o is initial turbidity of wastewater and T_f is final turbidity of treated water by coagulation.

Table 1. Factors and their levels for the chemical treatment by a factorial experimental design2^2

Code	Factor	Low level (-1)	High level (+1)
X_1	Dose of coagulant, polyaluminum chloride 15 % (PAC)	2.5 $g.L^{-1}$	3.8 $g.L^{-1}$
X_2	Dose of flocculant, polyacrylamide (PA)	0.005 $g.L^{-1}$	0.015 $g.L^{-1}$

Table 2. Factors and their levels for the bio-treatment by a factorial experimental design2^2

Code	Factor	Low level (-1)	High level (+1)
X_3	Dose of biocoagulant, extract of *C. spinosa* pods	6.5 $g.L^{-1}$	10.8 $g.L^{-1}$
X_4	Dose of flocculant, polyacrylamide (PA)	0.01 $g.L^{-1}$	0.03 $g.L^{-1}$

Chemical and physical characterization of water

The samples used in this project consisted in effluents from a local leather industry in Ambato (Ecuador). Samples were obtained from the tannery liming drum process. Chemical oxygen demand (COD) was determined by digestion at 148ºC with chrome (VI) and measured at 620 nm according to the photometric method M-N Ref. 985 012 in a photometer Macherey-Nagel D500 (Germany). Biochemical oxygen demand (BOD) was determined by a manometric respirometric test with the OxiTop Control system (WTW Weilheim, Germany). The measurement range of 0–4000 mg/L was chosen for wastewater. Sample volumes were thus 22.7 mL according to the test. The bottles were filled with the sample and sealed with a rubber sleeve containing sodium hydroxide pellets. A nitrification inhibitor n-allylthiourea was added. The bottles were incubated at 20ºC for five days (Roppola, Kuokkanen, Rämö, Prokkola, and Heiska, 2007). Turbidity was measured using a turbidimeter Hanna HI 88713 in nephelometric units (NTU). Salinity (% NaCl), pH, total dissolved solids ($g.L^{-1}$) and electrical conductivity ($mS.cm^{-1}$) were measured using a multiparameter Hanna HI 2550. An UV-visible absorbance scanning of wastewater and treated water was made in range 280 - 400 nm using a spectrophotometer Nanocolor II UV-VIS (Macherey-Nagel, Germany).

RESULTS AND DISCUSSION

Effect of initial pH on turbidity removal

Initial pH of wastewater has a direct effect on turbidity removal, as well as sludge quality and compaction (Bazrafshan, Mostafapour, Ahmadabadi, and Mahvi, 2014). Figure 1 shows the efficiency of turbidity removal using *C. spinosa* (tara) under different pH with tannery liming drum wastewater. A constant dosage of 10.8 $g.L^{-1}$*C. spinosa* extracts was experimented as natural coagulant and 0.015 $g.L^{-1}$ of PA as flocculant. A turbidity removal of 87% was obtained at pH = 1, 92.1% at pH = 3, 79.4% at pH = 6, 81.6% at pH = 10 and a final removal of 99.2% at pH = 12.5. Best sludge quality according to bibliography can be achieved at basic pH (Bazrafshan *et al*., 2014).

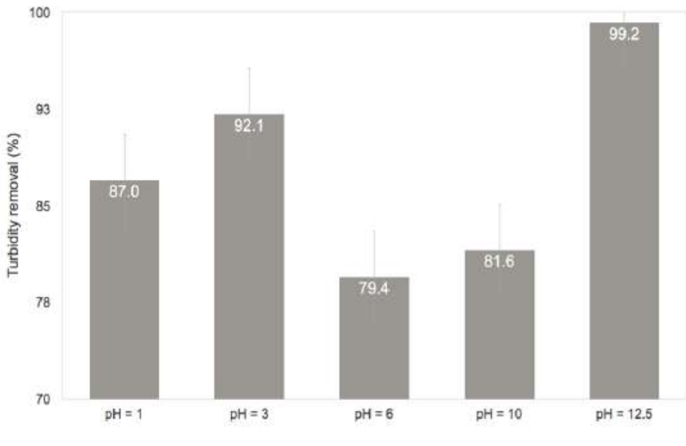

Figure 1. Effect of pH on turbidity removal using *C. spinosa* extracts

Best results of turbidity removal at pH 3 and 12.5 may be linked to the structure of the tannin which probably undergoes denaturation and hydrolysis (Beltrán-Heredia, Sánchez-Martín, and Rodríguez-Sánchez, 2011). Turbidity removal at basic pH might also presumably due to adsorption effect of precipitation and adsorption onto hydroxide flocs. Best results were at original pH 12.5, therefore it is not necessary to change initial pH of wastewater. According to the scientific literature, *Pistacia atlantica* and *Moringa oleifera* extracts had no effects on pH, electrical conductivity and alkalinity after coagulation (Yarahmadi *et al*., 2009; Bazrafshan *et al*., 2014).

Coagulation effect and phenol content of plant extracts

The coagulation effectiveness of plant extracts to remove turbidity from tannery liming drum wastewater is presented in Figure 2 (left axis). Extracts from *C. spinosa*, *Eucalyptus spp., P. granatum* and *V. vinifera* removed colloidal contamination up to 97.3%. Thus, all plant extracts showed a potential as coagulant. PAC removed 99.5% of turbidity. Bark extracts from *Eucalyptus spp* removed 97.3% of colloidal contamination. Seed extracts from *V. vinifera*removed 98.9%. Pod extracts from *C. spinosa* removed 99.2%.Maximum removal of 99.7% was obtained by *P. granatum* peel extracts. Doses of all natural treatments were 10.8 g.L^{-1} of coagulant and 0.01 g.L^{-1} of PA per 500 mL of tannery liming drum wastewater. To obtain natural coagulants, an extraction process using an organic solvent (approx. 60% acetone) was performed. Then, tannin extracts were crystallized into a cold brine solution (3.5% NaCl) and then resuspended in sodium bisulfate solution, thus an electrolyte suspension was formed. It is suggested that such an electrolyte medium might enhance the solubility of coagulating active compounds like tannins, thus diminishing electrostatic repulsion between contaminants and coagulant.

Figure 2 (right axis) shows, phenol index (PI) of plant extracts. Bark extracts from *Eucalyptus spp* had 8.2 mg.L^{-1} PI. The seed extracts from *V. vinifera*had 10.7 mg.L^{-1} PI. The pod extracts from *C. spinosa* had 14.5 mg.L^{-1} PI.A maximum PI by *P. granatum* peel extracts of 20.0 mg.L^{-1} was obtained. These results show that *P. granatum* extracts from peels and *C. spinosa* from pods had the highest PIs. Both *C. spinosa* and *P. granatum*are a good source of tannins, a naturally occurring plant polyphenols (Ben Nasr, Ayed, and Metche, 1996; Chambi *et al*., 2013). According to bibliography, *C. spinosa* pods has atannin content of approx. 40-60% (w/w) and a gallotannin content of 55.1g gallic acid equivalents/100 g tara pods (Chambi *et al*., 2013). Gallotannins can be hydrolyzed into gallic acids. Because gallic acid is a polar and cationic phenolic compound, it may be deprotonated and consequently take part in the coagulation process by a charge neutralization mechanism. Besides, an inter-particular bridging effect might take place. It is because in a basic medium hydroxyl ions might reactwith the polyphenols to produce stable polymers and complexes, which precipitate negative charged colloids, thus improving the flocculation (Chambi *et al*., 2013; Thakur and Choubey, 2014). Studies showed that the dominant mechanism in turbidity removal by *Moringaoleifera* seed extract was adsorption and charge neutralization (Yarahmadi *et al*., 2009).

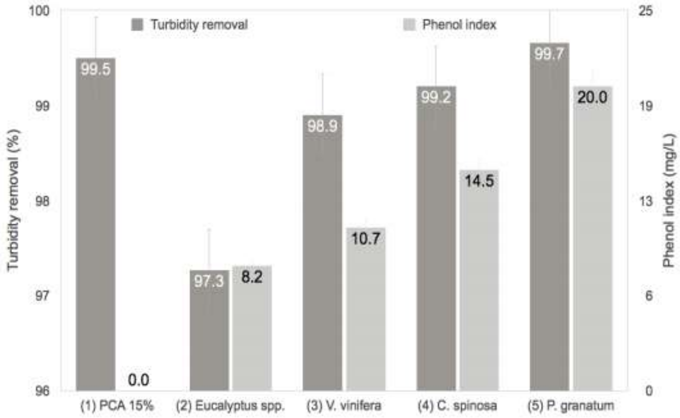

Figure 2. Right axis: Turbidity removal (%) using PAC, plant extracts and PA; left axis: phenol index (mg.L^{-1}) of plant extracts. Treatment doses are (1) 3.8 g.L^{-1} of PAC 15% and 0.03 g.L^{-1} of PA; treatments doses (2) to (5) are 10.8 g.L^{-1} of natural coagulant and 0.01 g.L^{-1} of PA. N = 15 replicates

A positive correlation was observed between PI and turbidity removal (Fig. 3) with a correlation r = 0.8612. This provides an indication that the more phenolic groups are available in a tannin extract, the more effective its coagulation capability. And also it suggests that colloidal remotion is due to the hydrolization effect of polyphenols. As consequence of these results, *P. granatum*and *C. spinosa* tannin extracts were used to perform a remediation process (Figures 5 and 6).

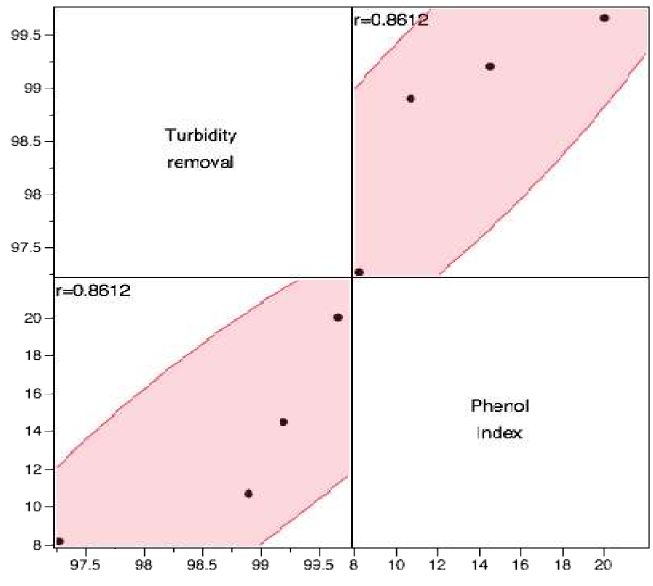

Figure 3.Pearson correlation between turbidity removal (%) and phenol index (mg.L^{-1})

Effect of coagulant dose on turbidity removal

Coagulation processes are generally affected by colloid charges and besides coagulant dosage is directly related with charge destabilization (Ramavandi and Akbarzadeh, 2014). Therefore, coagulant dosage is one of the most important parameters to optimize. To find out the statistical effect of low and high doses of coagulant and flocculant into tannery liming drum wastewater, two factorial designs 2^2 were applied (Tables 1 and 2). Based on the results of those designs (Figs. 4

and 5), doses ranges of coagulant and flocculant were obtained. The data, in Figure 4 (A), determine themaineffects when dosing low and high concentrations of coagulant PAC and flocculant PA. Low and high doses were 2.5 - 3.8 g.L^{-1} for PAC and 0.005 - 0.015 g.L^{-1} for PA. Both factors showed a linear behavior (R^2 = 0.8414 and $p < 0.05$, n = 16). Therefore, PAC and PA were statistically significants. This means that, 3.8 and 0.015g.L^{-1}were optimal doses of PAC and PA respectively, because the lowest turbidity of treated waterwas obtained. A turbidity removal of 99.5% was obtained by these means. These results suggest that chemical coagulation was due mainly to deprotonation: a complex-ion effect of aluminium monomers when they are added to wastewater (Mertens *et al*., 2012). This also suggests that contaminants in tannery liming drum wastewater from a leather industry in Ambato (Ecuador) had mainly a negative ionic charge. Thus, aluminium monomers of the polyaluminum chloride combined with active sites of wastewater colloids and consequently a polymerization effect took place. Figure 4 (B) presents the main effects at low and high concentrations of *C. spinosa* extracts and PA.Low and high doses were 6.5 - 10.8 g.L^{-1} for *C. spinosa* extracts and 0.01 and 0.03 g.L^{-1} for PA. Only one factor (*C. spinosa* concentration) showed a linear behavior (R^2 = 0.9544 and $p <$ 0.05, n = 16). Therefore, *C. spinosa* extracts was statistically significant at 10.8 g.L^{-1}and flocculant concentrations bellow 0.01 g.L^{-1} would be enough in the remediation process. A turbidity removal of 99.2% was determined by these means.

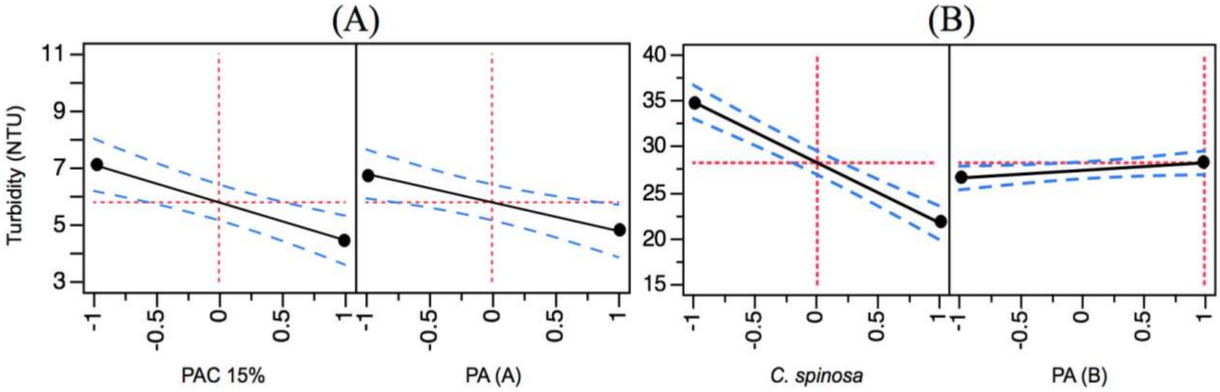

Figure 4. Main effects plot. Where (A) Main effects plot when dosing 2.5 and 3.8 g.L^{-1} PAC and 0.005 and 0.015 g.L^{-1} PA and (B) Main effects plot when dosing 6.5 and 10.8 g.L^{-1} *C. spinosa* extracts and 0.01 and 0.03 g.L^{-1} PA. N = 32 replicates

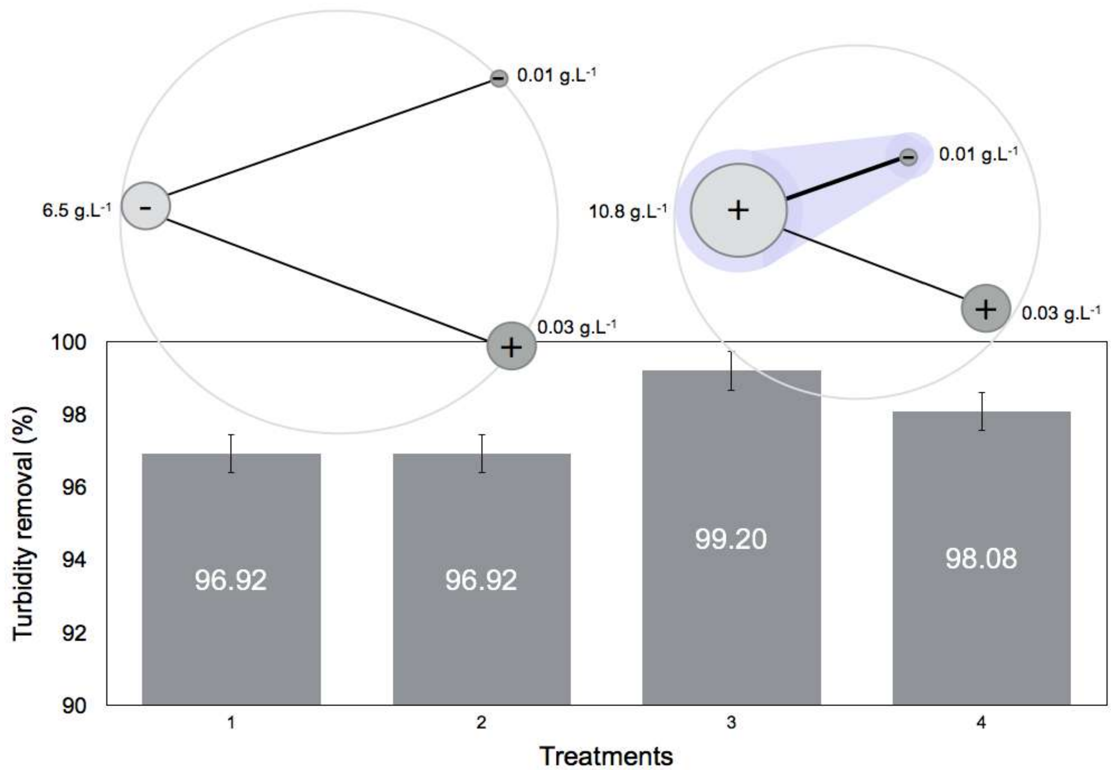

Figure 5. Percent of turbidity removal using *C. spinosa* extracts and PA according to Table 2.Where treatment (1) 6.5 g.L^{-1} of *C. spinosa* extractsand 0.01g.L^{-1} PA, (2) 6.5 g.L^{-1} of *C. spinosa* extractsand 0.03g.L^{-1} PA, (3) 10.8 g.L^{-1} of *C. spinosa* extractsand 0.01g.L^{-1} PA, (4) 10.8 g.L^{-1} of *C. spinosa* extractsand 0.03g.L^{-1} PA. N = 16 replicates

Table 3. Physical and chemical analysis of water before and after the remediation process usingPAC,*C. spinosa and P. granatum* extracts

Parameter	WW	CP	CS	CS + H_20_2	PG	PG + H_2O_2
pH	12.5	9.4	11.3	8.8	11.5	9.2
EC ($mS.m^{-1}$)	18.4	14.3	18.5	14.3	10.7	20.9
TDS ($g.L^{-1}$)	9.2	8.2	9.3	7.1	5.3	10.5
NaCl (%)	1.3	1.1	1.3	0.9	0.7	1.5
Turbidity (NTU)	1131.3	6.2	9.2	4.1	2.4	2.1
COD ($mg.L^{-1}$)	10550.0	8.2	5800	8.2	3440.8	19.4
BOD_5($mg.L^{-1}$)	300.0	64.0	220	45	250	80

Although the high dose of natural coagulant *C. spinosa* had the highest effect on turbidity removal, it can be noticed in Fig. 5 that even at low dose (6.5$g.L^{-1}$) the natural coagulant was efficient showing a 96.9% of turbidity removal. The data presented in Fig. 4 illustrates that *C. spinosa* pod extracts (99.2% efficiency) had practically the same effect as polyaluminum chloride (99.5% efficiency).

Optimization of *P. granatum* dosage on turbidity removal

In order to study the optimal dosage of natural coagulant *P. granatum*, various concentrations were experimented and then represented as a mathematical model using a RSM package in R-project (Fig. 6). Doses of *P. granatum* (0.4 - 13.0 $g.L^{-1}$) and polyacrylamide (0.001 - 0.03 $g.L^{-1}$) were added into 500 mL of tannery liming drum wastewater. Doses exhibiting the highest turbidity removals (96.9 - 99.6%) were between 7.0 - 11.7 $g.L^{-1}$ of *P. granatum* and 0.02 - 0.03 $g.L^{-1}$PA. Initial turbidity was 1131.3 NTU. A polynomial model was obtained from 30 trials using *P. granatum* as coagulant.

$$\text{(Eq. 2) \% Removal} = 91.83 + 54.78\,(B*F)_1 - 41.78\,(B*F)_2 + 23.85\,(B*F)_3 - 14.35\,(B*F)_4$$

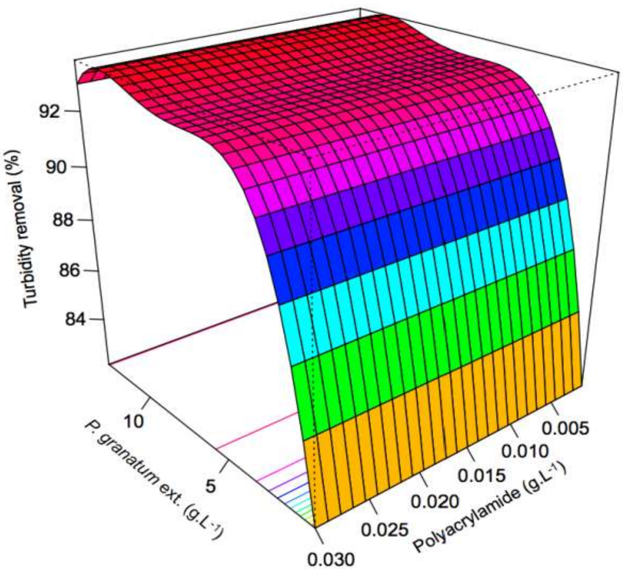

Figure 6. Response surface for turbidity removal using *P. granatum* extracts and PA. RSM model: adjusted R^2 is 0.9907 and p-value: < 2.2e-16. N = 30 replicates

Effect of oxidation on the remediation process

The natural coagulation process left color residuals in treated water because of tannins. Therefore, an oxidation process with hydrogen peroxide 5% solution was applied to removed color residuals. The results presented in Table 3 demonstrate that chemical oxidation byhydrogen peroxide is effective to enhance the removal of residuals after using natural coagulants. Table 3 summarizes three remediation processes. The first remediation process (CP) is due to 3.8 $g.L^{-1}$ PAC and 0.015 $g.L^{-1}$ PA. The second process shows results from wastewater treatment with *C. spinosa* (CS) and its oxidation process (CS+H_2O_2). Finally, Table 3 resumes the data of the third remediation process with results from treated wastewater with *P. granatum* (PG) and its oxidation process (PG+H_2O_2). Both natural coagulants were added at 10.8 $g.L^{-1}$using 0.01 $g.L^{-1}$ PA. In general, natural coagulation did no affect significantly the pH, EC, TDS and NaCl values in contrast with chemical coagulation, in agreement with literature (Song *et al*., 2004; Alo, Anyim, and Elom, 2012; Banuraman and Meikandaan, 2013). The chemical oxidation demand (COD) was reduced to 99.9% using PAC, 45.0% using *C. spinosa extracts* and 67.4% using *P. granatum* extracts. After the addition of hydrogenperoxide 5% solution, COD was reduced to 99.9% in the process in that *C. spinosa extracts* were used and 99.8% in the process in that *P. granatum extracts* were used. According to Table 3, biochemical oxidation demand (BOD) was reduced to 78.7% using PAC, 26.6% using *C. spinosa extracts* and 16.6% using *P. granatum* extracts. After the addition of hydrogenperoxide solution, BOD was reduced to 85.0% in the process in that *C. spinosa extracts* were used and 73.3% in the process in that *P. granatum extracts* were used.

WW = Tannery liming drum wastewater, **CP** = Water treated by3.8 $g.L^{-1}$ PAC and 0.015 $g.L^{-1}$ PA, **CS** = Water treated by 10.8 $g.L^{-1}$*C. spinosa* peel extracts and 0.01 $g.L^{-1}$ PA, **CS + H_2O_2** = Treatment CS + hydrogen peroxide 5% solution, **PG** = Water treated by 11.7 $g.L^{-1}$*P. granatum* peel extracts and 0.03 $g.L^{-1}$ PA, **PG + H_20_2** = Treatment PG + hydrogen peroxide 5% solution.

UV-VIS scanning

As presented in Figure 7, the UV-visible absorbance of ultra-pure water (type I), wastewater and treated water after *P. granatum* and hydrogen peroxide treatments were measured. According to the UV-visible absorbance, a maximum absorbance was observed at 280 nm from wastewater; this high peak decreased as the treatments were applied. Ultra-pure water practically does not show any response at 280 nm. The absorbance peak at 280 nm decreased to a minimum level when hydrogen peroxide treatment was applied. The significant changes occurring in absorbance indicate that removal of contaminants by natural coagulation and oxidation takes place.

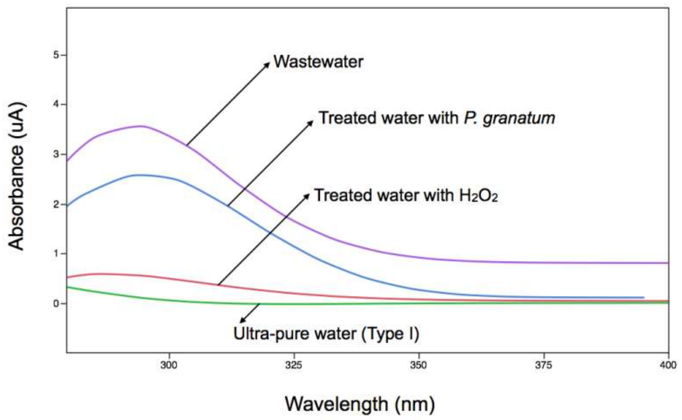

Figure 7. UV-VIS absorbance spectra of ultra-pure water (Type I), tannery liming drum wastewater and treated water with *P. granatum* and hydrogen peroxide

Conclusion

In the present study, the coagulation potential and efficiency on turbidity removal from *C. spinosa*, *Eucalyptus spp.*,*P. granatum* and *V. vinifera* were experimentally evaluated. Phenol index helped to identify which plan extracts had the highest turbidity removal effects: *C. spinosa* and *P. granatum*. Coagulation potential was measured at different pH values. Best results were at original wastewater pH 12.5, and therefore it was not necessary to change initial pH for all studies. The optimum dosages for coagulation with *C. spinosa* and *P. granatum*were 2.8 times higher than PAC. To remove color residuals from natural coagulation processes, it was necessary an oxidation using hydrogen peroxide. All natural coagulants had no significant effects on pH, electrical conductivity, salinity and total dissolved solids. According to experimental results, it can be concluded that *C. spinosa*, *Eucalyptus spp.*,*P. granatum* and *V. vinifera* follow adsorption-charge neutralization and inter-particular bridging as coagulation mechanisms. It was found that *C. spinosa* and *P. granatum* had practically the same high efficiency as PAC. Therefore, these plant extracts seems to be suitable as powerful coagulants for treatment of tannery wastewater.

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REFERENCES

Alo, M. N., Anyim, C., and Elom, M. 2012. Coagulation and Antimicrobial Activities of *Moringa oleifera* Seed Storage at 3° C Temperature in Turbid Water. *Advances in Applied Science Research*, *3*(2), 887–894.

Banuraman, S., and Meikandaan, T. 2013. Treatability Study of Tannery Effluent by Enhanced Primary Treatment. *International Journal of Modern Engineering Research (IJMER)*, *3*, 119.

Bazrafshan, E., Mostafapour, F. K., Ahmadabadi, M., and Mahvi, A. H. 2014) Turbidity removal from aqueous environments by *Pistacia atlantica* (Baneh) seed extract as a natural organic coagulant aid. *Desalination and Water Treatment*, 1–7. http://doi.org/10.1080/19443994.2014.942704

Beltrán-Heredia, J., Sánchez-Martín, J., and Rodríguez-Sánchez, M. T. 2011. Textile wastewater purification through natural coagulants. *Applied Water Science*, *1*(1-2), 25–33. http://doi.org/10.1007/s13201-011-0005-2

Ben Nasr, C., Ayed, N., and Metche, M. 1996. Quantitative determination of the polyphenolic content of pomegranate peel. *Zeitschrift Für Lebensmittel-Untersuchung Und Forschung*, *203*(4), 374–378. http://doi.org/10.1007/BF01231077

Chambi, F., Chirinos, R., Pedreschi, R., Betalleluz-Pallardel, I., Debaste, F., and Campos, D. 2013. Antioxidant potential of hydrolyzed polyphenolic extracts from tara (*Caesalpinia spinosa*) pods. *Industrial Crops and Products*, *47*, 168–175. http://doi.org/10.1016/j.indcrop.2013.03.009

Corcoran, E., Nellemann, C., Baker, E., Bos, R., Osborn, D., and Savelli, H. 2010. *Sick water?: the central role of wastewater management in sustainable development : a rapid response assessment*. Arendal, Norway: UNEP/GRID-Arendal.

El-Bestawy, E., Al-Fassi, F., Amer, R., and Aburokba, R. 2013. Biological Treatment of Leather-Tanning Industrial Wastewater Using Free Living Bacteria. *Advances in Life Science and Technology*, *12*(2), 46–65.

Harris, J., and McCartor, A. 2011. The world's worst toxic pollution problems. Blacksmith Institute and Green Cross Switzerland. Retrieved from http://www.worstpolluted.org/files/FileUpload/files/2011/Worlds-Worst-Toxic-Pollution-Problems-2011-Report.pdf

Kazi, T., and Virupakshi, A. 2013. Treatment of Tannery Wastewater Using Natural Coagulants. *Development*, *2*(8). Retrieved from http://ijirset.com/upload/august/29A_Treatment.pdf

Lefebvre, O., and Moletta, R. 2006. Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Research*, *40*(20), 3671–3682. http://doi.org/10.1016/j.watres.2006.08.027

Mangale Sapana, M., Chonde Sonal, G., and Raut, P. D. 2012. Use of Moringa oleifera (Drumstick) seed as natural absorbent and an antimicrobial agent for ground water treatment. *Research Journal of Recent Sciences*, *2277*, 2502.

Mertens, J., Casentini, B., Masion, A., Pöthig, R., Wehrli, B., and Furrer, G. 2012. Polyaluminum chloride with high Al30 content as removal agent for arsenic-contaminated well water. *Water Research*, *46*(1), 53–62. http://doi.org/10.1016/j.watres.2011.10.031

Mwinyihija, M. 2010. Main Pollutants and Environmental Impacts of the Tanning Industry. In M. Mwinyihija, *Ecotoxicological Diagnosis in the Tanning Industry* (pp. 17–35). New York, NY: Springer New York. Retrieved from http://link.springer.com/10.1007/978-1-4419-6266-9_2

Naumczyk, J., and Kucharska, M. 2011. Tannery wastewater treatment by anodic electrooxidation coupled with electro-Fenton process. *Environment Protection Engineering*, *37*(3), 47–54.

Pallavi, N., and Mahesh, S. 2013. Feasibility Study of Moringa Oleifera as a Natural Coagulant for the Treatment of Dairy

Wastewater. *International Journal of Engineering Research*, *2*(3), 200–202.

Ramavandi, B., and Akbarzadeh, S. 2014. Removal of metronidazole antibiotic from contaminated water using a coagulant extracted from *Plantago ovata*. *Desalination and Water Treatment*, 1–8. http://doi.org/10.1080/19443994.2014.928909

Roppola, K., Kuokkanen, T., Rämö, J., Prokkola, H., and Heiska, E. 2007. Comparison Study of Different BOD Tests in the Determination of BOD7 Evaluated in a Model Domestic Sewage. *Journal of Automated Methods and Management in Chemistry*, *2007*, 1–4. http://doi.org/10.1155/2007/39761

Seifu, E. 2015. Actual and Potential Applications of *Moringa stenopetala*, Underutilized Indigenous Vegetable of Southern Ethiopia: A Review. *International Journal of Agricultural and Food Research (IJAFR)*, *3*(4). Retrieved from https://www.sciencetarget.com/Journal/index.php/IJAFR/ article/view/381

Song, Z., Williams, C. J., and Edyvean, R. G. J. 2004. Treatment of tannery wastewater by chemical coagulation. *Desalination*, 164(3), 249 – 259. http://doi.org/ http://dx.doi.org/10.1016/S0011-9164(04)00193-6

Thakur, S. S. and Choubey, S. 2014. Use of Tannin based natural coagulants for water treatment: An alternative to inorganicchemicals. Retrieved from http://www.sphinxsai.com/ 2014/ch_vol_6_7/3/(3628-3634)%20O14.pdf

UN-WATER. 2014. Water pollution. The United Nations Inter-Agency Mechanism on All Freshwater Related Issues, including Sanitation. Retrieved from http://www.unwater.org/statistics/statistics-detail/en/c/211800/

Vishali, S., and Karthikeyan, R. 2014. *Cactus opuntia* (*ficus - indica*): an eco-friendly alternative coagulant in the treatment of paint effluent. *Desalination and Water Treatment*, 1–9. http://doi.org/10.1080/ 19443994.2014.945487

Yarahmadi, M., Hossieni, M., Bina, B., Mahmoudian, M. H., Naimabadie, A., and Shahsavani, A. 2009. Application of Moringa oleifera seed extract and poly aluminium chloride in water treatment. *World Appl Sci J*, *7*(8), 962–967.

Yongabi, K. A. 2010. Biocoagulants for Water and Waste Water Purification: a Review. *International Review of Chemical Engineering-Rapid Communications*, 2(3), 444–458.

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