

Green Silver Nanoparticles in Improvement of Physicochemical and Microbiological Properties of Tannery Wastewater

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The water used in the industries becomes wastewater and is discharged into the receiving water bodies or soil without prior treatment to mitigate environmental pollution. The objective of this research was to evaluate the percentage of improvement in the quality of wastewater from a tannery industry by applying silver nanoparticles (AgNPs) obtained by the green method. The treatment was carried out with silver nanoparticles synthesized with *Aloysia triphllo* extract. As a result, the chemical oxygen demand (COD), biochemical oxygen demand (BOD), oils and greases (O and G), total suspended solids (TSS) and *Escherichia coli* were reduced by 93.38, 93.27, 77.71, 91.78 and 100 %, respectively, after 30 minutes of treatment. The results indicated that the silver nanoparticle technology was efficient for the improvement of physicochemical and microbiological parameters of tannery industrial wastewater, but this should be further investigated by proposing other operating conditions such as other doses of silver nanoparticles. This proves that nanotechnology is a viable alternative with environmental advantages for the treatment of industrial wastewater when using nanoparticles obtained by environmentally friendly methods.

1. Introduction

The tanning industry is one of the most important industries due to the products generated, which are necessary mainly for the footwear and clothing industry. It is estimated that the U.S. is the largest exporter of leather in the world with 26.4% and China is the largest importer with 36.0% (NLC, 2021). This means at the same time the generation of large volumes of potentially contaminated wastewater that must be treated before being discharged into receiving bodies in order not to have a negative impact (Aquiye et al., 2021). According to a United Nations (UN) report, in Latin America and the Caribbean, only approximately 60% of the population has a sewage system and only 30-40% of the wastewater collected is treated (Rodríguez et al., 2020), which is a major problem in search of solutions. Likewise, wastewater from the leather industry is generated between 25 to 80 m³ per ton of raw material processing (Mannucci A. et al., 2014) and has very dangerous characteristics due to the type of pollutants it may contain, such as acids, alkalis, tannins, biocides, phenols, dyes, sulfates, heavy metals, chromium salts, among others (Lofrano G. et al., 2013).

One method considered environmentally sustainable is bioremediation, i.e. when using various microorganisms such as *Ochrobactrum intermedium* (Yadav P. et al., 2021), *Enterobacter sp.* (Ashraf S., 2018), *Pseudomonas aeruginosa* (Sivaprakasam S. et al., 2008), *Acinetobacter sp.*, *Bacillus cereus* (Kumari V., et al., 2016), *Citrobacter freundii* (Vijayaraj A. et al., 2018), among others.

In recent times, the use of nanotechnology has been tested as a method for the treatment of tannery wastewater, investigating the use of magnetite nanoparticles with chitosan for absorption of chromium present in these effluents (Zahra M. et al., 2022). Nanomaterials such as carbon nanotubes, zinc oxide and titanium oxide have also been used for the same purpose (Maity S. et al., 2020). Within this context, the research aimed to treat wastewater from a tannery industry using silver nanoparticles synthesized with plant extract to reduce

physicochemical and microbiological parameters such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), electrical conductivity (EC), temperature, oils and greases (O and G) and *Escherichia coli*.

2. Methodology

2.1 Treatment process

The treatment of the tannery wastewater had the following stages, as shown in Figure 1.

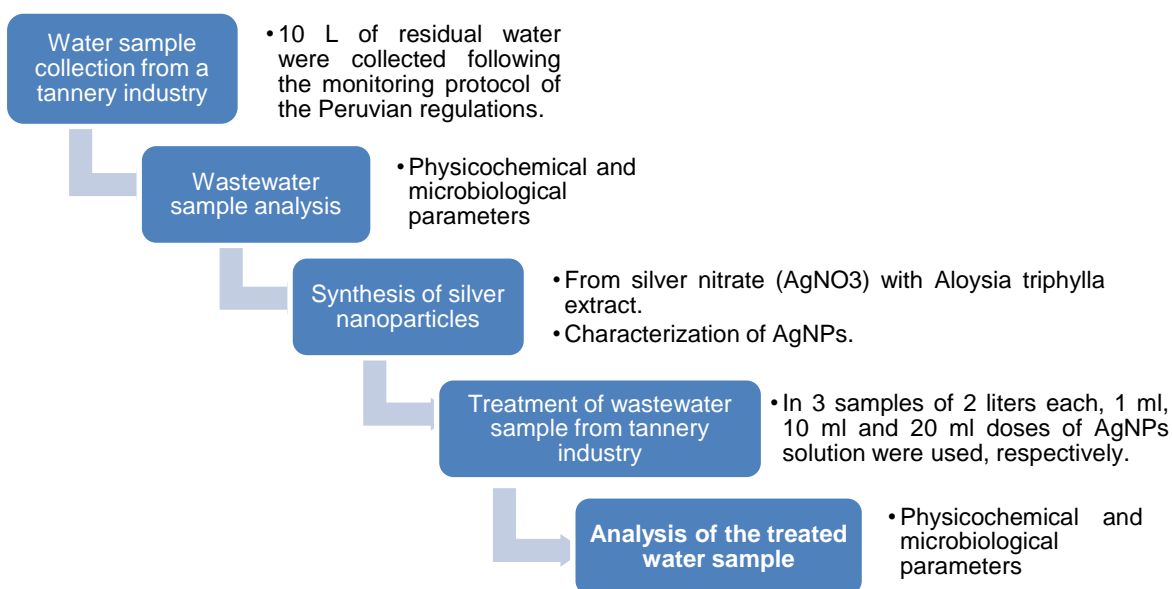


Figure 1: Scheme of the treatment process

2.2 Synthesis of silver nanoparticles (AgNPs)

The research is not exclusively focused on the synthesis of nanoparticles but also on their application. To obtain this nanomaterial, the procedure of Gómez-Garzón M. (2018) was followed and adapted, being carried out in two steps: First, the extract of the plant *Aloysia triphylla* (commonly known as lemon verbena) was obtained. The next step was to take 3 mL of plant extract, and to this was added dropwise 5 mL of 0.001 M silver nitrate solution, observing a change of amber color to light yellow indicating the presence of nanoparticles. Subsequently, the nanoparticles were characterized at the nanomaterials laboratory of the National University of Engineering in Lima, Peru.

2.3 Analysis methods of physicochemical parameter

It was performed in laboratory at Universidad César Vallejo in Lima, Peru, following the standardized protocols described in the undergraduate thesis of Tafur R. (2019):

SMEWW-APHA-AWWA-WEF Part 5210 B, 22nd Ed: For BOD₅.

SMEWW-APHA-AWWA-WEF Part 5220 D, 23rd Ed: For COD.

SMEWW-APHA-AWWA-WEF Part 5220 D, 23rd Ed: For total suspended solids.

SMEWW-APHA-AWWA-WEF Part 5520 B, 23rd Ed: For oils and greases.

Growth by interpolation of bacteria on MacConkey Agar: For *Escherichia coli*.

3. Results and discussion

The action of silver nanoparticles obtained by green synthesis (plant extract) is given by the antioxidant capacity of the plant species (*Aloysia triphylla*), which thanks to plant phytochemicals of antioxidant characteristic that reduce metal ions and produce nanoparticles (Prabhu and Poulouse, 2012).

Nanoparticles to reduce certain parameters have special characteristics that make it more efficient compared to particle level, due to the high surface/volume ratio and the resulting high surface reactivity (Nie et al., 2010; Barros et al., 2021) that increases when the size of the nanoparticles is smaller (Karlsson et al., 2009). The action of silver nanoparticles on microbes can occur through the ability to anchor to the bacterial cell wall and subsequently penetrate it, thus causing structural changes in the cell membrane until causing cell death (Prabhu and Poulouse, 2012).

3.1 Physicochemical characteristics of tannery industrial wastewater

The tannery wastewater presented high values of physicochemical and biological parameters that exceeded the maximum admissible values stipulated by Peruvian legislation (D.S. 021-2009-vivienda), with the exception of temperature. These values are shown in Table 1.

Table 1: Physicochemical and biological parameters of tannery wastewater

Parameter	Units	Value	Maximum permissible limit (MPL)
Temperature	°C	19	35
EC	µS/cm	2637	-
TSS	mg/L	713	-
pH	-	12.02	6.5-9.5
BOD	mg/L	859	500
COD	mg/L	1883	1000
Oils and greases	mg/L	126	100
<i>Escherichia coli</i>	MPN/100 mL	2400	-

3.2 Characterization of silver nanoparticles

The silver nanoparticles (AgNPs) synthesized with plant extract were characterized by dynamic light scattering (DLS), resulting in a diameter with an average size of 10.9 nm.

3.3 Physicochemical parameters of tannery wastewater treated with AgNPs

After performing tests on three samples (sample 1 with 1 mL, sample 2 with 10 mL and sample 3 with 20 mL) of AgNPs solution, with three replicates for each, the average values of the physicochemical properties of the treated wastewater were obtained and are presented in Tables 3 to 8.

Temperature

A slight increase in temperature occurred in the three samples (Table 3), mainly between the treatment times of 30 and 60 min. All temperature values did not exceed the maximum admissible values established by Peruvian legislation, which is 35 °C.

Table 3: Wastewater temperature during treatment

Treatment time (min)	Temperature (°C)		
	Sample 1 (1 mL of AgNPs)	Sample 2 (10 mL of AgNPs)	Sample 3 (20 mL of AgNPs)
30	20.40	20.00	19.50
60	21.67	21.77	22.00
90	22.00	21.50	21.67
120	21.63	21.73	21.73

Biochemical oxygen demand (BOD₅)

The AgNPs acted with good efficiency, maintaining a reduction range between 90.56 and 93.27 % with solutions of 1, 10 and 20 mL of silver nanoparticles, as shown in Table 4. The reduction of BOD₅ occurred from 30 minutes of treatment and had a slight progressive increase until 120 minutes of treatment, obtaining values required by Peruvian environmental regulations (MVCS, 2009).

Table 4: Biochemical Oxygen Demand (BOD₅) of wastewater during AgNPs treatment

Treatment time (min)	Sample 1 (1 mL of AgNPs)			Sample 2 (10 mL of AgNPs)			Sample 3 (20 mL of AgNPs)		
	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)
30	859	81.13	90.56	859.00	76.22	91.13	859.00	75.29	91.24
60	859	70.94	91.74	859.00	69.58	91.90	859.00	71.56	91.67
90	859	64.36	92.51	859.00	65.17	92.41	859.00	65.93	92.32
120	859	57.83	93.27	859.00	58.60	93.18	859.00	59.68	93.05

The activity that AgNPs do for the reduction of BOD₅ and COD is by surface interaction with metabolites and proteins present in the organic load of the wastewater (Metz et al., 2015), forming coatings on the nanoparticles by adsorption while oxidation-reduction processes occur (Navarro E. et al., 2008).

Chemical Oxygen Demand (COD)

The results obtained using doses of 1, 10 and 20 mL of AgNPs showed close values in COD reduction, observing that the samples had reductions from 91.73 % to 93.38 % for 30 to 120 minutes of treatment (see Table 5).

Table 5: Chemical oxygen demand (COD) of wastewater during AgNPs treatment

Treatment time (min)	Sample 1 (1 mL of AgNPs)			Sample 2 (10 mL of AgNPs)			Sample 3 (20 mL of AgNPs)		
	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)
30	1883	155.67	91.73	1883	142.67	92.42	1883	136.33	92.76
60	1883	130.33	93.08	1883	128.38	93.18	1883	132.33	92.97
90	1883	144.00	92.35	1883	146.30	92.23	1883	145.06	92.30
120	1883	126.33	93.29	1883	126.00	93.31	1883	124.67	93.38

Oils and greases

This parameter suffered a reduction around 77.71 % when 1 mL of AgNPs was used with a treatment time of 120 minutes (See Table 6). This due to the fact that greases have affinity in ion exchange with silver nanoparticles when ionized because of their instability (Murru, 2017).

Table 6: Oils and greases in wastewater during AgNPs treatment

Treatment time (min)	Sample 1 (1 mL of AgNPs)			Sample 2 (10 mL of AgNPs)			Sample 3 (20 mL of AgNPs)		
	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)	Initial (mg/L)	Final (mg/L)	Reduction (%)
30	126	42.09	66.60	126	37.12	70.54	126	37.07	70.58
60	126	35.20	72.06	126	33.74	73.22	126	33.21	73.64
90	126	30.10	76.11	126	30.65	75.68	126	30.06	76.14
120	126	28.08	77.71	126	28.30	77.54	126	28.84	77.11

Escherichia coli

After 30 minutes of treatment using the three doses of nanoparticles studied, *Escherichia coli* in tannery wastewater was reduced to 100% (see Table 7). This is due to the fact that the nanoparticles have a nanometric size that gives them a larger surface area of action, and also present high biological reactivity with microbicide characteristics due to the high exposure of the metal's electronic plasma with very small amounts of mass that increases the electrostatic and kinetic energy of the interaction electronic plasma to a good level (Noguez, 2007; Lynch and Dawson, 2020). On the other hand, silver has antibacterial properties and is a natural biocide (Gonzales A. and Garcia A., 2020), reaching an efficiency of elimination of *Escherichia coli* of 100%.

Table 7: *Escherichia coli* in wastewater during AgNPs treatment

Treatment time (min)	Sample 1 (1 mL of AgNPs), sample 2 (10 mL of AgNPs) and sample 3 (20 mL of AgNPs)		
	Initial (NMP/100 mL)	Final (NMP/100 mL)	Reduction (%)
30	2400	0.00	100.00

Other parameters

The parameters such as pH, total suspended solids (TSS) and electrical conductivity (EC) of the tannery wastewater after treatments with samples 1, 2 and 3 of 1, 10 and 20 mL of AgNPs, respectively, are shown in Table 8. The pH of the original sample decreases from 12 to a value of 7.90 at 90 min of treatment using 1 mL of AgNPs, being the lowest value and the most efficient. However, in all the tests there was a good reduction, leaving this parameter within the maximum admissible value of the environmental standard, which is between 6 and 9.

Total suspended solids (TSS) decreased in the treatment with AgNPs, reaching a reduction of approximately 91.78 %, which is below the maximum admissible value established (713 mg/L). This is attributed to the adsorption capacity of the nanoparticles due to their high contact surface area (Nie et al., 2010).

The electrical conductivity increased and sometimes decreased because AgNPs are unstable and transform to their ionic form (Larue et al., 2014). This parameter is not registered in Peruvian environmental regulations.

Table 8: pH, TSS and EC in wastewater during AgNPs treatment

Treatment time (min)	Sample 1 (1 mL of AgNPs)			Sample 2 (10 mL of AgNPs)			Sample 3 (20 mL of AgNPs)		
	pH	TSS (mg/L)	EC (μ S/cm)	pH	TSS (mg/L)	EC (μ S/cm)	pH	TSS (mg/L)	EC (μ S/cm)
30	8.17	74.51	1024.00	7.97	68.57	1082.00	7.97	68.39	1070.33
60	8.20	61.77	1044.67	7.97	60.49	1187.67	8.07	58.62	1161.33
90	8.23	67.07	1016.33	7.90	67.66	1014.67	8.07	66.07	1080.33
120	8.23	68.70	1276.33	7.97	68.07	1237.00	8.10	67.22	1262.33

4. Conclusion

Using silver nanoparticles of green synthesis, physicochemical parameters such as total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and oils and greases (A&G), as well as *Escherichia coli* from the wastewater of a tannery industry, were reduced to the maximum admissible levels allowed by the Peruvian environmental standard. It was observed that the maximum reduction of the different parameters studied depends on the dose of AgNPs and the treatment time, reaching values of 93.27 %, 93.38 %, 91.78 %, 77.71 % and 100 % for BOD, COD, TSS, A&G and *Escherichia coli*, respectively. Thus, it is established that this method is feasible and environmentally friendly by using nanoparticles from natural products.

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