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Green Silver Nanoparticles for Effluent Treatment with BRL Blue Dye in the Textile Industry

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The use of reagents and synthetic dyes products in the textile industry makes the effluents originated in the industrial process have a high danger of contamination in the receiving bodies in surface water or soil. In search of a solution for the treatment of these discharges, the research has the objective of decreasing the concentration of the BRL blue dye, by means of silver nanoparticles (AgNPs) synthesized according to a green chemistry route. The methodology consists on synthesizing AgNPs by using *Petroselinum crispum* (parsley) extract as reducing and stabilizing agent. Characterization of the prepared samples revealed in the best case AgNPs having 24.25 nm size. These AgNPs have been used for the treatment of model effluent samples, obtaining a reduction of the BRL blue dye until 80.46%. The obtained result shows that the prepared AgNPs can be successfully used for the treatment of residual waters of one of the industries that have been causing high contamination lately, and the results is more promising considering that the AgNPs have been obtained with an environmentally friendly method.

1. Introduction

The textile industry has been growing rapidly due to the great demand due to trends and fashions in the clothing of the population, but at the same time it has become one of the industries that generates the most pollution in aquatic environments (Brañez, 2018). A garment widely acquired in many parts of the world are jean pants with the characteristic color blue and synthetic dyes are used to obtain this presentation, including BRL blue with a molecular chemical structure resistant to degradation with traditional methods. This stability to environmental conditions results in a negative impact on the environment because they are not easily biodegradable, even conventional treatments are not efficient (Gordón, 2015). One of the recent technologies for this purpose with the use of nanoparticles is tested in this research.

In the dyeing process, approximately 100 to 150 liters of water can be used per kilo of product (Aimacaña, 2019), which are then discharged as effluents with a high load of dye residues to the receiving bodies. These textile effluents will alter important characteristics of the water such as pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids, etc. These discharged waters contain up to 15% of the dyes used (Deza et al., 2017) and the impact on the waters can be a problem of eutrophication.

There are various methods for the treatment of contaminated wastewater from the textile industry, such as the use of sonocatalysis in the presence of MgO nanoparticles, achieving an 85% reduction in the COD of wastewater (2.4 g / L of MgO, in 141 min) and with 0.11 M periodate in the solution (Cheshmeh et al., 2016).

The objective of the research was to quantify the reduction of the BRL blue textile industrial dye by means of silver nanoparticles synthesized with *Petroselinum Crispum* extract; Also, at the same time, the conditions for obtaining the nanoparticles and the importance of the method of their synthesis from reduction with plant extract, also called green chemistry due to environmental advantages, unlike the chemical method, are taken into account. Nanoparticles of this type have been tested to reduce turquoise blue textile dye achieving up to 96.8% (Banerjee et al., 2014). Nanoparticles of this type are also effective in soil treatment (Orizano et al., 2020). In other cases, good results of use as an antibacterial were obtained (Da Silva et al., 2018).

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2. Materials and methods

2.1 Characteristics of the BRL blue dye

Synthetic water with blue BRL dye was prepared with concentrations similar to those discharged in the textile industry, taking into account the scientific literature. 3 samples were prepared with concentrations of 40 ppm (Aimacaña, 2015), 50 ppm (Treissy, 2015) and 69.61 ppm (Zavala, 2015).
These samples were determined for their pH, temperature, and absorbance. The characteristics of BRL Blue dye are shown in Table 1.

Table 1: General Characteristic of Dye BRL Blue

Dye name	Type of dye	Molecular formula	IUPAC name	Molecular Weigh (g/mol)
BRL Blue (Direct Blue 1)	Diazoic	$C_{34}H_{24}N_6Na_4O_{16}S_4$	Tetrasodium; 5-amino-3-[[4-[4-[2-(8-amino-1-oxo-3,6-disulfonatonaphthalen-2-ylidene)hydrazinyl]-3-methoxyphenyl]-2-methoxyphenyl]hydrazinylidene]-4-oxonaphthalene-2, 7-disulfonate	992.82

The BRL Blue dye has a chemical structure shown in Figure 1.

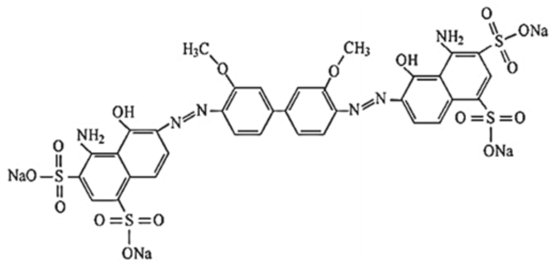

Figure 1: Chemical structure of the BRL blue dye

2.2 Synthesis of silver nanoparticles

To obtain silver nanoparticles, two solutions are used: *Petroselinum crispum* as a reducer and silver nitrate as a precursor.

A. Preparation of the extract of *Petroselinum crispum:* 10 g of washed and dried *Petroselinum crispum* leaves were crushed and placed in a flask, then 200 mL of distilled water were added. The mixture was heated to 65° C under stirring at 350 rpm for 20 minutes, after a slow filtration. To obtain a higher concentration of extract, the mixture was heated to 65° C under stirring at 350 rpm for 20 minutes, finally to separate the solids from the liquid, the mixture was filtered in the vacuum pump equipment with a Whatman slow filter paper.
B. Preparation of the silver nitrate solution: 3.38 g of silver nitrate was diluted in 200 mL of distilled water.
C. Preparation of the silver nanoparticles: 30 mL of silver nitrate solution previously prepared ware placed in a 100 mL balloon and 10 mL of *Petroselinum crispum* extract was added dropwise. The mixture was heated and maintained at 65°C for 8 minutes under stirring (400 rpm) then was exposed to a UV lamp, observing the change in color of the solution to a light brown color, indicating the formation of AgNPs. The procedure was repeated with the same amount of nitrate solution but this time it was added to 20 and 30 mL of *Petroselinum crispum* extract. The colloidal suspension so obtained have been indicated as AgNPs1, AgNPs2 and AgNPs3 and then characterized.

2.3 Characterization of silver nanoparticles (AgNPs)

A 10 ml colloidal mixture of silver nanoparticles was placed in an ultrasound machine (Brand: Branson Ultrasonic, Model: CPX-952-338R) at 60Hz for 1 minute to disperse them. To obtain pure nanoparticles from the mixture, the solution was centrifuged (centrifuge Make: BOECO Germany, Model: SC -8) at 6000 revolutions per minute, for 30 minutes. The precipitate was dispersed in 10 ml of distilled water and the centrifugation process was repeated twice more in order to remove any residual biomass. The colloidal silver was then decanted and collected and analyzed in a UV-vis spectrophotometer (UV/VIS Spectrophotometer, Brand: Pg instruments, Model: T80 + UV-Vis, detection limit: 190nm-1100nm), in order to know the wavelength, and by its result, to identify the presence of silver nanoparticles. Dynamic light scattering (DLS) technology (Dynamic Light Scattering: Brand: 90 PLUS Particle Size Analyzer, Model Brookhaven Instruments, detection limit: Range >1nm to 6μm) was used to analyses the distribution profile and size of silver nanoparticles in the suspension. The characterization of the nanoparticles was made in the Materials and Environment Laboratory of the Faculty of Sciences of the National University of Engineering.

2.4 Treatment of synthetic wastewater contain the DRL blue dye with silver nanoparticles (AgNPs)

In a flask, 1 mL of synthetic waste water with a concentration of 40 ppm BRL blue dye was placed and 8 mL of distilled water was added. To improve the reaction rate of the process (according to scientific literature), 1 mL of 0.1 M sodium borohydride ($NaBH_4$) was added and stirred (stirrer Model: MS7-H550- Pro, DLAB) for 5 min. To this mixture with BRL blue dye, 2 mL of colloidal solution of silver nanoparticles was added in an ultraviolet light chamber for 5 min (UV-A Fluorescent Lamp, size: 33 (L) x 2.5 (D) - Tubular 10 W - 368nm, Model F10T8 / BL368, GLEECON brand). The addition of sodium borohydride and exposure to UV light is to stability and enhance the speed of the process of action of the nanoparticles in reducing the dye. The removal of the silver nanoparticles from the treated water is done by centrifugation. The final concentration of the dye in the treated wastewater was determined by UV-vis spectrophotometry.
Research is continuing to determine the efficiency of these AgNPs in the treatment of coloured wastewater without addition of $NaBH_4$ or exposure to UV radiation, as well as using solar radiation

3. Results and Discussion

3.1 Physicochemical characteristics of the Petroselinum crispum extract sample

The plant extract of Petroselinum crispum, presented a pH of 6.1 around the neutral, see Table 2, this solution presents flavonoids with antioxidant activity (Martinez-Florez, 2002) that allows to have a reducing power in the presence of metals such as silver, it is this characteristic that allows the synthesis of silver nanoparticles. The Petroselinum crispum, its taxonomy is from Kingdom Plantae, Magnoliophyta Division, Magnoliopsida Class, Apiales Order, Apiaceae Family, Apioideae Subfamily, Petroselinum Genus, Petroselinum crispu Species. Its common name is "parsley" (Reyes et al., 2012). This extract, like others with similar characteristics, allows the synthesis of nanoparticles of various metals such as gold NPs using kiwi juice and gold chloride solution (Zuorro et al., 2020).

Table 2: Petroselinum crispum (parsley) extract characteristics

Sample	Concentration (g/ml)	Temperature (°C)	pH
Abstract	10	65	6.1

3.2. Characterization of silver nanoparticles (AgNPs)

Three samples of colloidal silver solution were analysed in the UV-vis spectrophotometer. The samples were found to have similar wavelengths close to 400 nm. From these, sample M2 (AgNPs2) was chosen to be used in the treatment of the wastewater sample with BRL Blue dye. Sample M2 had a shorter wavelength and a higher absorbance level. See Table 3

Table 3: UV-vis spectrophotometric parameters of AgNPs

Samples	Sample code	Wavelength (nm)	Absorbance (Abs)
M1	AgNPs1	431.5	0.86104
M2	**AgNPs2**	**431.1**	**0.95205**
M3	AgNPs3	432.7	0.51294

3.3 Characterization of silver nanoparticles (AgNPs) by dynamic light scattering (DLS)

Through the DLS it is observed that the smallest size of the AgNPs samples was 24.25 nm, so it was with this size of nanoparticles that the treatment of contaminated water with BRL blue dye was carried out, see Table 4 and Figure 2. The size of the nanoparticles synthesized with plant extracts depend on the presence of the reducing agents found and the operating conditions in the process, hence other researchers have found different sizes such as those obtained by Zuorro et al. (2020) with a mean size of 30 nm; However, when comparing with the synthesis carried out by Roy et al., (2019) that found silver nanoparticles of size 30 nm using *Petroselinum crispum*, this is undoubtedly due to the concentrations of the extract and the silver nitrate solution to be reduced.

Table 4: Size characterization of AgNPs by DLS

Sample code	Size (nm)	Polydispersion
AgNPs1	56.99	0.221
AgNPs2	24.25	0.192
AgNPs3	30.56	0.226

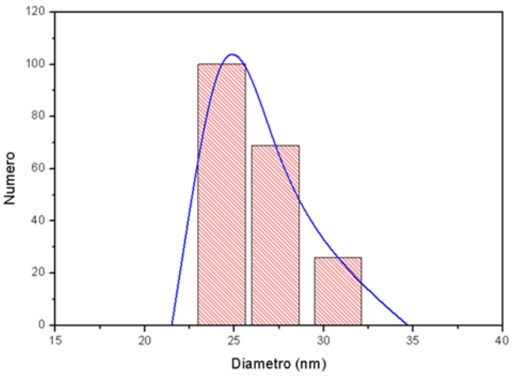

Figure 2: DLS result for AgNPS2 sample.

The colloidal solution with AgNPs after 3 hours of synthesis was subjected to analysis by DLS observing the respective chain of custody, despite the advantage of the silver colloidal solution to be very stable due to the presence of boron acid used and its reaction with the polyhydroxyl components of the reducing extract (parsley) giving antimicrobial characteristics to the formed nanoparticles (Bentacur, 2016).

3.4 Initial and final physicochemical parameters of the water sample with BRL blue dye

With the synthesized nanoparticles of size 24.25 nm (AgNPs2), the coded samples M1, M2 and M3 were treated with concentrations of dye indicated in Table 5. Table 6 shows the results of the final concentration of the dye BRL blue after treatment with silver nanoparticles synthesized with extract of the plant Petroselinum crispum. It was determined that for the three samples at the end they present a reduction of 84.25%, 80.46% and 77.014% respectively. These results are lower than that achieved by Aimacaña (2019) who reduced 91.25% with the fenton and persulfate method and what was obtained by Zavala (2015) who used a UASB upflow anaerobic reactor with activated carbon that reduced 87% of the same colorant, but it exceeded the result achieved by Treissy (2016), which reduced 63.07% using heterogeneous photocatalysis with titanium dioxide.

The results indicate that the silver nanoparticles turn out to be good agents in reducing the BRL blue dye with environmental characteristics, low toxicity, in physicochemical processes. On the other hand, it can be seen that the pH undergoes an increase due to the treatment, probably due to the greater presence of the OH radical that is generated in the process.

Table 5: Initial concentration of blue dye BRL and parameters in samples.

Sample code	Initial concentration of BRL blue dye (ppm)	Temperature (°C)	pH
M1	40.00	21.00	8.04
M2	50.00	21.00	7.90
M3	69.61	21.03	7.85

Table 6: Final concentration and percentage reduction of BRL blue dye

Sample code	Final concentration of BRL blue dye (ppm)	Initial concentration of BRL blue dye (ppm)	BRL blue dye reduction percentage	Temperature (°C)	pH
M1	6.30	40.00	84.25	20.06	9.84
M2	9.79	50.00	80.46	20.03	9.79
M3	16.00	69.61	77.01	20.01	9.65

Figure 2 shows the difference in colors before and after applying silver nanoparticles to the three samples. It is determined visually that sample 1 is more discolored, which is consistent with the result presented in Table 5

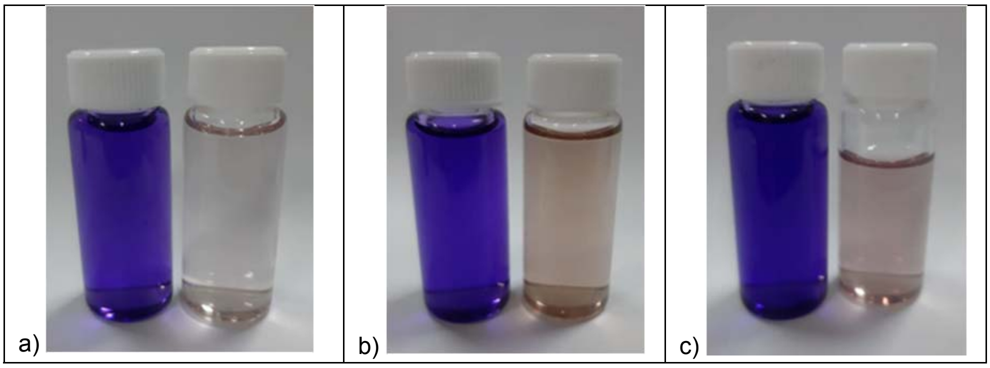

Figure 2: a) Initial and final color of sample M1, b) Initial and final color of sample M2, c) Initial and final color of sample M3

4. Conclusion

An appreciable result was obtained in the degradation of the blue textile dye BRL textile with the use of silver nanoparticles. The method is promising both for the observed decolorization capacity (after treatment there is a reduction of the dye content of 80.46%) and the synthesis of silver nanoparticles by a green chemistry method exploiting the extract of the vegetable plant *Petroselinum crispum*. This treatment can contribute to improve the quality of industrial effluents before being discharged into water bodies avoiding pollution and negative impact.

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