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Removal of cationic dyes utilizing natural coffee pulp coagulant

Felipe Correa Mahecha* [a], Diana Cuesta Parra[a], Juan A. Sandoval[a], Manuel A. Mayorga[b], Samuel A. Ortiz[a]

[a]Chemical Engineering Department, Fundación Universidad de América, Bogotá, Colombia
[b]Chemical Engineering, Universidad ECCI, Bogotá, Colombia

*felipe.correa@profesores.uamerica.edu.co

The color removal activity of polyphenolic extracts obtained by maceration of coffee pulp with the *Coffea arabica* species was evaluated in synthetic waters prepared with three commercial dyes: methylene blue, malachite green and crystal violet. The extract was prepared by maceration using milled coffee pulp in a hydroalcoholic solution with a volume ratio of 1:1 and a solid: solvent ratio of 1:20 (g: mL). Additionally, total polyphenols were quantified using the Folin-Ciocalteu method and pH effects were evaluated based on the color removal percentages at fixed doses of 2.5 mg GAE / L (gallic acid equivalent per liter). Maximum removals with the values of 61.74%, 91.65% and 86.47% were obtained for malachite green, crystal violet and methylene blue at a pH of 4.26, 8.40 and 9.22, respectively. The present study confirms the potential use of waste extracts from the coffee industry for the removal of cationic dyes by coagulation.

Keywords- Cationic coagulants, Polyphenols, coffee pulp.

1. Introduction

Dyes are commonly used in the textile industry but many of these products represent a real risk to the environment, because their annual discharges into waters are between 2.0 to 2.3 million tons. This produces high levels of Chemical Oxygen Demand (COD), biological toxicity and alterations in color and pH levels (Han et al. 2020). For these reasons, development of treatment processes for this type of waste is an urgent need.

Different physical, chemical, and biological processes have been studied for dyes removal from industrial wastewaters. Physical methods such as adsorption, extraction, and filtration with membranes are widely used (Li, Mu, & Yang, 2019; Maiti, Mukhopadhyay, & Devi, 2017). From the three methods mentioned above, adsorption offers a simple, effective, and profitable solution, which is why it is currently the most attractive waste management treatment approach (Wang & Wang, 2016). On the other hand, coagulation is considered the most effective and economical technique for the removal of contaminants (Dotto et al. 2019). However, very few studies have been reported on the use of organic materials for the coagulation and flocculation of cationic dyes (Jeon et al., 2009; Kuppusamy et al., 2017). It is known that tannins and other polyphenols can interact with cationic dyes through ion-ion and ion-dipole forces (Leopoldini, Russo, & Toscano, 2006), thus achieving the formation of three different complexes, an initial supramolecular interaction, the formation of colloidal flocs and their precipitation (Jeon et al., 2009).

Methylene blue, malachite green and violet are cationic dyes commonly used in different industries to dye cotton, wood, paper, silk, and wool (Álvarez, Castro, & Tinoco, 2019), but they present complications in removal, due to their cationic nature, since the most frequently used chemical coagulants, such as ferric chloride and aluminum sulfate, are usually ineffective. Cationic dyes are also used as model compounds due to the presence

of numerous common functional groups in various types of dyes (Kuppusamy et al. 2017). The presence of tints in natural waters can cause serious problems in aquatic life because it increases the amount of chemical oxygen demand and toxicity, and reduces light penetration. In addition, some colorants such as methylene blue can cause damage to human and animal health (Salleh et al. 2011).

The coffee pulp is the main waste residue of the coffee industry, representing 29% of the weight of the whole fruit and due to its high content of nutrients its use as animal feed has been evaluated. However, tannins and caffeine limit its use to a proportion of 20% or less of a daily diet since higher doses tend to produce nutritional problems (Noriega Salazar et al. 2008). Coffee pulp has also been studied to obtain alcohol (Rodríguez, 2013), refreshing drinks (Heeger et al. 2017), as a substrate to produce mushrooms and enzymes (Janissen & Huynh, 2018), and for wastewater treatment with dyes (Jeon et al., 2009; Kuppusamy et al., 2017). It also has a high source of polyphenols with high antioxidant activity (Tobón Arroyave 2015; Serna Jiménez et al. 2018). The objective of this work is to evaluate the action of coffee pulp extracts as natural agents for the coagulation of synthetic waters with cationic dyes.

2. Methods & Materials

Coffea arabica coffee pulp was provided by the Coffee Innovation Technology Park Corporation -Tecnicafé-Supracafe, located in Cajibío, a town in the department of Cauca, Colombia. The pulp was dried and shipped afterwards to the laboratory.

The humidity of the sample was determined according to the Colombian Technical Standard NTC 2558 (ICONTEC, 2011) by determining its mass loss at 103 ºC. The sample was crushed with a Premium Model PB323 blade mill, China. The average of three measurements was registered.

The extraction was carried out by maceration, using a solution of ethanol in deionized water at a volume ratio of 1:1 and a solid: solvent ratio of 1:20 (g: mL), for a period of 30 hours at room temperature of 15±3 ºC. The phases were separated by filtration, and the extract was concentrated using a Heildoph G3 Hei-Vap Precision rotary evaporator, Germany, at a temperature of 70 ºC and a pressure of 180 mBar. The dried extract was stored at 4 ºC. Tests were carried out afterwards.

The polyphenol content of the extract was established using the Folin-Ciocalteu method, as described by (Muñoz Bernal et al. 2017). Reading was taken at 765 nm with a Genesis 30 spectrophotometer using Folin-Ciocalteu reagents (Sigma Aldrich®) and sodium carbonate (Rodaquímicos®). For the calibration of the standard curve, 6 solutions of anhydrous analytical reagent gallic acid (Merck®) were prepared and quantified three times, which resulted in a linear correlation with a coefficient of determination (R^2) of 0.9911.

Synthetic water with the three dyes was prepared using the methodology described by Chaibakhsh et al. (2014). A total of 25 mg of each dye were taken and dissolved in a beaker with water. Then, analytical transfer was carried out to volumetric flasks of 1000 mL filled to the mark with deionized water.

The maximum wavelengths used to estimate the concentration were determined by scanning between 350 and 750 nm with a Genesis 30 spectrophotometer. These values were used to measure the absorbance of the different dye solutions before and after treatment.

For the pH measurement, a Schott handy lab PH11 pH meter was used and calibrated with Schott solutions, Germany.

To evaluate the behaviour of the extract, jar tests were performed in accordance with NTC 3903 standard (ICONTEC, 1996) on synthetic water samples, using sulfuric acid and sodium hydroxide. The operation pH was adjusted by using Gallic acid at 2.5 mg GAE / L (Gallic acid equivalent per litre), value used by Beltrán (2009). Colour removal percentage was calculated with the following equation:

$$\%\ \text{Colour removal} = \frac{\text{Abs}_o - \text{Abs}_f}{\text{Abs}_o} \quad (1)$$

Where Abs_o is the absorbance before treatment and Abs_f is the absorbance after treatment. The experimental results are presented in the following section.

3. Results and discussion

The moisture content obtained was 15.76 ± 0.11%, which is a value close to the 15.99% reported by other authors for sun-dried pulps (Galanakis, 2017). In the extraction method by maceration, the concentration of total polyphenols in the analysed pulp was 8.471 ± 1.743 mg GAE / g dry base, which is close to the value reported by Duangjai et al. (2016) for three different types of pulps of the same variety (*Coffea arabica L.)*.
Figure 1 shows the spectral sweeps of the solutions with the three cationic dyes, as well as the molecular structures, which were used to determine the removal percentages.

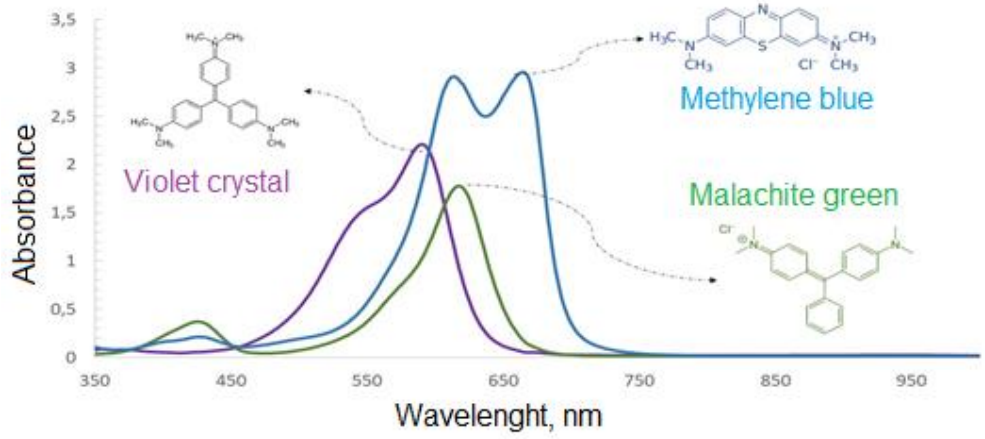

Figure 1: Spectral scans of three cationic dyes, with their molecules and respective wavelengths of maximum absorption.

The values obtained for the crystal violet were based on the maximum absorbance wavelength of 590 nm, close to the value reported by Fabryanty et al. (2017). For methylene blue and malachite green, wavelengths of 665 nm and 617 nm were obtained, which are almost the same as the ones reported by Chaibakhsh et al. (2014) with values of 666 nm and 615 nm.

Figure 2 shows the removal percentages of malachite green as a function of pH for a fixed dosage of coffee pulp extract, where the maximum value is achieved at a pH of 4.26. Additionally, it can be observed that for all pH values tested the removal percentages was greater than 36%.

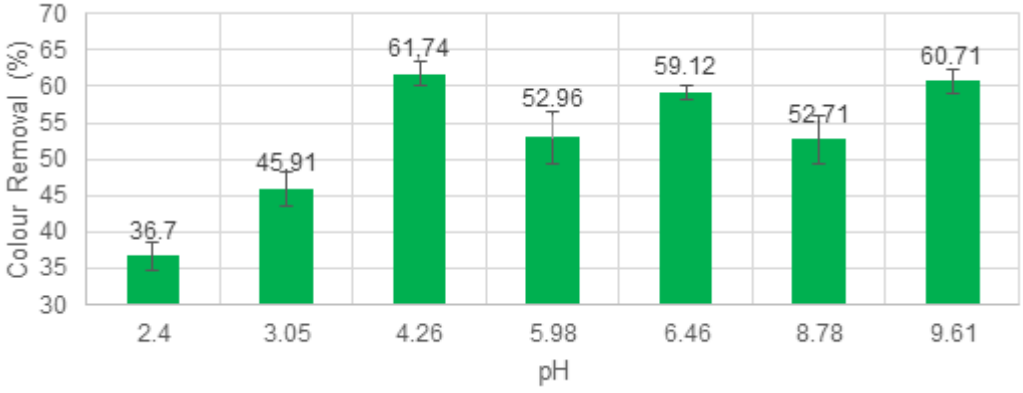

Figure 2: Colour removal for malachite green at different pH values and a fixed dose of 2.5 mg GAE / L.

Figure 3 shows the results for the removal of the violet crystal, whose maximum removal percentage achieved was 91.65% at pH 8.4 and all removals were greater than 60%.

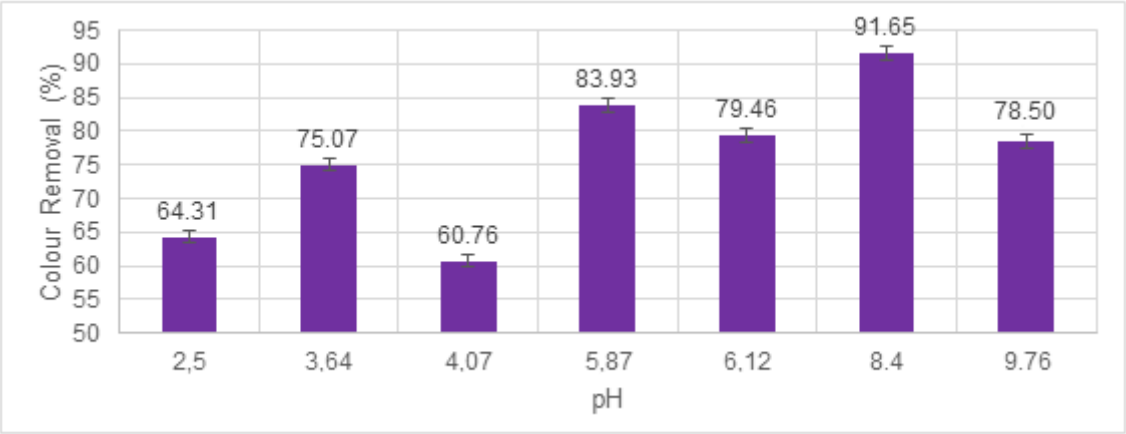

Figure 3: Colour removal for crystal violet at different pH values and a fixed dose of 2.5 mg GAE / L.

Finally, Figure 4 shows the results of methylene blue removal, where the best removals occur at an alkaline pH level with a maximum removal percentage of 86.47%.

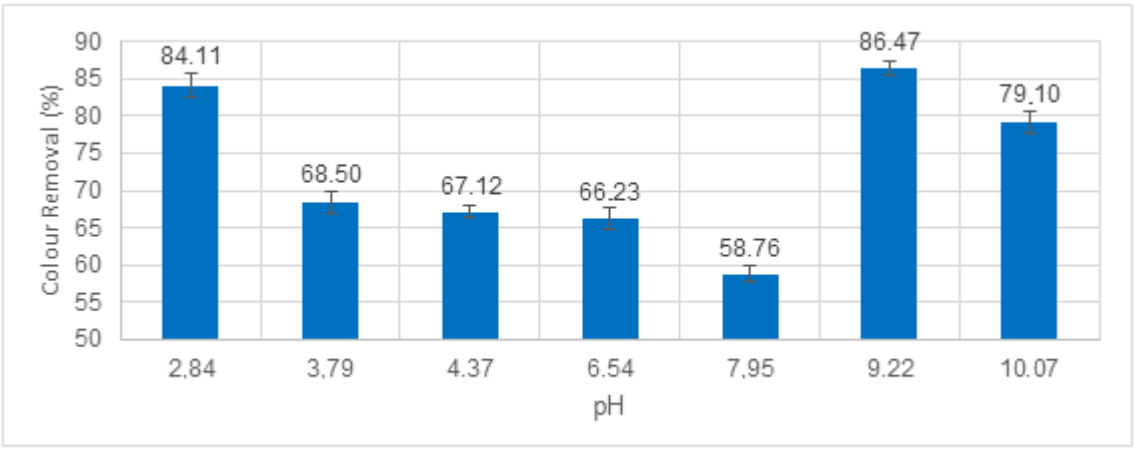

Figure 4: Colour removal for methylene blue at different pH values with a fixed dose of 2.5 mg GAE / L. Error bars represent the standard deviation of the tests.

According to Figures 2 to 4, colour removal was greater for violet crystal than for blue methylene and malachite green, which presented the lowest removal percentage. The basic pH seems to favour colour removal, especially in the case of methylene blue. However, more research must be done to explain the high removal percentage at a pH of 2.84.

4. Conclusions

This study preliminarily confirms that waste extracts from coffee pulp (*Coffea arabica)* have a potential use as natural coagulants for cationic dyes removal.

It was also found that the pH and the dose of the extract have an important influence on the coagulation action. Additional studies are required to establish the optimal conditions for the flocculation - coagulation process in real wastewater, as well as the combination of natural materials that improve the stability of the clots and increase their sedimentation rate.

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