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Removal of Azo Dyes through a Natural Coagulant Obtained from Coffee Waste (*Coffea Arabica)*

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The present work evaluated the performance of coffee (Coffea Arabica) Caturra variety waste extracts for the removal of two azo dyes used in the textile industry. Ultrasonic extractions were performed to evaluate the effect of particle size and type of residue on the concentration of polyphenols in the extracts, finding that the dehydrated pulp with a particle diameter of 3.375 mm is the residue with the highest yield with 6.96 ± 0.08 milligrams of Gallic Acid in a gram of dry base (mgGAE/gBD); The extract of polyphenolic compounds was dosed in synthetic waters with azo dyes to test its efficacy as a coagulant, using a jar test by varying the doses and pH. It was found that the maximum removal for the acid red dye was 59.37 % of the acid red dye #88 (RD-88) at a concentration of 15 milligrams per liter (mg/L) of the natural coagulant at acid pH and 49.76 % of the acid yellow dye #36 (YD-36) at a concentration of 15 mg/L of the polyphenolic extract at neutral pH. Finally, the results obtained were compared with the performance of aluminum sulfate (AS), which achieved a 65.44% removal of YD-36 at a concentration of 15 mg/L at neutral pH and 95.04% of RD-88 at a concentration of 10 mg/L of metallic coagulant at acid pH. natural coagulants obtained from coffee residues have the potential to be used in the removal of cationic dyes by coagulation processes, it is necessary to carry out tests to optimize the process and improve the coagulant by means of chemical modifications and the use of complementary flocculants.

1. Introduction

Due to their functional characteristics, range of colors, ease of synthesis and low price, azo dyes are widely used in the textile industry, they represent about 70% of the synthetic dyes market, however, they have important environmental and sanitary implications, they are toxic substances, recalcitrant and difficult to eliminate by conventional methods of wastewater treatment (Oyetade et al., 2022). Their color is determined by the azo bonds in their chemical structure and their associated chromophore and auxochrome groups (Benkhaya et al., 2020). Prominent among them are Acid Yellow 36 (YD-36), a non-biodegradable dye under aerobic conditions, with degradation intermediates such as aromatic amines that are carcinogenic, which can pose a serious threat to the aqueous environment (Aghdasinia et al., 2016), and Acid Red 88 (DR-88) dye is discharged into industrial wastewater at a concentration ranging from 10 to 50 mg/L, causing breakdown products that cause skin sensitization and mutagenicity (Malik, 2009). A wide range of high-value technologies have been reported to be used for their removal, including photocatalytic degradation with zinc nanoparticles synthesized in plant extracts (Dihom et al., 2022), advanced oxidation with ozone, ultraviolet radiation (Dadban Shahamat et al., 2022) and microbial electrolytic reactions coupled to plant microbial fuel cells (Liu et al., 2023), for these reasons there have been urgent calls for the treatment of effluents containing azo dye residues to eliminate them or convert them into useful and safe products (Benkhaya et al., 2020). On the other hand, coffee is one of the most popular beverages in the world, its production process generates large amounts of waste that are normally discarded, causing contamination of water and soil sources, coffee pulp is the main residue of the wet milling process in producing countries.

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From which valorization alternatives have been developed such as composting, animal feed, production of edible fungi and biogas (Manasa et al., 2021), as well as tests for the removal of cationic dyes from synthetic waters with coffee pulp extracts (Correa et al., 2021).
Polyphenols such as Gallic, Caseic and Ferulic acids have in their structure the union of carbohydrates with hydroxyl and carboxyl groups, capable of donating a proton to a water molecule that hydrolyzes, for the formation of hydronium ions and hydroxides in insoluble colloidals, capable of accepting protons and adsorbing particles, favoring the precipitation of a wide range of pollutants (Quiñones et al., 2012). Coffee pulp extract contains phenolic compounds (PC) that can form insoluble complexes, so they have the potential to be used as natural coagulants. This work performs the extraction and evaluation of the azo dye removal activity of polyphenols extracted from coffee industry residues.

2. Method

All the tests mentioned in this section were carried out at the facilities of the Tecnoparque Research Center (SENA), Bogotá, Colombia. The Dehydrated Pulp (DP) and Threshed Green Coffee (TGC) residues were supplied by SUPRACAFÉ-TECNiCAFÉ (Coffee Innovation Technological Park) collected in the town of Cajibío (Cauca) in southwestern Colombia during the first semester of 2022.

2.1 Coffee Waste Pretreatment

First, particle size reduction is performed in a disk mill followed by sieving, as shown in Table 1 for 100 g sample of each residue respectively.

Table 1: Sifting of the coffee waste

# Sieve	Opening [mm]	Particle diameter [mm]	Dehydrated Pulp (DP)		Threshing Green Coffee (TGC)	
			Retained mass [g]	Mass fraction Xi	Retained mass [g]	Mass fraction Xi
Auxiliary: 3.5	5.60	-	-	-	-	-
4.0	4.75	5.175	18.5	0.1979	28.5	0.3275
10.0	2.00	3.375	41.0	0.4385	41.0	0.4713
Auxiliary: 12.0	1.70	1.850	34.0	0.3636	17.5	0.2012
∑	-	-	93.5	1.0000	87.0	1.0000

The samples retained in the particle diameters (Pd) of 3,375 mm and 1,850 mm are chosen, to which the humidity is determined as indicated by the Colombian Technical Standard 2558 (ICONTEC, 2000) at a temperature of 103°C, in a thermobalance that allows graphing the humidity curve, to observe its behavior.

2.2 Calibration Curve of Gallic Acid (GA)

For this, it is necessary to prepare standard solutions, such as 5% sodium carbonate solution, a stock solution of Gallic Acid (GA) at 50 ppm using Ethanol:Water (50:50) V:V as solvent, from which dilutions are prepared at 10, 20, 30 and 40 ppm; the Folin-Ciocalteu assay is performed (Cicco et al., 2009) with 3 replicates for each concentration and a blank, the samples in test tubes are placed on a rack in a thermostatized bath previously heated to 40 °C for 30 minutes. After allowing to equilibrate at room temperature, all samples are read in triplicate in a UV-visible spectrophotometer (Thermo Fisher United States Scrientific model GENESYS 30) at a wavelength of 765 nm, to graph the result of absorbance vs concentration (mg GA/L).

2.3 Itrasonic-wave Assisted Extraction

For the extraction of polyphenolic compounds, the methodology described by Cuesta and Correa (Cuesta Parra and Correa Mahecha, 2018) is followed where Ethanol:Water (50:50) V:V is used as extractive solvent and a residue-solvent ratio of (1:20) g:mL. Ten grams of residue are taken in 200 milliliters of solvent and taken in amber containers to an ultrasound bath (WiseClean Germany model WUC-D06H) with a frequency of 40 KHz for 30 minutes; Subsequently, they are vacuum filtered, the liquid phase of interest (Extract) is separated and distilled in a rotary evaporator (HeidolphTM Germany model Basis Hei-Vap Precision HL) at 60°C, 1 mBar and 60 rpm to purify the extract and recover the solvent used.
A 2^2 factorial design of experiments is proposed, as a dependent variable the type of residue to be evaluated with two levels (DP and TGC), and as an independent variable the particle diameters obtained from the sieving process with two levels (3,375 mm and 1,850 mm). Finally, the response variable is the total PC concentration (mg GAE) in grams of dry base (g DB). In this way, the extract that presents the highest concentration of PC will be chosen to be applied in the coagulation tests in the azo dyes (YD-36 and RD-88).

2.4 Coagulant Activity of Natural Extract

Previously, a spectral scan is performed to find the maximum wavelength, with a 50-ppm solution of each dye, a length of 442 nm is obtained for acid yellow No. 36 and 505 nm for acid red No. 88. In order to evaluate the extract in 25 ppm dye solutions, the Cuesta-Parra (Cuesta-Parra et al., 2022) methodology is followed and a 3^2 factorial design of experiments is proposed as study variables the pH range and coagulant doses (10, 15 and 20 mgGAE/L), as response variable the percentage of removal calculated with Equation (1) is taken.
Subsequently, the tests are carried out by means of a jar test with 400 mL dye samples at the same initial concentration, shaken at a speed of 120 rpm for one minute to mix the coagulant, then at 35 rpm for 20 minutes, let it rest for 15 minutes (ICONTEC, 2010) and filter through quantitative paper by gravity.

$$\%\, Color\ removal = \frac{Abs_0 - Abs_f}{Abs_0} \times 100 \quad (1)$$

2.5 Removal Performance of Conventional Coagulant

In order to compare the removal obtained by the natural coagulant, as Dotto (Dotto et al., 2019) does in his research between an organic coagulant (Moringa extract) and an inorganic coagulant (Aluminum Sulfate) applied to textile wastewater from an industrial laundry. The use of granulated aluminum sulfate (AS) is decided to compare the results obtained; a decrease in its particle size is made with the help of a ball mill in order to improve its dissolution in the colored waters. In the same way, the same design of experiments described in the previous section is repeated with the difference of using the inorganic coagulant.

3. Results y Discussion

3.1 Moisture Curves

It is important to emphasize that the supplier of the coffee residues gave us the dry samples at room temperature, however, one of the parameters of great importance for the characterization of the extract is the determination of humidity, for this reason, the curves of humidity as observed in Figure 1, for each of the samples analyzed. It is obtained for the DP with Pd: 3,375 mm a humidity percentage of 10.53% and for a Pd: 1,850 mm a humidity percentage of 10.78%; both within the theoretical specification between 10 and 12% (Franco, 2017). On the other hand, a humidity of 3.40% is obtained for the TGC with Pd: 3,375 mm and for a Pd: 1,850 mm a humidity of 7.13%, which means that it increases by 2.93% compared to the theoretical (3.0-4.2%) (Clifford, 1975), phenomenon attributed to the type of material and its porosity. As its surface area increases, its moisture retention increases (Perry, 1992); Thus, only the sample with Pd: 3,375 mm is within the theoretical moisture specification.

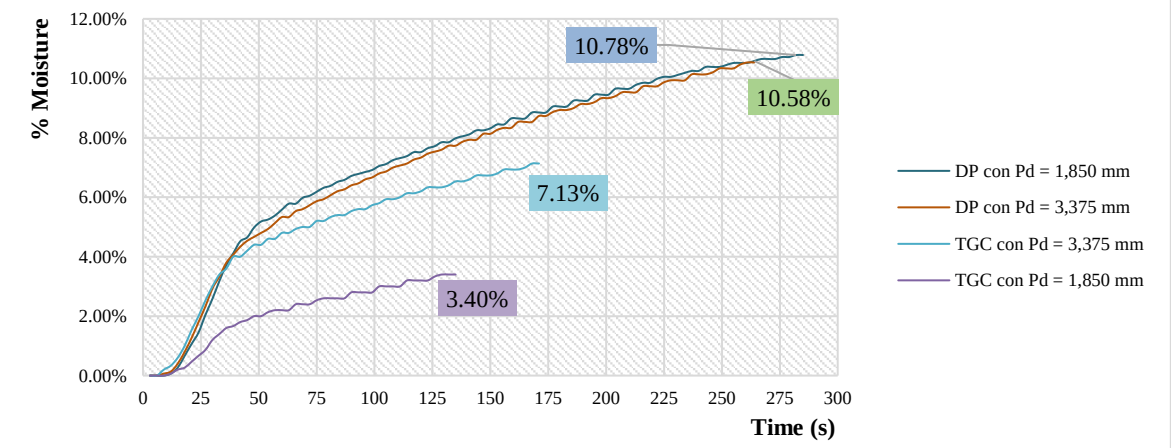

Figure 1: Moisture graph for coffee residues.

3.2 Calibration Curve of Gallic Acid (GA)

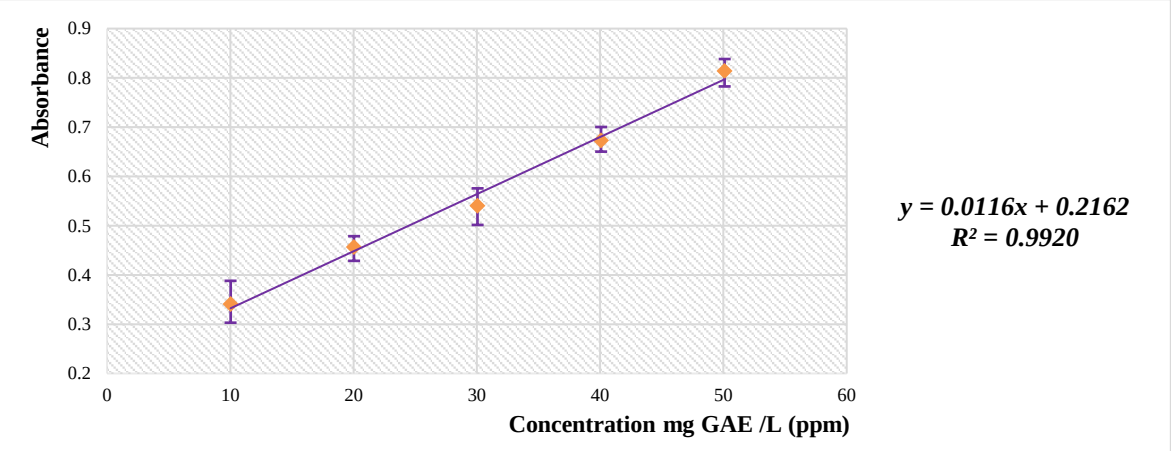

Figure 2: The figure shows the calibration curve with Gallic acid.

As shown in Figure 2, the calibration curve for Gallic acid is obtained; After a linearization of the data, an equation of the line (2) is obtained, with a coefficient of determination R^2 of 0.9920 very close to 1, which means that they fit the chosen linear model and predict reliable results.

$$y = 0.0116\,x + 0.2162 \quad (2)$$

3.3 Polyphenolic Compounds of the Coffee Waste

Table 2 shows the results obtained from the extraction and quantification of PC for all coffee residues. In this way, the DP with a particle diameter of 3,375 mm is chosen as the one with the highest average quantity of PC (6,962 mg GAE/g BS). In the same way, the phenomenon is observed with respect to the variation of the particle diameter taken as an independent variable, well, the results indicate that the larger the surface, the greater its solvent absorption capacity and its ultrasound-assisted extraction.

Table 2: Concentration of polyphenols in coffee waste using the Folin-Ciocalteu methodology

Coffee Waste	Particle diameter [mm]	Absorbance [Abs]	Concentration mg GAE / L [ppm]	Concentration mg GAE / gBD
Dehydrated Pulp	3.375	0.697	870.01	6.962
	1.850	0.621	733.43	6.148
Threshing Green Coffee	3.375	0.586	669.86	5.894
	1.850	0.574	648.14	5.583

3.4 Percentage of Color Removal at Different Doses of Natural Coagulant

Taking into account, the minimum dose reported by Cuesta and Correa (Cuesta Parra and Correa Mahecha, 2018) was 42.5 mg/L and the phenomenon presented above, it was decided to work with a concentration lower than 15 mg/L, with the execution of a target. In order to calculate the percentage of total color removal, the absorbance measurement before adding the extract and filtering it is taken as a reference, and it is compared with the absorbance measurement after adding the extract and filtering the solution with qualitative paper.
As observed in Figure 3, for YD-36 maximum removal percentages are obtained at a pH of 7.10 together with an optimal dose of 15 mg GAE/L (49.76%), followed by the dose of 20 mg GAE/L (47.70%) and finally 10 mg GAE/L (44.65%) due to pH variation, natural coagulant and filtration. In the same way, for RD-88, maximum removal percentages are obtained at a pH of 5.24 together with an optimal dose of 15 mg GAE/L (59.37%), followed by the dose of 20 mg/L (58.10%) and by last of 10 mg/L (57.56%) due to pH variation, natural coagulant and filtration. It is observed that the polyphenols present in the coagulant cause the formation of colloids with the dye particles that are removed from the solutions.

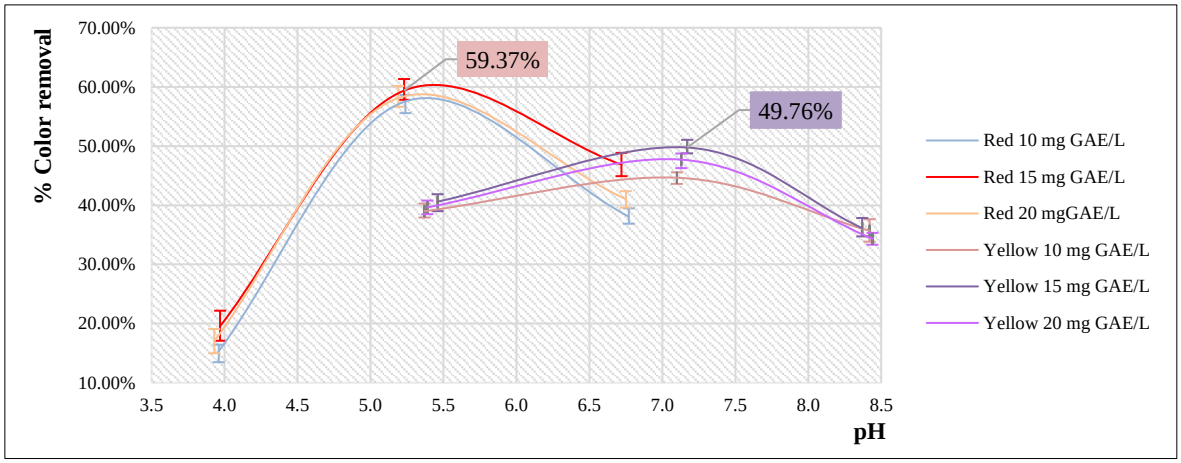

Figure 3: The figure shows the color removal percentages for Acid Yellow #36 Acid Red #88 at different doses of natural coagulant, vertical bars represent standard deviation.

3.5 Percentage of Color Removal at Different Doses of Aluminum Sulfate

Mainly, it is verified that the decrease in the particle size of the granulated synthetic coagulant (AS) allows a better solubility in the dye water sample. The total color removal percentage obtained with a synthetic coagulant AS and our natural PC coagulant is compared, the absorbance measurement before adding the AS and filtering it is taken as a reference, and it is compared with the absorbance measurement after add the AS and filter the solution through qualitative paper.

As observed in Figure 4, for YD-36 a maximum removal percentage is obtained at a pH of 7.14 at a dose of 15 mg AS/L (65.44%), in the same way, for RD-88, it is obtained a maximum percentage of removal at pH of 5.21 at a dose of 10 mg AS/L (95.04%), which indicates that the extract of coffee residues is less effective to coagulate in both cases, since aluminum sulfate has a higher affinity for azo dyes. However, the natural coagulant removes more than 50%, which demonstrates its possible uses and represents a first step to investigate its applicability.

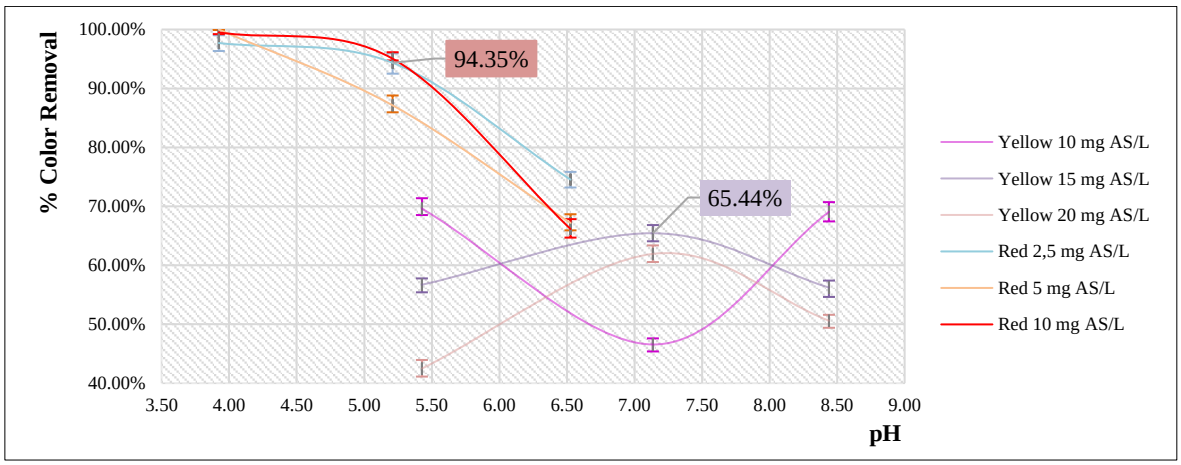

Figure 4: The figure shows the color removal percentages for Acid Yellow #36 Acid Red #88 at different doses of Aluminum Sulfate, vertical bars represent standard deviation.

For the experimental designs proposed throughout this investigation, an ANOVA statistical analysis is performed, from which the calculated F is greater than the critical F for the two variables chosen in each of the cases, which indicates that there is a statistically significant difference between them.

4. Conclusions

The removal of the azo dyes acid yellow No. 36 and acid red No. 88 was evaluated using a coagulant extracted from dehydrated coffee pulp of the Coffea Arabica species. A removal of 49.76% was achieved for the yellow dye and 59.37% for the red dye, it is important to take into account that the natural coagulant is derived from a by-product of coffee, which implies a lower total cost compared to traditional chemical coagulants like aluminum

sulfate. Besides the use of natural coagulants extracted from the coffee industry can be a valorization alternative in application of green chemistry principles and sustainable circular economy, further studies are required to optimize the coagulation process, evaluate chemical modifications and the synergistic effect with natural and synthetic flocculants.

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