Ingeniería y Universidad
ENGINEERING FOR DEVELOPMENT

Vol. 27
Continuous Publication
2023

ISSN: 2011-2769 (Online) | ISSN: 0123-2126 (Print)

Artículos de Investigación

Increasing the pH of Coffee Wet Mill Wastewater Using Eggshells*

Aumento del pH del agua residual del beneficio húmedo del café, utilizando cáscaras de huevo

DOI: https://doi.org/10.11144/Javeriana.iued27.ipcw

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Received: june , 02, 2020
Accepted: september , 25, 2023
Published: december , 15, 2023

Abstract:

In this investigation, chicken eggshells, which contain high contents of calcium carbonate, were used to increase the pH of acidic residual water products from conventional wet coffee processes, as these products are commonly discarded in water sources and cause chemical contaminations. Through experimental tests and an exploratory process, the eggshell was crushed, mashed and passed through sieves classified by American Society for Testing and Materials (ASTM) . This was performed to determine the particle size and most suitable concentrations for treating waste water with an acid pH (4.05), which was obtained from the coffee zone of the municipality of Líbano, Tolima, Colombia. To neutralize the acidic pH of the residual water, an eggshell with a maximum particle size of 0.15 mm, which corresponds to the No. 100 sieve of the ASTM classification, was mixed with the water. These methods offer an alternative process for treating wastewater generated in coffee-growing areas, which is characterized by the presence of acids that negatively impact the environment, especially bodies of water. Considering that coffee is an essential good and is consumed daily by most families in Colombia, abundant levels of coffee residues are extracted from wastewater.
Keywords: pH, eggshell, coffee, wastewater.

Resumen:

En la investigación se utilizó el cascarón de huevo de gallina, aprovechando su alto contenido de carbonato de calcio, para aumentar el pH del agua residual ácida, producto del proceso convencional de beneficio húmedo del café, arrojada comúnmente en fuentes hídricas con la consecuente contaminación química de cuerpos de agua. Mediante pruebas experimentales y proceso exploratorio, se trituró y maceró el cascarón de huevo, pasándolo a través de tamices de la clasificación ASTM, para determinar el tamaño de las partículas y las concentraciones más indicadas para tratar el pH ácido de agua residual, cuyo valor es de 4,05 y tomada de la zona cafetera del municipio de Líbano, Tolima, Colombia. Se neutralizó el pH ácido del agua residual mezclando con cascarón de huevo con tamaño máximo de partícula de 0,15 mm, que corresponde al que pasó el tamiz No. 100 de la clasificación ASTM, siendo una alternativa en el proceso de tratamiento de este tipo de aguas residuales que se generan en zonas cafeteras, caracterizadas por contener ácidos que ocasionan impacto ambiental negativo, especialmente a cuerpos de agua, cuya obtención es abundante, considerando que hace parte de la canasta familiar y se consume diariamente por la mayoría de familias en Colombia.
Palabras clave: pH, cascarón de huevo, café, agua residual.

Introduction

Colombia is among the four main coffee producers worldwide [1]. Global consumption is close to 40 liters of water per kilogram of traditional dry parchment coffee processing, which involves pulping, washing, and transportation stages, known as wet processing. This results in wastewater with physicochemical characteristics that are harmful to the environment, as the water possesses low hydrogen potential (pH),

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complex chemical compositions due to with organic matter, and dissolved solids that correspond to pollutant levels 60 to 240 times higher than domestic wastewater. The electrical conductivity is higher than 1900 µS/cm, dissolved oxygen is less than 3.1 mg/L, and chemical oxygen demand (COD) is greater than 1500 mg/L [2, 3], with pH values between 4 and 4.05 [4]. When wastewater is discharged without prior treatment, surface and groundwater sources become contaminated by agro-toxic residues, as evidenced by research conducted in Manhuaçu, Minas Gerais, Brazil [5, 6], in Coipa, Bolivia [7], and in the Chopim River and its tributaries, Palmas municipality, Brazil, where the contamination of surface sediments was investigated [8].

Research is underway on treatments to remove pollutant loads and stabilize the pH of wastewater, which indicates the level of water alkalinity or acidity [9]. For Colombia, this corresponds to a minimum pH value of 5 according to current regulations for agro-industrial wastewater produced in coffee processing (for both traditional and ecological processes) [10]. Various technologies are being employed, including electrocoagulation [11], artificial wetlands with macrophytes [7], anaerobic digestion with manure for methane production [12, 13], and anaerobic treatment [14].

Many methods are used to increase pH, including phytoremediation with macrophytes [15] and oxygenation lagoons [16]. Quicklime is currently used for pH adjustments. It results from the calcination of limestone at high temperatures, ranging between 650-900 °C [17], and is mainly composed of calcium carbonate and other alkalinizing agents, such as sodium hydroxide, sodium carbonate, and sodium bicarbonate [18, 19]. Water with a high carbonate content has an alkaline pH [20]. Therefore, chicken eggshell, composed mostly of calcium carbonate, can be used to alkalize coffee processing wastewater. As eggs are a widely consumed household product, they could be produced in coffee plantations as a productive diversification option [24]. The calcium in the chicken's diet influences the weight and thickness of the eggshell, as well as storage time [25, 26, 27], producing more calcium carbonate per egg.

Coffee solid waste is being researched for potential applications, such as activated carbon production with phosphoric acid [28], alcohol from pulp [29], and mucilage [30]. Coffee wastewater treated with leachate from coffee pulp inoculated with efficient microorganisms is used as a bioinput for vegetable production [31]. This adds value to these residues and contributes to the mitigation of negative environmental impacts.

At the Research Laboratory of the Universidad Cooperativa de Colombia, Ibagué-Espinal campus, chicken eggshells were prepared by cleaning, crushing, and maceration steps. The shells were used to treat the acidic pH of coffee processing wastewater obtained from a coffee farm in the municipality of Líbano, Tolima, Colombia, with a pH of 4.05. The material was passed through a series of sieves with American Society for Testing and Materials (ASTM) classification numbers 30 to 140, which contained openings from 0.600 to 0.106 mm, respectively. Through this process, the most efficient size of the process was determined, as well as the necessary concentration to increase the pH to 5, which is the minimum value established by current regulations for this type of water before being discharged into the environment [9]. Therefore, chicken eggshells would be useful as a simple, accessible, and effective alternative to alkalize acidic residual water. As a result, this solid domestic waste can be utilized rather than discarded in landfills.

Materials and Methods

The research was conducted through experimental tests to evaluate the use of eggshell for increasing the pH of acidic wastewater from the wet processing of coffee. The preparation steps involved washing the eggshell to remove adhered material and removing the testaceous membrane inside the shell, which does not contain calcium carbonate [32] and is not useful for the purpose of this research. The eggshell was then crushed using a 600-watt electric blender at 10,000 rpm for approximately 20 seconds and further ground in a mortar. The sample was dried in an oven at 120 °C for a maximum of three hours to eliminate microorganisms and remove moisture.

Before the trial process, the eggshells without the testaceous membrane were left at room temperature (average 24 °C) for eight days to check for decomposition and unpleasant odor. This was performed to permit further storage and use in coffee farms to increase the pH of wastewater.

The crushed material was sieved through stainless steel wire mesh sieves in the ASTM series from No. 30 to No. 140, with openings ranging from 0.600 mm to 0.106 mm, respectively. The retained samples were separately stored in closed glass containers to prevent contamination, as depicted in Figure 1.

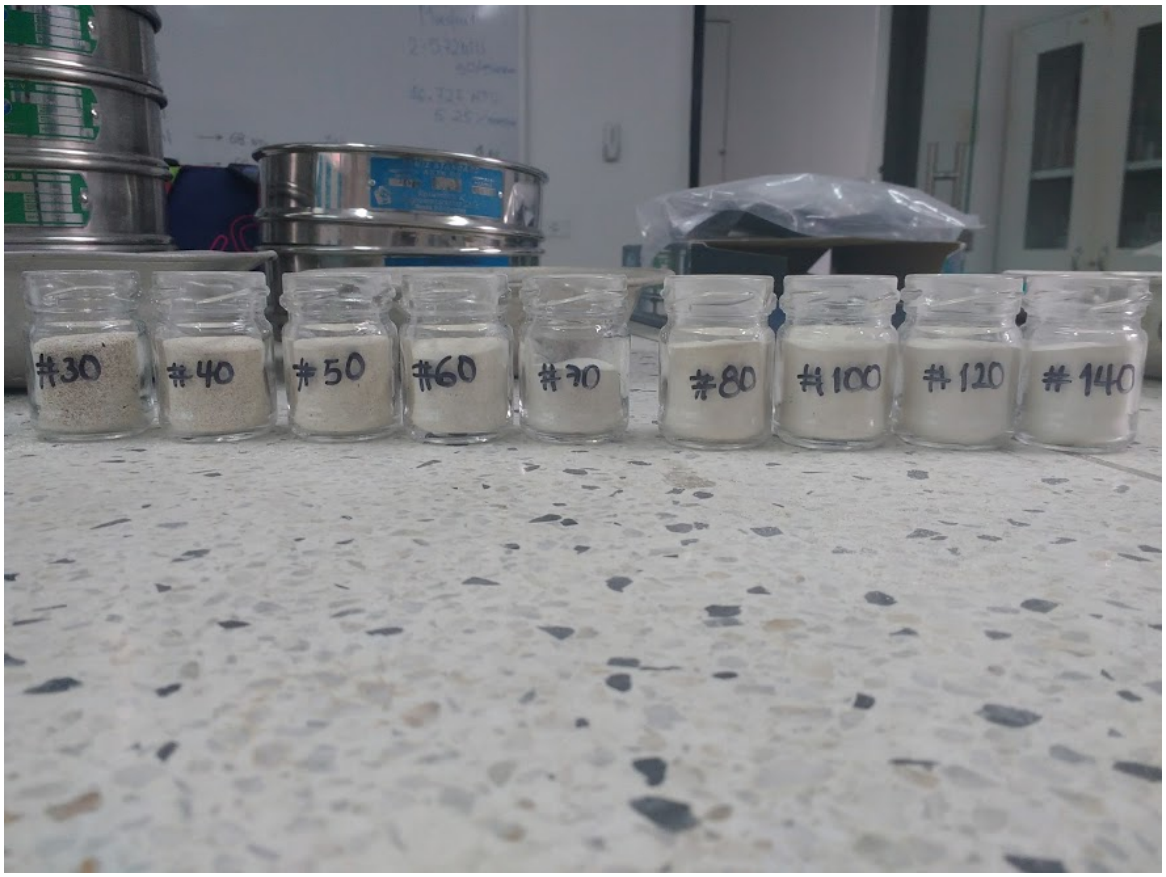

FIGURE 1.
Eggshells for each material retained on ASTM sieves
Source: Authors of this manuscript.

The eggshells were applied to wastewater through manual mixing. Specifically, 200-milliliter samples of raw water with varying concentrations of eggshell were weighed using a precision balance and the residual pH for each concentration and particle size obtained in the sieves were evaluated. The goal was to achieve a pH greater than 5 to establish trend lines for the results between the eggshell concentration and pH. The pH measurement of wastewater was conducted using a pH meter for wastewater with an electrode and integrated temperature sensor, with hundredth-degree precision.

Results

After eight days of storage at room temperature, the clean eggshell without the testaceous membrane showed no odor, physical changes, or decomposition. Therefore, the shell does not require special preservation processes for use, but contact with humid environments should be avoided. Laboratory tests were performed using this material, and the pH in the wastewater from wet coffee processing was evaluated using a volume of

200 ml for each sieve size in the ASTM series from No. 30 to No. 140. The concentration of applied eggshell was changed until a pH value greater than 6 was obtained, as indicated in Table 1.

TABLE 1.
pH values for different eggshell concentrations applied to wastewater for each sieve used in the ASTM series

Eggshell in Honey Water (mg/L)	pH								
	SIEVE No. 30	SIEVE No. 40	SIEVE No. 50	SIEVE No. 60	SIEVE No. 70	SIEVE No. 80	SIEVE No. 100	SIEVE No. 120	SIEVE No. 140
0	4,05								
2,5	4,34	4,62	4,55	5,30	5,70	5,71	5,80	5,80	5,82
5,0	4,53	5,15	4,97	5,81	6,00	6,05	6,14	6,18	6,14
7,5	4,80	5,53	5,41	6,05	6,16	6,22	6,33	6,31	6,31
10,0	5,01	5,83	5,80	6,15	6,35	6,40			6,41
12,5	5,30	6,02	6,00	6,32					
15,0	5,52	6,13	6,15						
17,5	5,74	6,34	6,28						
20,0	5,95		6,40						
22,5	6,02								
25,0	6,15								

Source: Authors of this manuscript.

An increase in wastewater pH was observed when crushed eggshell was applied, as shown in Figure 2. A pH range of 5 was established as the minimum requirement for coffee processing wastewater, as per Colombian regulations [10]. Concentrations ranged from 1 to 10 mg/L eggshell, depending on the sieve size selected.

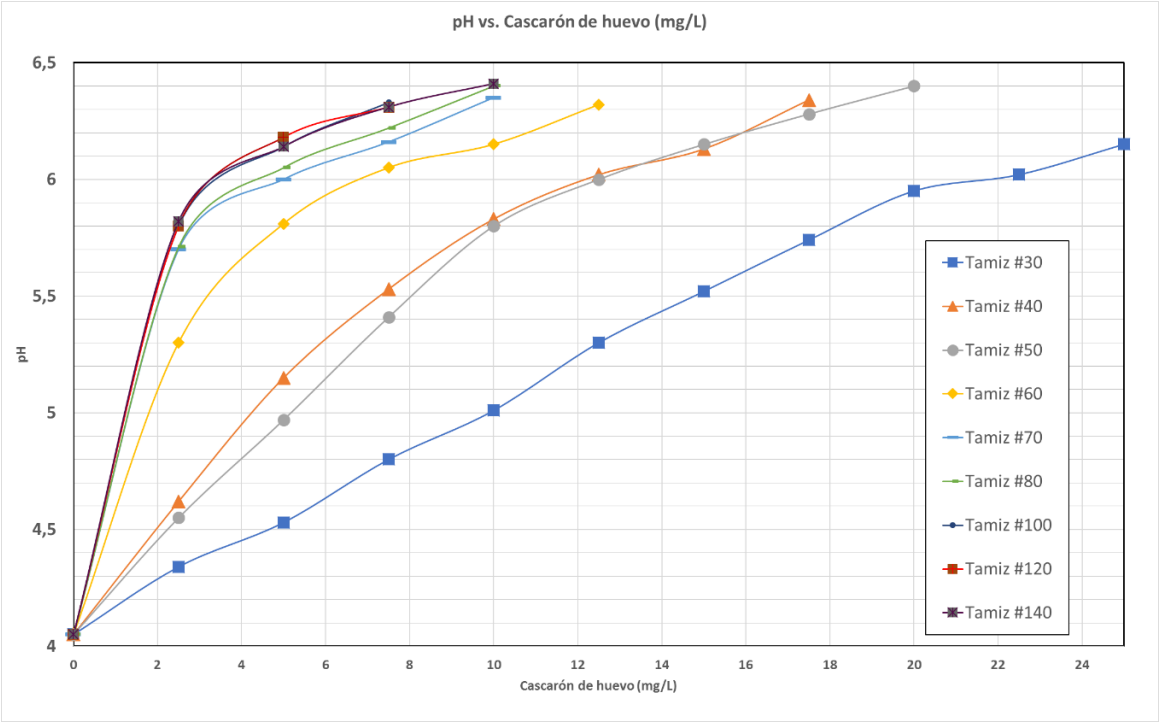

FIGURE 2.
pH vs. eggshell (mg/l) for ASTM sieves
Source: Authors of this manuscript.

Lower concentrations of eggshell were needed for sieves No. 100 (0.150 mm), No. 120 (0.125 mm), and No. 140 (0.106 mm), which attained similar pH results, as shown in Figure 2. It can be inferred that smaller particle sizes dissolve better in water. Sizes up to 0.150 mm (No. 100 sieve) are suitable for increasing the pH of wastewater from wet coffee processing. Figure 3 describes the trend line for pH values obtained with the No. 100 sieve, with a polynomial curve and an R^2 correlation coefficient of 1, indicating a perfect linear fit. Equation 1 is as follows:

$$pH = 0{,}0134 \times C^3 - 0{,}2136 \times C^2 + 1{,}15 \times C + 4{,}05 \quad (1)$$

where
C: Concentration of eggshell (mg/L)

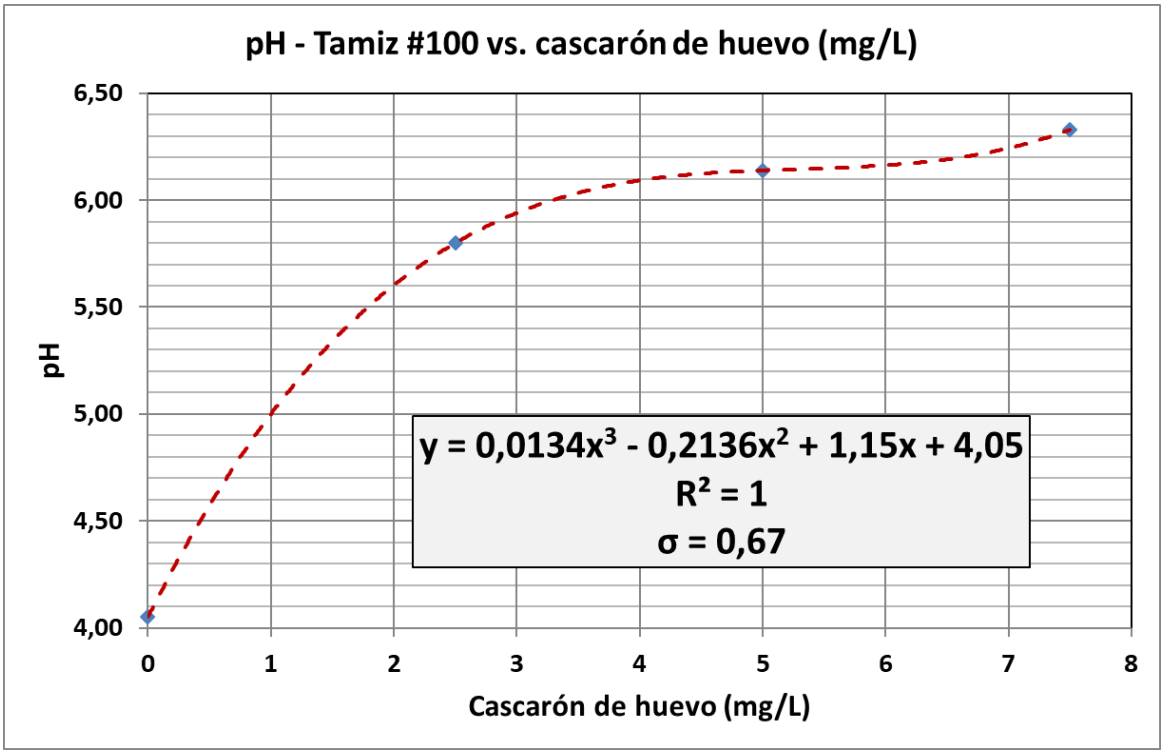

FIGURE 3.
pH vs. pH vs. eggshell (mg/l) for No. 100 sieves of the ASTM series
Source: Authors of the manuscript.

In wastewater generated by coffee wet processing at a coffee farm in Líbano, Tolima, the concentration of eggshell needed to increase the pH from 4.05 to 5 (the minimum value established by Colombian regulations for disposal in water bodies) is 1.001 mg/L based on the equation obtained for the No. 100 sieve, as indicated in Figure 4. The same equation was applied to achieve a neutral pH of 7 in wastewater, and 6.23 mg/L eggshell was needed.

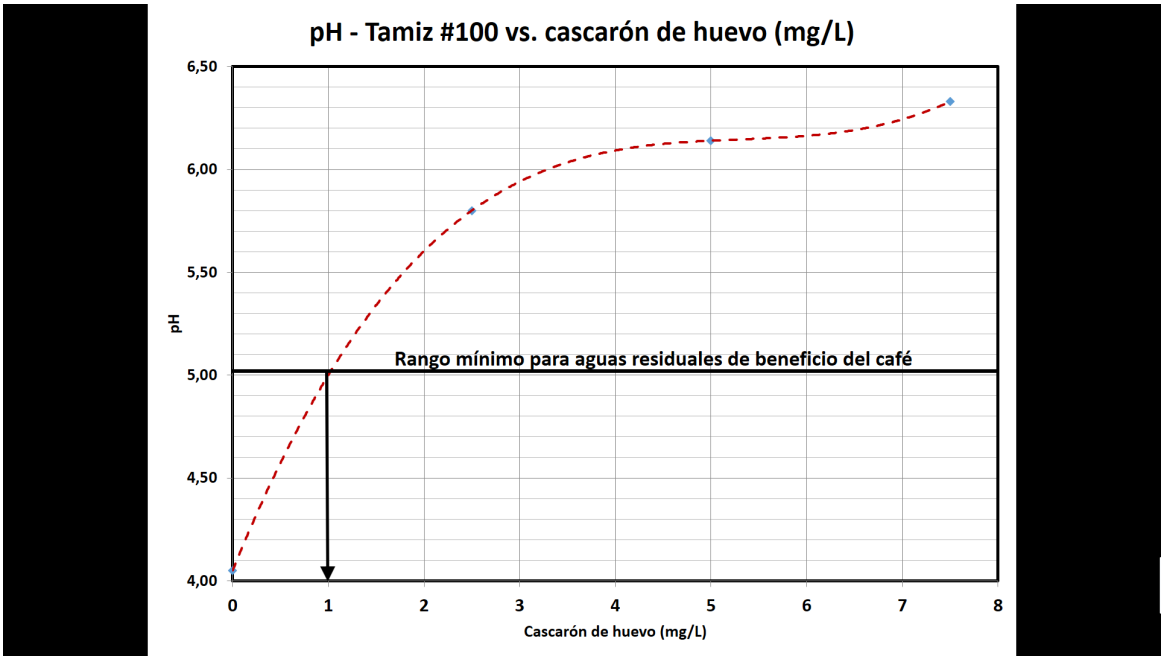

FIGURE 4.

Eggshell concentration (mg/L) to achieve pH=5, SIEVE No. 100 sieve of the ASTM series

Source: Own elaboration.

The pH obtained for eggshell concentrations varying every 0.5 mg/L, according to the equation obtained for the No. 100 sieve, is described in Table 2 and ranged from 4.05 to 6.56.

TABLE 2.
pH values for different eggshell concentrations that each varied by 0.5 mg/l, No. 100 sieve of the ASTM series

Honey Water Mixed with Eggshell (mg/L)	pH of Wastewater Mixed with Eggshell
0,0	4,05
0,5	4,57
1,0	5,00
1,5	5,34
2,0	5,60
2,5	5,80
3,0	5,94
3,5	6,03
4,0	6,09
4,5	6,12
5,0	6,14
5,5	6,14
6,0	6,15
6,5	6,18
7,0	6,23
7,5	6,31
8,0	6,44
8,4	6,56

Source: Authors of the manuscript.

Discussion of Results

Wastewater from coffee processing requires a neutral pH value of 7 to eliminate pollution during treatment processes, especially secondary treatment, and to minimize odors [33]. This can be achieved using chicken eggshells, and a concentration of 6.23 mg/L is theoretically needed according to the trend equation obtained for SIEVE No. 100. Notably, in this research, the experimental results approached a pH close to 6.30. If a pH of 6.5 is considered, which corresponds to the minimum pH needed for drinking water according to current regulations in Colombia [34], 6.18 mg/L eggshell material from SIEVE No. 100 is needed based on

the obtained equation. The standard deviation was low, indicating that most data points clustered around the mean.

The Colombian regulation that governs discharge limits defines a minimum pH of 5 for coffee processing wastewater [10]. This value is low and subject to revision, especially considering that the same regulation sets a pH of 6 for wastewater used in fruit and vegetable processing [10]. A pH of 5 may also affect the treatment process, particularly nitrogen removal [35]. This pH range (between 5.65 and 4.70) is slightly acidic [36], lower than the minimum value for wastewater from the coffee processing industry established in the Mexican standard, which is 6 [37].

The research involved neutralizing the acidic pH of wastewater from wet coffee processing using calcium carbonate. This provides the possibility of investigating other parameters, such as alkalinity and total hardness, which are not regulated in current standards [10]. This type of wastewater has total hardness concentrations below 40 mg/L [38], whereas up to 300 mg/L is permissible for drinking water [34].

Conclusions

The obtained results lead to the conclusion that chicken eggshells are a viable option to increase the pH of wastewater from wet coffee processing. This solution can be applied in coffee-growing regions of countries in which wastewater is discharged into water bodies without any treatment, leading to negative consequences by decreasing pH.

Chicken eggshells are a domestic solid waste with limited use and are often deposited in open dumps, landfills, and dumpsites, wasting its potential as a raw material. As the bioceramic structure of eggshells contains organic and inorganic components, the percent of primarily calcium carbonate exceeds 95% in the form of calcite; thus, eggshells can be useful for various anthropogenic activities.

Eggshell crushing sizes below 0.15 mm achieve better dissolution in wastewater and, consequently, greater increases in pH. In addition to wastewater from coffee processing, this utility extends to other types of agro-industrial, domestic, and industrial wastewater in general. Therefore, further research is necessary. Additionally, eggshells from other oviparous animals, such as ostriches and quails, can be considered for their potential to increase wastewater pH.

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Notes

* Research article.

How to cite this article: Ospina Zúñiga, O. E., Aldana Giraldo, A., Rojas García, O. E., "Increasing the pH of coffee wet mill wastewater using eggshells." Ing. Univ. vol. 27, 2023. https://doi.org/10.11144/Javeriana.iued27.ipcw