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Determination of the point of zero charge of pineapple (*Ananas comosus* L.) peel and its application as copper adsorbent

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ABSTRACT

Objective: To determine the optimum pH at which the pineapple peel can adsorb the greatest amount of copper.

Design/methodology/approach: *Sorbent material.* The size of the pineapple peel was reduced to 0.250 mm; it was chemically modified with 0.2 M NaOH and 0.2 M CaCl₂. *Point of zero charge (PZC).* Six solutions were prepared with 0.5 g of sorbent in an aqueous medium (with a 3-8 pH range), they were stirred at 225 rpm for 48 h. The derivative method was used to plot the initial pH versus final pH, in order to determine the PZC. *Copper adsorption.* CuSO₄ solutions were prepared in 2, 4, 6, 8 10 mg/L concentrations; 0.1 g of pineapple biomass was added adjusting the pH to 5. The solutions had a contact time of 0 to 24 h.

Results: The pineapple peel had a 5.0 point of zero charge (PZC) value, which indicates that pH values higher than the PZC are required to obtain an adsorbent with a negatively charged surface and favor the copper adsorption. A 50% copper removal was obtained in all concentrations after a 1 h contact time.

Limitations on study/implications: This research had no limitations.

Findings/conclusions: The point of zero charge is a reliable parameter that allows the adsorption process to take place and provides a greater certainty to the metal adsorption process. Meanwhile, pineapple peel can be used as an adsorbent material, consequently reducing its accumulation in open dumps.

Keywords: Pineapple peel, point of zero charge, copper adsorption.

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INTRODUCTION

The climate, soil, temperature, rainfall, and altitude conditions of the humid tropics region of Mexico is suitable for pineapple (*Ananas comosus* L.) production. The states of Veracruz, Tabasco, Chiapas, and Campeche have the highest potential surface for its



production. In Mexico, 44,182 ha of pineapple are currently grown; the total production is 1,041,161 t (SIAP, 2020). However, only 780 t are used for fresh consumption or to make juice, jams, and preserves (Vélez-Izquierdo *et al.*, 2020). This difference between production and consumption leads to an environmental and economic problem, as a consequence of the generation of a large volume of pineapple waste (including peel, crown, and pulp); all this inedible portion accounts for 41% of the fruit. Therefore, looking for alternative uses for this waste —based on effective techniques that can contribute to its reduction— is necessary.

Fruit peels —particularly from citrus fruits— have been studied as pollutant adsorbents (Romero, 2018; Pathak *et al.*, 2016). They have high metal adsorption capacity, as a result of their pectin content. Pectin contains carboxylic groups, which in its anionic form attracts cationic species such as metals (García Villegas *et al.*, 2011).

The CaCl_2 -modified orange peel can adsorb 36.1 mg/g of Cu (II) at a pH of 4.86 (Villanueva, 2007); the peanut shell adsorbs 60% Cu (II) ions at a pH of 3 (Tapia, 2018); the pomegranate peel had a maximum adsorption of Cu (II) at a pH of 5.6-5.8 (El-Ashtoukhy *et al.*, 2008). The pH is a factor that must be taken into account in the adsorption process, as it can indicate the degree of ionization of the adsorbent surface and its interaction with the adsorbate. Based on the point of zero charge, the pH at which the adsorbent retains anions or cations and thus optimizes the removal process can be determined (Amaringo-Villa and Hormaza-Anaguano, 2013). Several studies have been made about the use of pineapple residues as metal and dye adsorbent (Urrego *et al.*, 2018). Succinic anhydride-modified pineapple peel has a maximum adsorption capacity of Cu (II) ions of 27.68 mg g^{-1} at a pH of 5.4 (Hu *et al.*, 2011). However, most of those studies do not describe the determination of the point of zero charge. Therefore, the objective of this study is to establish a parameter that enhances the adsorption process and establishes an improved adsorbent-adsorbate interaction.

MATERIALS AND METHODS

The peel was obtained from Cabezona pineapples (*Ananas comosus* L.) acquired at the municipal market of Cárdenas, Tabasco.

Physical Modification of the Pineapple Peel

Drying: the pineapple peel is washed with plenty of water, cut into small fractions of approximately 5 cm, dried in the sun for 3 days, and dehydrated at 60 °C for 5 h in a drying oven. Crushing and sieving: once the material is dry, it is crushed until a small particle is obtained, which is then sieved through a #40 mesh (upper part) and a #60 mesh (lower part).

Chemical Modification of Pineapple Peel with CaCl_2

10 g of the dry material are added to 250 mL of a 0.2 M NaOH solution; the mixture is stirred for 2 hours, then filtered and washed until the excess NaOH is eliminated. Afterwards, it is dried at 40 °C for 2 h. Once dry, it is added to 250 mL of a 0.2 M CaCl_2 solution, adjusting the pH to 5, and stirred at a steady 200 rpm for 24 h. It is filtered and washed with deionized water and dried at 60 °C for 6 h.

Determination of the Point of Zero Charge

Six solutions were prepared in 100-mL Erlenmeyer flasks. Fifty mL of distilled water were added to each flask and their pH was adjusted with standard NaOH and 0.1 M HCl solutions, in a 3-8 pH range. Pineapple biomass (0.5 g) at room temperature was added to each solution and it was constantly stirred at 225 rpm for 48 h. At the end of this process, the pH value was measured. The initial pH versus the final pH was plotted and the PZC was determined by the derivative method. The pH readings were taken with a Hanna HI98103 Checker pH meter.

Adsorption Study

Five CuCl₂ solutions were prepared at different concentrations (2, 4, 6, 8 and 10 mg/L). Adsorbent (0.1 g) was added to each solution and the pH was adjusted to 5. The mixtures were placed in contact time for 24 h. A sample was taken every hour and its Cu (II) removal percentage was determined, using the following equation:

$$\% Removal = \frac{C_0 - C_{eq}}{C_0} \times 100\%$$

Where: C_0 =initial concentration; C_{eq} =balanced concentration.

Copper Identification by Scanning Electron Microscopy Coupled with Elemental Analysis

It was carried out in a JEOL JSM 610 LA model Scanning Electron Microscope (SEM-EDX).

RESULTS AND DISCUSSION

Determination of the Point of Zero Charge (PZC)

The PZC is defined as the pH value corresponding to a balance point of (external and internal) charges on the adsorbent material (Sposito, 1998). pH values higher than PZC indicate that the surface is negatively charged, while pH values lower than PZC mean that the surface is positively charged (Amaringo and Hormaza, 2013). The PZC corresponds to the point where the curve of the final pH—versus the initial pH— crosses the diagonal. Figure 1 shows the graph of the initial pH versus final pH. The pineapple peel had a 5.0 PCZ value; therefore, pH values higher than PZC will favor uptake during the metal ions adsorption in aqueous media.

Copper Adsorption

In order to demonstrate the application of the point of zero charge in the adsorption process, the removal of different concentrations of Cu (II) from aqueous solutions with a contact time of 24 h was studied. The particle size, temperature, and stirring speed remained constant. Figure 2 shows the maximum adsorption reached during the study. During the first hour, a maximum percentage of 66 was reached for the concentration of

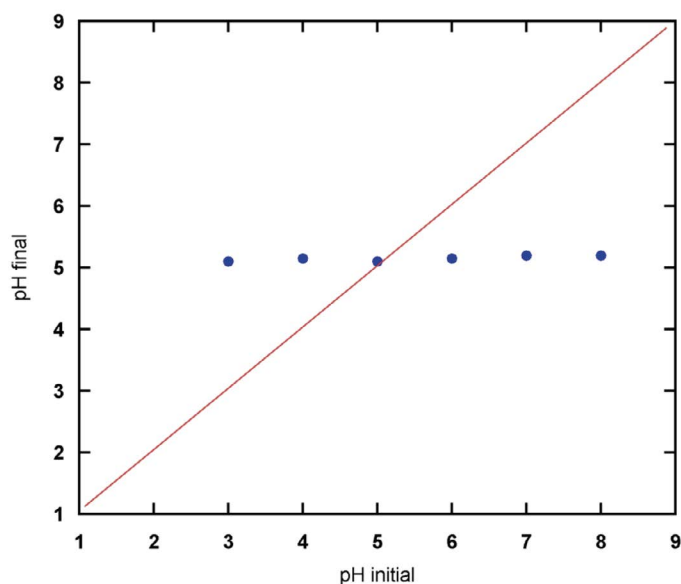


Figure 1. Point of zero charge of pineapple peel.

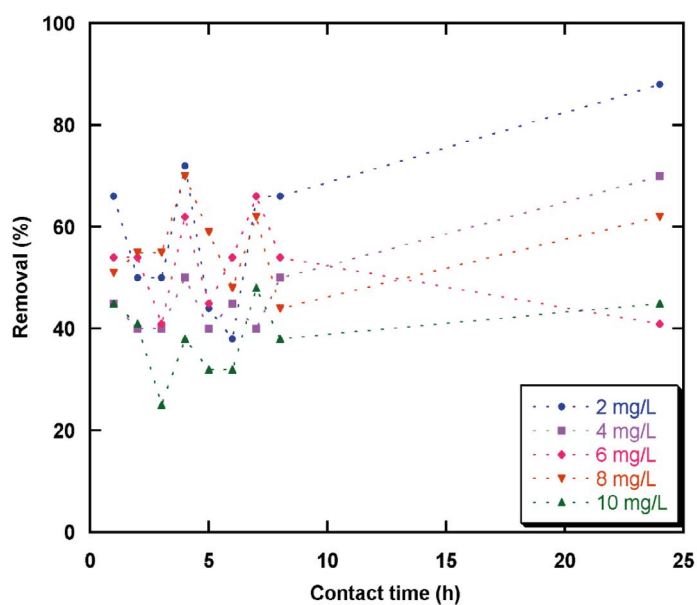


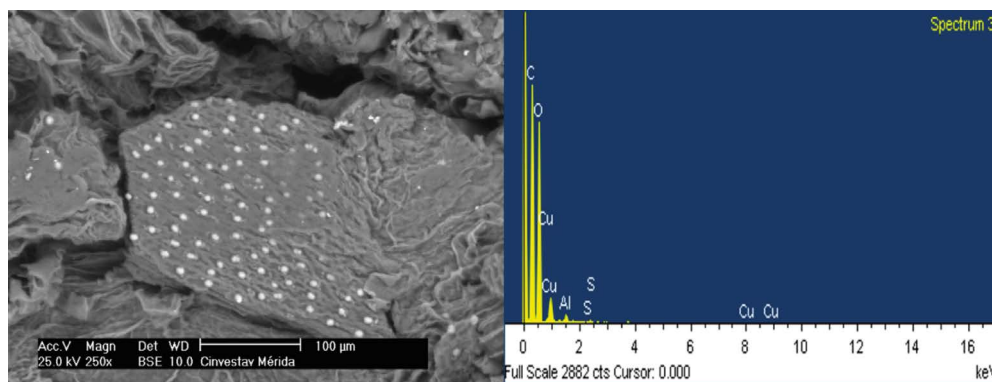
Figure 2. Removal percentage of Cu (II) at different contact times.

2 mg/L; from the 2nd to the 7th hour, there was a variation in the removal percentage, as a result of the balancing of the loads; at the 8th hour, the removal percentage was similar to the 1st hour. The maximum adsorption percentage is reached for all concentrations after 24 hours (Table 1).

Figure 3 shows the SEM image of the surface of the pineapple peel after it had adsorbed the copper ions—which can be seen as shiny particles lodged within the cavities of the adsorbent. The EDX elemental analysis confirms that its composition includes copper.

Table 1. Maximum removal percentage.

Time (h)	% R 2mg L ⁻¹	%R 4 mg L ⁻¹	%R 6 mg L ⁻¹	%R 8 mg L ⁻¹	%R 10 mg L ⁻¹
1	66	45	54	51	45
2	50	40	54	55	41
3	50	10	41	55	25
4	72	50	62	70	38
5	44	40	45	59	32
6	38	45	54	48	32
7	66	40	66	62	48
8	66	50	54	44	38
24	88	70	41	62	45

**Figure 3.** SEM image and elemental analysis of copper adsorption on pineapple peel.

CONCLUSIONS

Using the derivative method to determine the point of zero charge is a simple and fast procedure to establish the distribution of the charges on the surface of an adsorbent material. The CaCl₂-modified pineapple peel can adsorb up to 50% of Cu (II) ions dispersed in water at a pH of 5. The results of this study prove the potential of agricultural waste as metal adsorbents and consequently their capacity to avoid the negative environmental impact generated by its final disposal in open dumps.

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