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Investigation of the zero-charge point of orange biomass for further use as a metal biosorbent

https://doi.org/10.56238/alookdevelopv1-103

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ABSTRACT
Biosorption is characterized by the removal, retention, or recovery of metals present in toxic residues, through the adsorbent and adsorbate. For this, one of the characteristics to be evaluated in the determination of a good biosorbent is the zero-charge point. This value is defined by the pH value at which the biomass surface has a neutral charge, that is, the adsorption of H+ and OH- ions is equal. For the orange species studied, the values of the zero-charge point form between pH 4.5 and pH 5.8.

Keywords: Biosorption, zero charge point, pH.

1 INTRODUCTION

When exploring economic and food cultures, the toxicities of chemical elements to the environment and human health must be determined and known. Environmental impacts are characterized by changes in the environment, usually caused anthropically, to alter its physical, chemical, and biological properties. Being caused by any source of matter or energy, environmental impacts can affect the health, safety, and well-being of the population, in addition to compromising the quality of natural resources (Oliveira, 2016). Concomitantly, the daily consumption of industrialized products is one of the main responsible for the continuous production of garbage, since the industrialization process requires the use of metals for the production of the most varied products (Pinto, 2017).

The contamination of the environment using potentially toxic metals contributes directly to the pollution of the air, soils, and water, causing the death of species, as well as the intoxication of man (Barroco et al, 2018). Although some metals are essential for organisms such as copper, zinc, and iron, all forms of life are affected by these, depending on the dose and their chemical form. Some compounds are biologically active in the environment and can interact with the biota of the environment, interfering significantly with the metabolism and behavior of species, and causing various damages to living beings, from plants and even to humans (Rocha, 2009; Belisarius, 2009).

Considering the current context, the importance of the relationships between individuals and the environment with actions in favor of sustainability is recognized. Therefore, the planning of actions for environmental sustainability is an instrument that aims to plan and program the use of space, activities, development, and organization of society, in harmony with nature, making use of resources, and protecting the quality of the environment (Cavalcanti, 2011).

Thus, aiming at improving environmental conditions, biosorption emerges as an alternative, because it is characterized by using microorganisms or plant biomass for removal, recovery, or retention of metals present in toxic waste, involving a solid phase (adsorbent) and a liquid phase (adsorbate) in which, by various mechanisms, the adsorbate is attracted by the adsorbent (Silva et al, 2014).

Several aspects need to be considered for the use of a material as a biosorbent and one of them is pH. The zero-charge point (PCZ) is a parameter that indicates the pH value at which a given solid has a charge equal to zero on its surface. The PCZ has great importance in several chemical phenomena, such as adsorption, coagulation, dissolution in minerals, electrochemical phenomena, and interaction between particles, among others (Silva, 2012).

The PCZ can be defined as the pH value at which the adsorption of H+ and OH- ions are equal, that is, the surface of the biosorbent will have a neutral charge (Teixeira et al, 2017; Freitas et al, 2016). In addition, by knowing the PCZ, one can define the ionization of the functional groups of the surfaces and their interaction with metallic species in the solution (Silva, 2012). Given this, the PCZ can vary according to the formation of cationic or anionic complexes on the surface of the solid. Therefore, when the adsorbent is negatively charged in solutions with pH higher than PCZ, it may attract positive metallic species; on the other hand, when the adsorbent is positively charged in solutions with pH lower than PCZ, it may interact with negatively charged species (Freitas et al, 2016; Werneck et al, 2018).

Therefore, aiming to apply biosorption in the adsorption of metals and contribute to a more sustainable technique, this work proposes the investigation of PCZ in two species of oranges.

2 MATERIALS AND METHODS

The adsorbents used for analysis were orange peel species Pear, orange pomace species Pear, orange peel species Bahia, and orange bagasse species Bahia. For the preparation of the material, the shells and bagasse were washed with distilled water. After that, they were dried in an oven for 24 hours at 80 °C to eliminate moisture. After drying, they were crushed in a knife mill and sieved in 354 µm polyester membranes.

To determine the PCZ, the study was based on the 11-point experiment described by Regalbuto (2004). For this, about 50 mg of each adsorbent was weighed and 50 mL of distilled water was added and the pH was adjusted with HCl or NaOH 0.1 mol L^{-1} in 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 8.0; 9.0; 10.0;

11.0 and 12.0. The solutions were stirred for 24 hours at room temperature. After 24 hours of agitation, the pH was measured again with a digital pH meter.

3 RESULTS AND DISCUSSION

The PCZ corresponds to the point at which the pH values do not adsorb positive or negative ions. Figure 1 shows the biosorbent materials already sifted: where a) corresponds to the pomace of the orange Pear; b) peel of the orange Pear; c) Bahia orange pomace and d) Bahia orange peel.

Figure 1. Sieved biosorbent materials

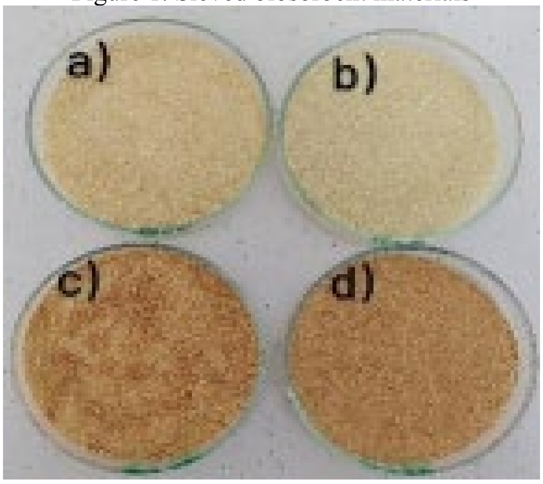

Table 1 shows the initial pH and final pH values for each type of biosorbent and Table 2 shows the variations in pH values (final pH - initial pH). In Graph 1, the results are arranged, indicating the biosorbents as BLP, pomace of the orange Pear; CLP, orange peel Pear; BLBh Bahia orange pomace and CLBh Bahia orange peel.

Table 1. Initial and final pH values

	Final pH			
pH initial	**BLP**	**CLP**	**BLBh**	**CLBh**
1,0	0,6	0,7	1,2	0,8
2,0	1,5	1,9	2,2	1,8
3,0	2,0	3,7	2,9	2,8
4,0	4,4	4,9	4,4	4,4
5,0	6,2	5,7	4,5	4,5
6,0	5,8	4,6	4,4	4,8
8,0	5,9	5,3	5,4	4,9
9,0	6,0	6,2	4,6	5,1
10,0	6,3	7,0	5,2	6,8
11,0	8,6	9,3	8,2	9,0
12,0	9,4	10,5	10,3	11,1

Table 2. Variations in pH values

	DpH			
pH initial	**BLP**	**CLP**	**BLBh**	**CLBh**
1,0	-0,4	-0,3	0,2	-0,2
2,0	-0,5	-0,1	0,2	-0,2
3,0	-1,0	0,7	-0,1	-0,2
4,0	0,4	0,9	0,4	0,4
5,0	1,2	0,7	-0,5	0,5
6,0	-0,2	-1,4	-1,6	-1,2
8,0	-2,1	-2,7	-2,6	-3,1
9,0	-3,0	-2,8	-4,4	-3,9
10,0	-3,7	-3,0	-4,8	-3,2
11,0	-2,4	-1,7	-2,8	-2,0
12,0	-2,6	-1,5	-1,7	-0,9

Graph 1: Identification of the PCZ

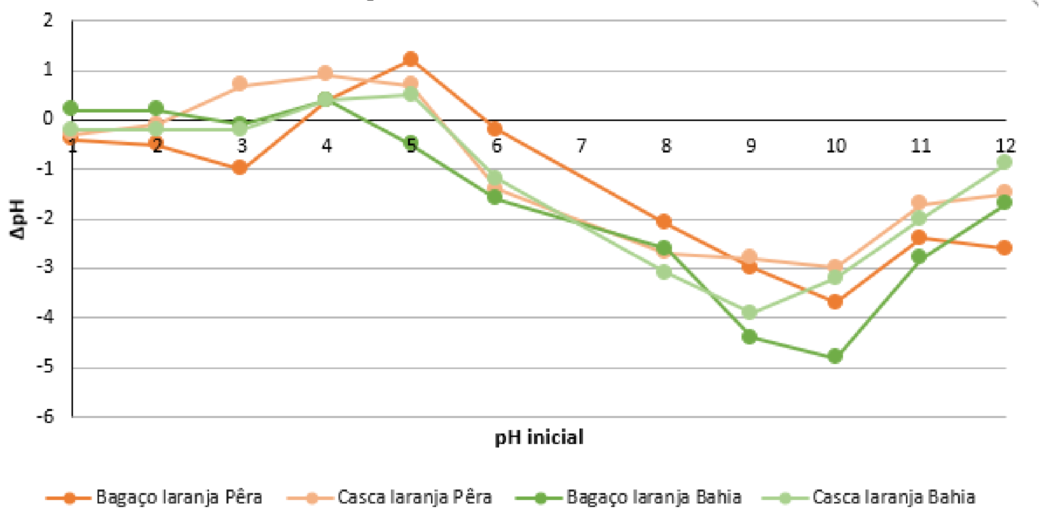

Chart 1 shows the PCZ values for each biosorbent.

Table 1. Result of the PCZ determination

Biomass	PCZ
BLP	5,8
CLP	5,5
BLBh	4,5
CLBh	5,5

This pH represents that the negative and positive charges are in equilibrium, presenting a neutral surface. For pH values below the PCZ, the biomass surface has positive surface charges, thus attracting negative ions. At values above PCZ, biomass has negative surface charges, attracting positive ions (Rech, 2014). Thus, the best pH to be used for metal adsorption tests with BLP is between 5.9 and 10.0; for CLP between 5.6 and 10.0. For tests with BLBh, it is indicated to be carried out experiments with pH between 4.6 and 10.0 and for CLBh between 5.6 and 9.0.

Aiming at the continuity of the studies, the pH value to be used will be 6.0 for all biomasses. This value is that pointed out by Freitas et al (2016), the pH value found was performed with the arithmetic mean of the points at which the pH remained constant, resulting in a value of 6.72. In Formica et al (2017), we worked on the adsorptive properties of the orange peel and the PCZ value found was 6.53 based on a graph made with the difference of the initial and final pH values.

4 CONCLUSIONS

According to the results obtained in the tests, it was possible to observe that orange residues, regardless of the species and organic part, have PCZ between pH values of 4.5 and 6.0. Thus, the adsorbent at pH lower than the PCZ behaves by adsorbing anions because it has a positive surface and for values greater than the PCZ, it will behave by adsorbing cations because it has a negative surface. However, given the observations throughout the experiment and the analyses made in the literature, it can be reported that orange can be used as an adsorbent material for metals.

Finally, it is worth remembering the importance of alternatives that contribute to the environment, especially those that use inorganic materials that would be discarded, biosorption being one of them. Presenting several advantages over other techniques, biosorption is cheaper and also effective. Reusing a natural adsorbent that provides a high rate of the ability to remove toxic metals present in nature, as well as reducing the metallic and toxic residues generated by industries, this method can be considered sustainable.

ACKNOWLEDGMENT

Institutional Program of Scientific Initiation Scholarships - PIBIC, Linked to the Unified Research Notice No. 03/2021 - DIPE/PROEPPI/IFPR

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