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CHEMICAL MODIFICATION OF PINEAPPLE (*ANANAS COMOSUS L. MERRIL*) PEEL WASTE FOR USE AS AN ADSORBENT OF FE (III)

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Abstract: The removal of metals dissolved in wastewater using agroindustrial waste turns out to be an economical and environmentally friendly method. These wastes contain functional groups that can be chemically modified, increasing their capacity to accommodate contaminants within their structure. In this work, the effect of chemical modification of pineapple peel with NaOH/ CaCl2 was studied for the adsorption of Fe(III) through an ion exchange reaction. The characterization was carried out by studying the surface of the materials and their elemental compositions by SEM-EDX scanning electron microscopy. The studies demonstrated the effectiveness of the adsorption process, since there was an exchange of Ca (II) ions for Fe (III) atoms, quantitatively. Therefore, pineapple waste could be incorporated into the value chain as low-cost, high-performance adsorbents for application in the treatment process of water contaminated by metals.
Keywords: Lignocellulosic waste, iron adsorption, bioadsorbent, ion exchange.

INTRODUCTION

Water pollution is one of the most worrying aspects of the degradation of natural environments, since not only plants and animals are affected but it also affects the quality of the water that is intended for human consumption. The main polluting agents in water have a chemical origin; Pesticides, hydrocarbons and heavy metals are those that cause the greatest environmental impacts. The high toxicity and low degradability of these contaminants causes natural imbalances (Domenech & Peral, 2008; Nava & Méndez, 2011). The industrial sectors that are sources of pollution mainly of heavy metals are mining, cement industry, paints, pigments, tanning, electroplating, textile manufacturing, among others (Fu & Wang, 2011; Higuera et al., 2009). There are towns where the drinking water that is distributed has a high iron content, which gives the water an unpleasant color, smell, and taste. Excess iron salts also favor the growth of bacteria that, although not pathogenic, generate waste that reduces water quality. These iron deposits accumulate in water tanks, bathrooms, and drains, making it impossible to use the water for both human consumption and washing, creating a problem for the population. According to NOM.127-SSA1-1994 and the US Environmental Protection Agency, the permissible limit of iron in water is 0.3 mg/L (Negrón, 2014).

There are various conventional methods for the treatment of water contaminated with metals, some of them are: chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane, evaporation (Zewail & Yousef, 2015). However, some of these methodologies are extremely expensive for the treatment of large quantities of wastewater, making large-scale use almost impossible. Adsorption is a technique that has been used to eliminate a wide variety of heavy metals present in water, due to its easy application and effectiveness in removing low concentration contaminants. (Caviedes et al., 2015, García-Rojas, 2012). The most used adsorbents are activated carbons due to their high surface adsorption, however their preparation is very expensive. Clays, polymers, zeolites, silica beads are also used and currently both plants and lignocellulosic waste with various chemical modification processes are being tested as adsorbents of heavy metals and other contaminants (Babel & Kurniawan, 2003).

There is broad interest in the use of lignocellulosic agroindustrial waste that previously had no use, as adsorbents not only for the removal of contaminants in water, but also to mitigate the environmental impacts generated by the waste on the environment (Marín et al, 2010; Wang et al., 2017). These wastes are made up of cellulose, hemicellulose, pectin and lignin, their structures are intertwined generating cavities capable of trapping organic or inorganic compounds and have an advantage over conventional adsorbents since they are low cost, easy to acquire and abundant, above all they can rejoin the environment in a friendlier way since due to their natural origin they do not generate major environmental impacts, complying with principle 10 of Green Chemistry which proposes to generate biodegradable products (Doria, 2009).

Bioadsorbents must preferably come from abundant and easily available waste in the region where they are located. In Table 1, some of the materials used in different investigations for the removal of heavy metals in aqueous media are recorded.

All the bioadsorbents mentioned in the table have certain characteristics in their structure (stiffness and porosity) and in their chemical composition (functional groups or active sites) that allow the formation of strong bonds with metal ions, and also determine the possible chemical modifications or physical actions that would be carried out to increase the adsorption potential of the biomaterial.

In the present research work, the chemical modification of the pineapple peel (*Ananas comosus L. Merill*) was carried out and its capacity as an Fe (III) adsorbent was studied, thus offering a simple, low-cost alternative to solve the problem of metal contamination in effluents.

MATERIALS AND METHODS

The pineapple peel was obtained from the Creole pineapple (*Ananas comusus L. Merril)* from the Ejido Salvador Neme Castillo located in the Chontalpa region, Tabasco, Mexico.

PREPARATION OF THE ADSORBENT

Drying: the pineapple peel was cut into small fractions of approximately 5 cm and subsequently washed with plenty of water. Subsequently, it was dried in the sun for 3 days, and dehydrated at 60°C for 24 h in a laboratory oven.

Crushed and sieved: once the material was dry, it was crushed with the help of a mill and an industrial blender. The material was sieved through a #40 mesh, a material with a particle size of 0.4 mm was obtained.

CHEMICAL MODIFICATION OF THE ADSORBENT

Demethoxylation: 30 g of dried pineapple peel were added to a solution of 500 ml of 0.2 M NaOH, the mixture was stirred for 2 h with a mechanical stirrer at 100 rpm, then the mixture was filtered by performing successive washes with distilled water to eliminate excess NaOH. The material was dried at 60°C for 24 h.

Crosslinking: 10 g of demethoxylated shell were added to a solution of 250 ml of 0.2 M CaCl2, adjusting the pH to 5, the solution was left stirring at 200 rpm for 24 h in a mechanical stirrer. The shell was washed several times with deionized water to remove excess calcium, filtered, and dried at 60°C for 24 h.

PREPARATION OF FE SOLUTION (III)

An aqueous solution of Fe2(SO4)3 was prepared at a concentration of 100 mgL-1 in deionized water.

ION EXCHANGE REACTION

500 mg of the adsorbent was weighed and mixed with 100 ml of a $Fe_2(SO_4)_3$ solution, setting the pH to a value of 5 with 0.1 M HCl, the contact time was 2 h, this process was carried out in triplicate.

Type of adsorbents	Bioadsorbent	Absorbed metal	Reference
Living organisms	Penicillium	Cu	(Xiao *et al.*, 2013)
	Aspergillus rizopus	Cu, Cr	(Bhuvaneshwari & Sivasubramonian, 2013)
	Paesilomyces sp	As	(Acosta *et al.*, 2013)
Biomass	Tamarind peel	Cd, Cu, Pb, Zn	(Know *et al.*, 2010)
	Orange peel	Pb, Zn	(Cardona *et al.*, 2013)
	Apple seed peel	Cr	(Selvi *et al.*, 2001)
	Barley (hordecum vulgare)	Cu	(Pehlivan *et al.*, 2012)
Biopolymers	Bentonite-chitosan	Cu, Pb, Ni	(Futalan *et al.*, 2011)
	Chitosan Epichlorohydrintriphos-phate	Cu, Cd	(Laus & de Fávere, 2011)
Activated carbons	From the coconut shell	Pb, Cu, Hg	(Anirudhan & Sreekumari., 2011)
	From orange peel	Cr	(Garzón & González, 2012)
Chemical modification	Reticulated biomass with $CaCl_2$	Pb	(Kawai *et al.*, 2014)
	Biomass modified with citric acid	Cu	(Zhu *et al.*, 2008)
Other materials	Sand	Cr, Pb, Cd, Cu	(Fonseca *et al.*, 2011)
	Zeolite	As, Cd, Cr	(Wu y Zhou, 2009)
	Fly ashes	Zn, Pb, Cd, Mn	(Mohan & Gandhimathi, 2009)

Table 1. Bioadsorbent materials used for the adsorption of heavy metals

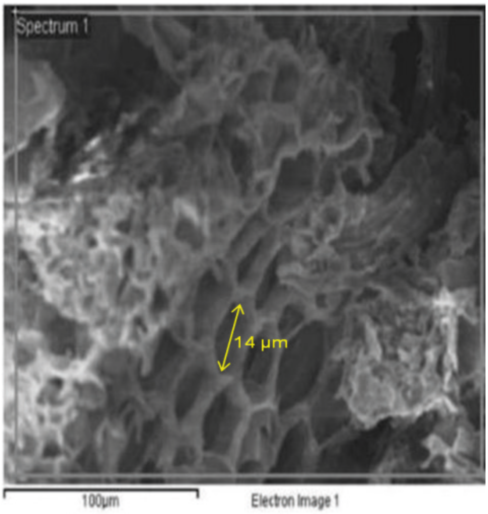
ADSORPTION STUDY

To evaluate the potential of pineapple peel as a metal adsorbent, the Scanning Electron Microscopy-Energy Dispersive X-ray technique was used in a Scanning Electron Microscope (SEM-EDX) brand JEOL model: JSM 610 LA. Micrographs of the biomasses were obtained using secondary electrons at 5kV. This technique scans the sample with an electron beam that allows obtaining high-resolution images, above 100,000x magnification, which make it possible to study details of its morphology. The energy dispersive X-ray spectrometer allowed analysis of the chemical composition of the samples generated.

RESULTS AND DISCUSSION

ADSORBENT CHARACTERIZATION

A sample of dried and crushed pineapple peel was taken, placed on a graphite support and studied by SEM-EDX. The image of the surface morphology as well as the elemental composition is shown in Figure 1.



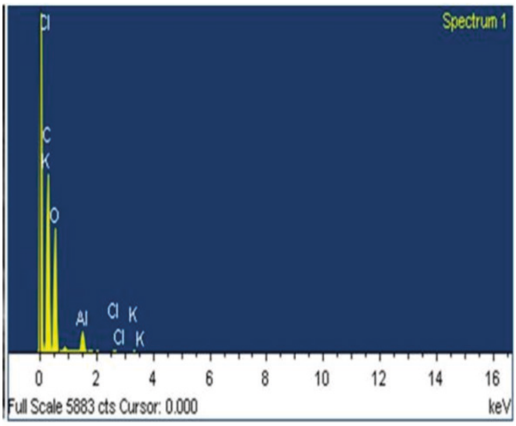


Figure 1. SEM-EDX of pineapple peel without modification

The image taken in the SEM shows a surface with a rough texture, with pores that have a radius of approximately 14 µm, classified by the IUPAC as mesopores (Castañeda Sánchez, et al., 2012). These pores present on the surface of the pineapple peel increase the contact area and facilitate the adsorption process. For its part, the elemental analysis acquired by EDX shows us that the pineapple peel is made up of the following elements with their respective atomic percentage: chlorine (% 0.14), carbon (50.22%), oxygen (47.40%), aluminum (1.89 %), potassium (0.35%).

CHARACTERIZATION OF THE MODIFIED ADSORBENT

According to what is reported in the literature, the carboxylic acid groups of the pectin contained in the peels of citrus fruits can be modified to acetate ions to trap metals (Cardona et al., 2013). The carboxylic acid groups of the pectin contained in the pineapple peel were modified using NaOH to form acetate ions. They were then treated with an aqueous solution of $CaCl_2$, leaving Ca(II) as the counter ion. The chemical modification is proposed according to the reaction in Figure 2.

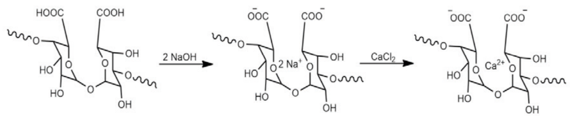


Figure 2. Chemical modification reaction of pectin

For analysis by SEM-EDX, a dry sample was taken and placed on a graphite support. Figure 3 shows the images obtained.

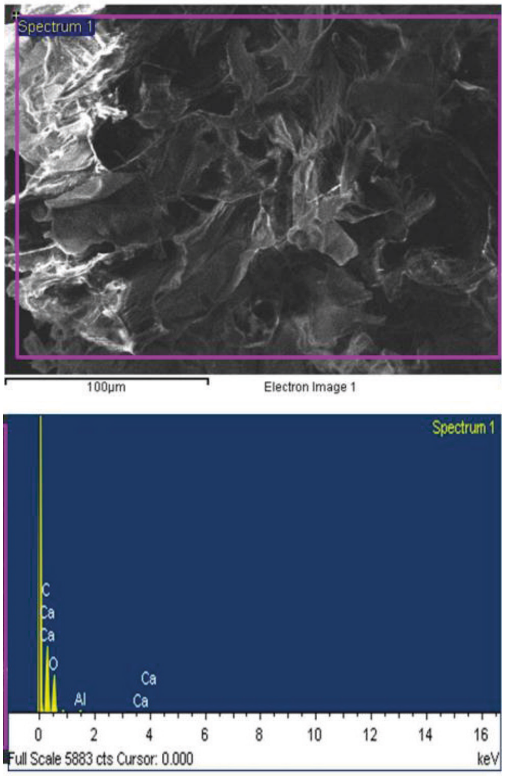


Figure 3. SEM-EDX of chemically modified adsorbent with NaOH /$CaCl_2$

In the image taken by SEM, a rough surface is observed, with large cavities, which favors the adsorption process. For its part, the elemental analysis acquired by EDX shows us that the chemically modified pineapple peel is made up of: carbon (56.98%), oxygen (42.93%), silicon (0.06%) and calcium (0.03%). The elemental analysis demonstrated the presence of Ca (II) ions in the adsorbent, this allowed us to continue with the adsorption process from an ion exchange reaction.

ADSORPTION OF FE(III) BY ION EXCHANGE

Ion exchange is a process used to trap metals dissolved in water. Ions in solution are transferred to a solid matrix which in turn releases ions of a different type without being chemically modified. The main advantages of this reaction are the recovery of metal value and selectivity (Zewail & Yousef, 2015). In this step the adsorbent was contacted with a Fe_2 solution$(SO_4)_3$ for 2 hours. During this contact time the color of the solution changed from red (characteristic color for Fe^{3+}) to yellow. The observed color change indicated that the Fe(III) was adsorbed. A dry sample resulting from this reaction was placed on a graphite support and analyzed by SEM-EDX, the images are shown in Figure 4.

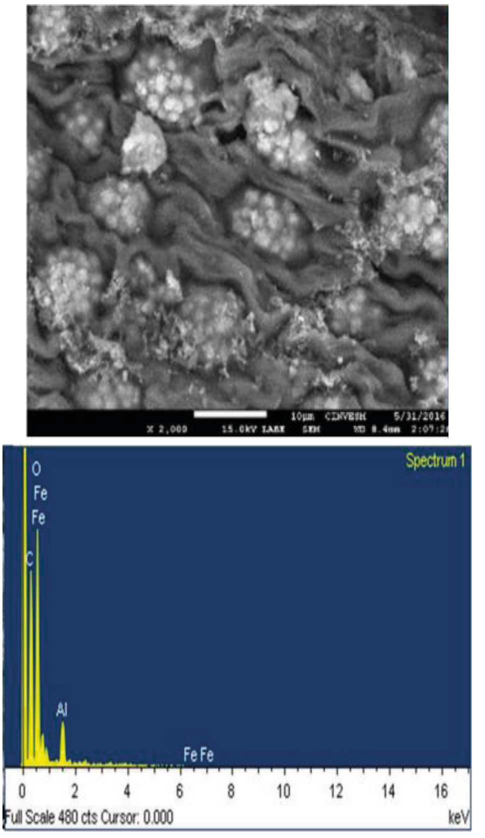


Figure 4. SEM-EDX of Fe(III) adsorption

In the image taken by SEM, the presence of brighter particles scattered throughout the surface and lodged within the pores is observed. These particles correspond to iron atoms. This was demonstrated with the elemental analysis acquired by EDX which shows that the material is made up of carbon (60.48%), oxygen (39.17%), silicon (0.19%) and iron (0.07%). The Ca(II) ions are no longer observed since they were displaced by Fe(III) ions, demonstrating that the ion exchange reaction proceeded quantitatively, the reaction proposal is presented in Figure 5.

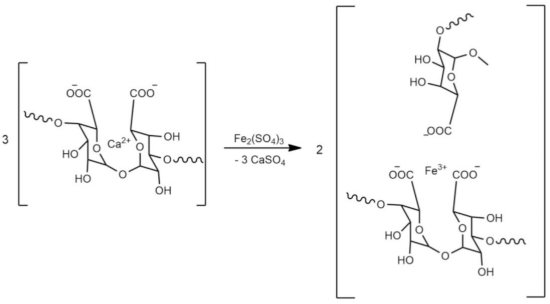


Figure 5. Ion exchange reaction of Ca (II) for Fe (III)

CONCLUSIONS

The chemical modification of pineapple peel with NaOH/CaCl2 generated acetate ions as active adsorption centers, facilitating iron adsorption. With the analysis carried out by SEM-EDX, it was demonstrated that pineapple peel has the potential to be used as a metal adsorbent material. This way, the sustainable use of pineapple waste as a bioadsorbent of metals in water will have benefits associated with the reduction of environmental impacts caused by the accumulation of waste derived from the industrial process of pineapple.

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