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Use of orange peel (Citrus sinensis) in the bioabsorption of potentially toxic metals from water resources through ICP-OES

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ABSTRACT

Water is the main resource for the world and humankind subsistence, being also used as a way to conduct nutrients and essential substances to life. The objective of this research was to evaluate the use of orange peel (*Citrus sineses*) as an adsorbent in water contaminated by heavy metals. To investigate this question, the group used calculations to know the recovery percentage of each analyzed metal, using 0.5g of adsorbent in solutions containing metals (Pb, Fe, Zn, Ni and Mn) with previously known concentrations in mg L^{-1}. The metal analyzes were performed in an inductively coupled plasma atomic emission spectrometer (ICP-OES). The analysis of the response surfaces indicated that the greater mass of adsorbent there was a greater adsorption rate. Based on the obtained responses, 13 mg L^{-1} of Pb were reduced to 0.44 mg L^{-1}, using 0.5 g of adsorbent, resulting in 96.7% of efficiency for the applied methodology. There was removal of metals in higher concentrations bands and mass, presenting efficiencies from 64.3% to 98.2%. The orange peel was adequate as an adsorbent for the removal of heavy metals from the solution.

Keywords: Metals; Orange peel; Adsorption

1 INTRODUCTION

According to Reichardt and Timm (2016), water is an abundant substance on Earth's surface that has a high importance in vital and physico-chemical processes. Being found in the atmosphere, makes it possible to adjust the temperature along with other elements on the planet that give the appearance and evolution of living beings. Excess rains cause overload that may cause soil loss by erosion or percolation, which is the water infiltratin in the soil and forming underground aquifers.

According to Brazil (2013), various human activities directly affect the water quality, contaminating affluent and underground and superficial resources. Some of these activities are agriculture, industry, mining, water infrastructure and domestic effluent treated or not. The

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disorderly growth of the cities causes intense modifications and, consequently, contribute to the contamination of soil and water resulting in the deposition of materials, chemicals, proliferation of bacteria, fungi and viruses, heavy metals, among other contaminants.

Metals are results from natural sources, such as weathering of rocks and washed soil, and anthropogenic sources. Also, being decompose in non-point sources, such as solid deposition, atmospheric and soil leaching, as well as punctual releases of industrial waste, domestic channels, landfills and waste from mining (CAMPOS; BENDO and VIEL, 2001).

The extractive activities of mining companies have a significant impact on water quality, since, drilling the ground also produce water in certain wells or use it to reduce the excess dust risen during the operation. The waters disposed from these activities have high levels of contamination in their composition containing metals such as: lead, copper, arsenic, zinc, sulfur compounds, mercury and other metals that are from extraction and processing (BRAZIL, 2013).

There are several modern methods to remove different metallic types from effluents, aiming to avoid negative results in the environment. The procedures include physical and chemical adsorption, coagulation, chemical precipitation, ultrafiltration, and others. Among these techniques, a viable option for removal of metals in effluents is the adsorption (YADLA, SRIDEVI and LAKSHMI, 2012).

This method is efficient, being used by species in aqueous solutions and depending on the adsorbent used in the procedure, having a lower cost when compared to other techniques used for the effluents treatment that present pollutants from distinct origins (2009).

Adsorption is a method with high capacity to transfer mass from a fluid phase to a solid phase. Thus, to better understand adsorption, the adsorbate is the species that adsorbs on the solid surface, while the solid with this characteristic is called adsorbent (NASCIMENTO *et al.*, 2014).

In this way, the selection of the solid is essential to achieve a high efficiency in the process. Thus, all solid material has some adsorption capacity, however, there are rare types with characteristics suitable to be employed in separation or industrial techniques of effluent treatment (HEUMANN, 1997).

Ciola (1981) highlights that the adsorbents are natural or artificial elements that have a good internal porosity available for a selective bond with solutes in a gas or liquid phase. Industrial adsorbents have to be specific, easy and inexpensive to be recovered, have mechanical immobility and do not react with the substrate or with regeneration reagents.

According to the literature, many biomass were effective in the extraction of aqueous contaminants, such as peanut shells (LIU *et al*., 2010), chestnut waste (YAO *et al*., 2010), sugar-canebagasse (SANTOS *et al*., 2011), rice husks (MIMURA *et al*., 2010) orange waste (SHARMA *et al*., 2012), among other elements.

The orange waste has peelings that stand out for being a by-product and evaluated as an agro-industrial residue purchased in greater quantity in Brazil. Despite being used in the production of feed for ruminants, it can be used for other purposes such as the removal of dyes from industrial effluents (FOSTER *et al*., 2010a; SHAH *et al*., 2012).

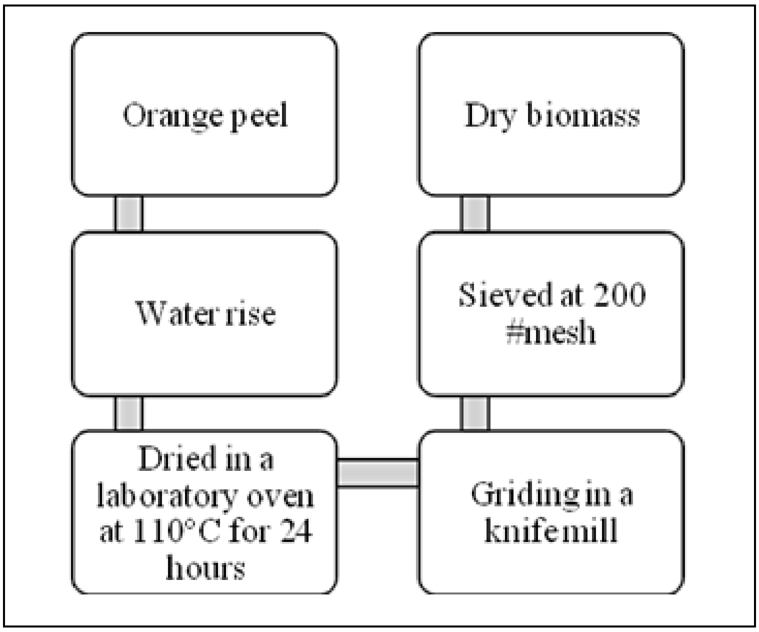
The orange peel contains 16.9% of soluble sugars, 9.21% of cellulose, 10.5% of hemicellulose and 42.5% of pectin, as the most significant element. The soluble sugars of orange peel are glucose, fructose and sucrose. The insoluble polysaccharides of its cell wall are composed by pectin, cellulose and hemicellulose (rich in galacturonic acid, arabinose, galactose and small amounts of xylose, rhamnose and glucose), in addition to essential oil, and D-limonene (GROHMANN CAMERON BUSLIG, 2005).

Biomass is used for the production of new chemical compounds with energetic utilization, merging the sustainability and possibility to commercialize its by-products, being one of the fundamental processes for pyrolysis conversion (BRIDGWATER *et al*.,1999; HUANG *et al*., 2011). Thus, Monteiro (2015) suggests the evaluation of the production and use of an adsorbent from orange peel as an alternative for the treatment of water contaminants.

2 METHODOLOGY

The research is of an experimental nature and aims to present the study of methods and equipment used in the analyses. Figure 1 has the steps of the biomass powdering process.

Figure 1 – Flowchart of the biomass spraying process



First, the orange peels (*Citrus sinensis*), most significant citrus species in Brazil, were rinsed in running water and placed in the sun for a few days to decrease its moisture, making them brittle (DONADIO, 1999).

Then, the samples were dried in a Solab laboratory oven (model: 1000) at 110 °C for 24h. After this process, they were fragmented in a Bermar knife mill (Model: 03-NR), passing through an ABNT sieve of #200 mesh in order to reduce the particle size and expand the surface area, leaving the solution more homogeneous and representative (BROWN and GALLAGHER, 1998).

2.1 Preparation of heavy metal solutions at known concentrations

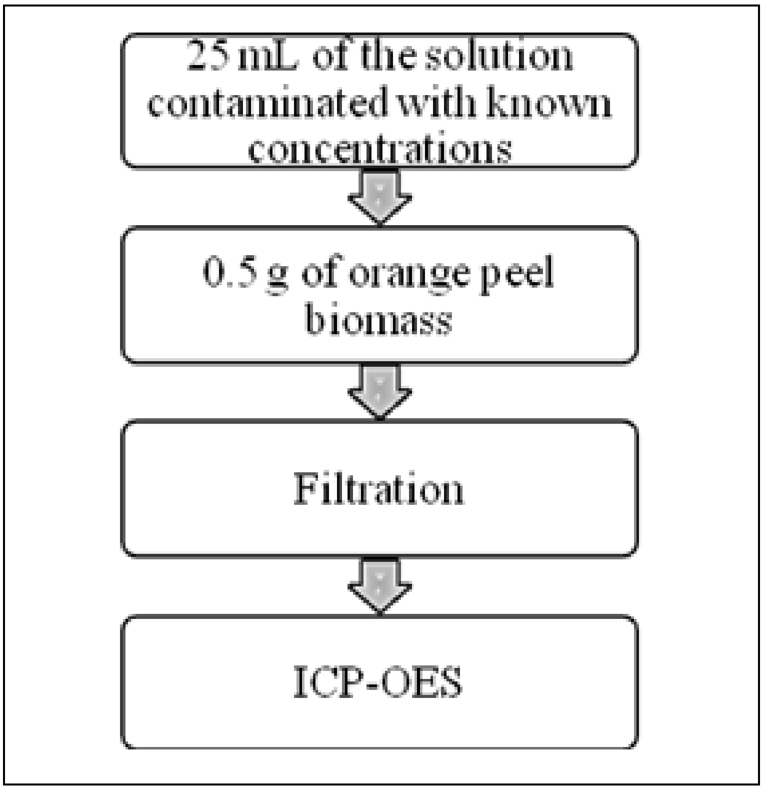
For the preparation of solutions at known concentrations with hevy metals, a micropipette Brand (1-10mL) was used to insert 3.9 ppm and 15.6 ppm of zinc (Zn) Accu Standard (concentration: 1000 µg/mL); 3.3 ppm, and 13.5 ppm of lead (Pb) Accu Standard (concentration: 1000 µg/mL); 3.2 ppm and 12 ppm of manganese (Mn) Accu Standard (concentration: 1000 µg/mL); 3.4 ppm and 14.5 ppm of iron (Fe) Fluka Analytical (concentration: 1000 µg/mL); 2.3 ppm and 9.5 ppm of nickel (Ni) Accu Standard (concentration: 1000 µg/mL).

The metals were added separately according to their type and concentration in a volumetric flask of 100 ml and were completed until the meniscus with distilled water.

2.2 Absorption kinetics

For the development of the research, it was necessary to follow steps of the adsorption kinetics, presented in Figure 2.

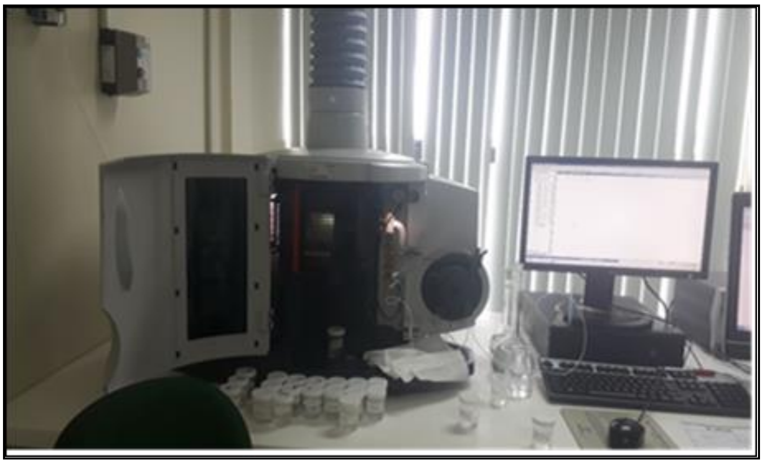
Figura 2 – Flowchartof the adsorption knetics



It was added 0.5g of orange peel powder into 25 mL of each solution, being mechanically stirred in an orbital shaker from Solab (model: SL-180/DT) at 110 rpm for 60 minutes. The samples were filtered in a slow process with about 120 seconds of duration.

After this procedure, the filtrates were analyzed in an inductively coupled plasma with optical emission spectrometer (ICP-OES) Thermo Scientific (model: ICAP 6300 Duo) as shown in Figure 3.

Figure 3 - Metal quantification via ICP-OES



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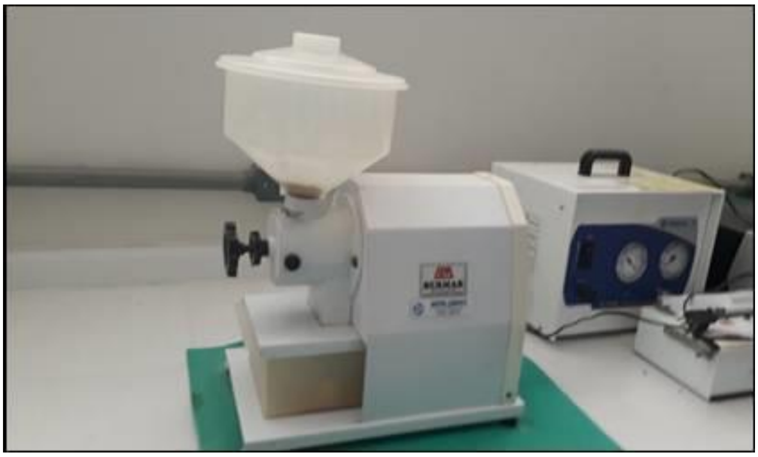
3 RESULTS AND DISCUSSION

The initial stage of this study investigated the possibility of using the orange peel biomass in an adsorption process of low and high concentrations metals. First, the orange peels were washed in order to remove residues that could interfere in the results, being dried in the sun for a few days. Then, they were placed into a laboratory oven at 110 °C for 24h.

After this process the peels were grinded in an industrial blender, being aware that this process may cause a significant amount of mass loss, then using a knife mill, in which it would produce small particles, as shown in Figure 4.

Figure 4 – Bermar knife mill



Source: Author

Figure 4 – Bermar knife mill

Source: Author

Then, the biomasses passed through a sieve of #200, being prepared to be used as an adsorbent. While for the other stage of the procedure, the preparation of the solutions was carried out in volumetric flask of 100 mL, in which the metals were added separately in low and high concentrations, being lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn) and iron (Fe).

An amount of 0.5g of biomass was used as a sorbent for each 25 mL of the water contaminated by the heavy metals, being left under agitation for 60 minutes. Thus, they were filtered in way that the needles were not clogging the equipment used.

The equipment used for the analysis was an optical emission spectrometer coupled by induced plasma (ICP-OES), which has the function of quantifying the metal content in the water. Thus, only contaminated water without the presence of the adsorbent was analyzed, in order to obtain the actual value of the metal present in the solution and samples they were analyzed after being trated in the adsorbent to make a comparative analysis if the efficiency of the applied method.

After all the samples were analyzed, the limit of detection, quantification of the equipment and the actual value of the metal present in the solution were obtained. After all data were collected, calculations were made to analyze the adsorption, Equation 1.

$$valor\ (\%) = \frac{100\,x}{y} \qquad (1)$$

Where:

$x =$ Final metal concentration (mg/L) – Sample with adsorbent

$y =$ Initial metal concentration (mg/L) – Sample without adsorbent

The results were:

Table 1 - Removal efficiency for metals at low concentrations

Hevay metals	Efficiency (%)
Lead	95.1
Zinc	78.7
Iron	-5.9
Nickel	86.9
Manganese	80.4

The results from Table 1 indicate that the values extracted from the metal removal at low concentrations were efficient, ranging from 78.7% to 95.1%. On the other hand, it was possible to observe that the biomass was not efficient in the removal of iron (Fe), being note that the value increased afterthe adsorption process.

According to Monteiro (2015), this can be associated to the chemical composition of the orange peel, once it has high content of organic and inorganic elements, among them iron, being possible that after the saturation, the biomass started releasing it instead of adsorbed it. In Table 2 is possible to see how the adsorbent behaves with metals of higher concentrations.

Table 2 - Removal efficiency for metals at high concentrations

Hevay metals	Efficiency (%)
Lead	96.7
Zinc	78.3
Iron	64.3
Nickel	98.2
Manganese	73.1

As observed in Table 2, all samples at high concentrations of metals had a positive efficiency, and the highest adsorption rate was contaminant for the nickel, 98.2%, followed by lead removal of 96.7%. The lowest rates were associated to iron 64.3%, manganese 73.1% and zinc 78.3%, but even showing lower values, they are also efficiently removed. Figure 6 and 7 present these values graphically.

Figure 6 – Analysis of the response surfaces at high concentration

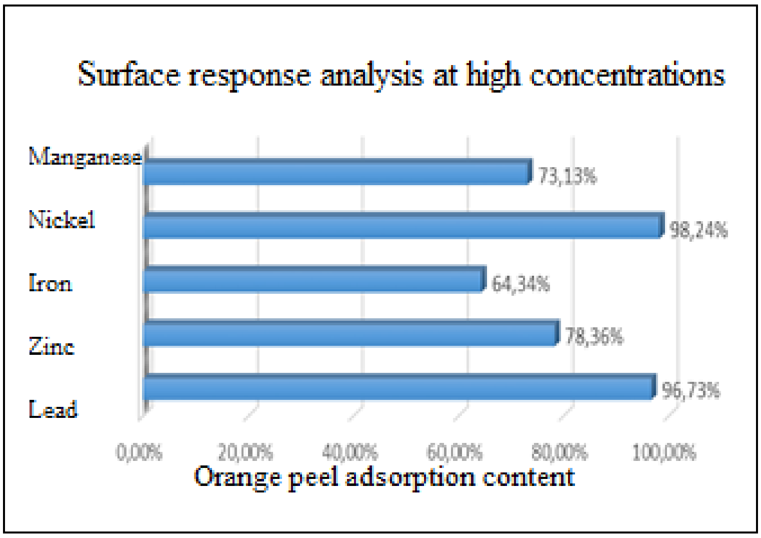
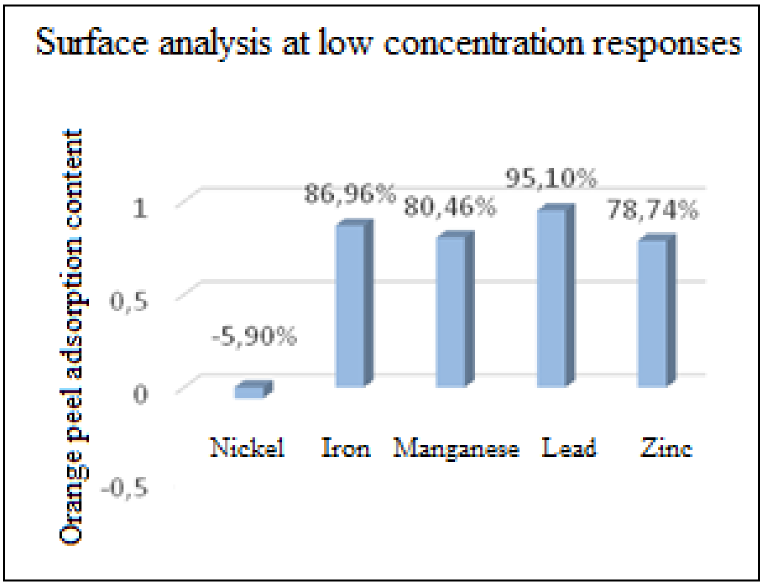


Figure 7 – Analysis of the response surfaces at low concentration



One can observe that the adsorptions for different metals and different concentrations presented similar profiles, being the highest removal percentage associated to lead (Pb) and nickel (Ni), for both concentrations. This result characterize that they were the metals with the greater affinity to the adsorbent material. The other metals presented significant removal values, although they were lower.

4 CONCLUSIONS

This work presented the potential use of orange peel as a decontamination agent for potentially toxic metals present in water sources. The obtained results indicate that the adsorption system of orange peel (*Citrus sinensis*) was efficient in the removal of all studied metals, except for iron (Fe) at high and low concentrations. The initial stage of this study investigated whether there is the possibility of using the orange peel biomass in the treatment of effluent contaminated by heavy metals, all procedures were simulated in the laboratory using metals solutions at known concentrations. In general, the results are in accordance with the literature, the orange peel proved to be an efficient alternative material for the removal of heavy metals from aqueous solution. Consequently, it can be an additional alternative in the removal of these metals in industrial liquid residues containing low and high concentrations.

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