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BATCH ADSORPTION STUDIES OF Ni (II) AND Mn (II) IN LIQUID EFFLUENTS USING SUGARCANE BAGASSE ASH

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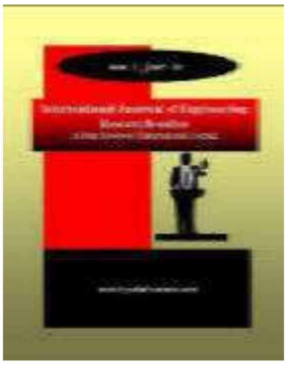

ABSTRACT

The liquid effluents of some industries have traces of harmful metals that have bio accumulative properties, which contributes to the increase of their toxicity. In view of industrial growth, and the consequent increase in emissions of contaminants in liquid effluents, adsorption is among the operations applied to reduce the concentration of metals in order to comply with current environmental regulations. Residual biomass has been gaining prominence in the treatment of these effluents because it is a renewable and low-cost material when compared to conventional adsorbents. The objective of this work is to evaluate the efficiency of sugarcane bagasse ash (CBA) in the adsorption of metallic ions Ni (II) and Mn (II) by means of adsorption isotherm tests. CBA was characterized in terms of its microstructure, chemical composition, specific surface area and morphology, and the adsorbate was analyzed by atomic flame absorption. CBA effectively presented itself as a bio adsorbent for both synthetic solutions, containing Ni (II) and Mn (II) ions, present in liquid effluents. The adsorption isotherms showed an increasing profile, indicating the average removal efficiency of 98.4 % for Ni (II) and 97% for Mn (II) and this material can be applied as an adsorbent in industrial effluents.

Keywords: bio adsorbent; sugarcane bagasse ash; adsorption; metals; liquid effluents

INTRODUCTION

The search for new materials and techniques that can be used as an alternative for the treatment of wastewater from industrial and mining processes has become a challenge in recent times. Recent studies have established the use of alternative methodologies for the adsorption of pollutants, such as heavy metals, which use materials of biological origin such as bacteria, algae and fungi, industrial, agricultural and urban waste, due to their great viability, low cost and high removal efficiency [1]. Within this broad set of biological materials, the application of citrus fruit peels (orange), marine algae or prickly pear stands out. One of the techniques used for these processes is biosorption, which consists of the selective transfer of one or more solutes from a liquid phase to a batch of solid particles of biological material and involves the participation of various physical and chemical mechanisms based on various factors [2]. Due to the natural origin of the substrates and the elimination of residual sludge during the removal process, this technological alternative constitutes a system that allows not only to remove the contaminating metal, reducing the environmental impact generated on the environment in which it is discharged [3], but also that also allows to recover it to integrate it into a new production cycle [4].

However, it's industrial, environmental and / or health application is generally limited by the chemical and structural instability of some materials used as biosorbents. [5] For this reason, it is necessary to carry out laboratory and / or scale tests that allow evaluating the removal efficiency of the various biomass of potential use and of the systems through which the bio sorption tests are carried out, to simulate the characteristics of the effluents in environmental conditions and establish the optimal ranges in which biomass is effective in each of the parameters involved in the process [6].

The removal of metal ions is a difficult task due to the high cost of treatment methods. There are several methods available for this removal in liquid effluents, including ion exchange, solvent extraction, reverse osmosis, precipitation, co-precipitation and adsorption [7]. With regard to adsorption, activated carbon and other carbon-based adsorbents are widely used because of their versatility in removing these metal ions. In view of the high cost and the exhaustive process for the synthesis and regeneration of activated carbon, there is a continuous search for low cost adsorbents, which demonstrate similar efficiency in the adsorption process [8].

Biomass - all renewable resources from organic matter (vegetable or animal) - has been arousing the interest of researchers in the production of bio-adsorbents, in the treatment of wastewater, as these are low cost and abundant in nature, in addition to requiring little processing 8. Biomass from the plant environment, particularly agricultural residues, rich in cellulose, hemicellulose, lignin, lipids, simple sugars, among other organic compounds, have great potential for adsorption of various pollutants [9]. Its chemical composition can guarantee a rich source for the production of activated carbon, which may contain low ash content and considerable fixed carbon content. Therefore, the conversion of agricultural waste into low-cost bio-adsorbents is a promising alternative for solving environmental problems as well as reducing the costs of preparing adsorbents. Among the agricultural residues used as bio-adsorbents 10], rice husk, corn cob , sugarcane bagasse stand out, mesocarp of coconut and ash from sugar cane bagasse (CBA) .

Sugarcane bagasse is used for energy cogeneration to replace fuel oil and other energy sources. However, the production process of the sugarcane industry generates huge amounts of solid waste in the form of ash. The amount of residue from the sugarcane bagasse ash generated is equivalent to about 0.5% by weight, in relation to the initial mass of the bagasse. In Brazil, around 1,200,000 tons / year of ash from sugarcane bagasse are produced in sugar and alcohol plants, but this co-product has an uncertain use for the sulco-alcohol industry. CBA is more economically viable compared to other adsorbents, such as activated carbon, which has a high initial cost, in addition to the need for an expensive regeneration system [11].

In the literature, among the studies observed with the use of sugarcane bagasse ash, the adsorption of acrylonitrile in aqueous solution stands out, widely used in the production of acrylic, resin and rubbers, as well as CBA was used for the removal of indole (heterocyclic aromatic organic compound), mercury, lead, cadmium, fluorine and benzoic acid decreasing concentrations considered toxic [12]. The present work aims to study the performance, through the analysis of the adsorption isotherm, of the sugarcane bagasse ash, as a bio-absorbent, evaluating its efficiency in removing Ni(II) and Mn(II) metals in their respective synthetic solutions, which simulate the concentrations present in the water produced in the oil industry. Effluent considered toxic, difficult to treat, with the largest flow of waste water in the process of oil exploration and production.

MATERIALS AND METHODS

The sample of ash from the sugarcane bagasse prepared by collecting sugarcane bio waste from Agricultural Land in Eluru, Andhra Pradesh, India as the method developed by Gaikwad (2010) [13] followed by washing with hydrochloric acid (2% HCl), under constant agitation for 4 h to remove impurities. The material resulting from the acid wash was washed with industrial water to neutralize the pH (~7.0), dried at 100 °C for 4 h and sieved for granulometric determination so that the ash was characterized under equal physical conditions. Subsequent procedures were performed with granulometry between 0.075 mm and 0.106 mm. The CBA was then calcined in a tubular oven at 700 ºC for 120 min, with a heating rate of 5 °C 1/min flow of N 2 300 mL/min .

Characterization of the adsorbent: the crystalline structure of the adsorbent was characterized by X-ray diffraction (XRD-7000, Shimadzu, radiation source Cu kα, angular range from 10 ° to 80 °). The chemical composition analyzed by X-ray fluorescence (Shimadzu, EDX- 720), with semi quantitative scanning of sodium to scandium and titanium to uranium; the samples were placed on polypropylene film for better beam penetration. The specific surface area was determined from data of adsorption isotherms of sorption in an analyzer (Nova 2000, Quantachrome) at the temperature of N 2liquid. Morphological analysis was performed using scanning electron microscopy (Shimadzu SSX-550 Superscan). The samples were deposited on a carbon ribbon and metallized with gold to obtain sufficient electrical conductivity, avoiding the accumulation of electrons on the surface, ensuring better image quality.

Adsorption tests: the adsorption tests were carried out in 250 mL conical flasks containing 20 mL of the precursor nitrate solutions of the nickel [$Ni(NO_3)_2.6H_2O$] and Manganese ions and Manganese(II) nitrate tetrahydrate, $Mn(NO_3)_2\ 4H_2O$- Sigma-Aldrich], respectively, in concentrations of 10, 20, 40, 60, 80 and 100 mg/L, with approximately 500 mg of the bioadsorbent (CBA). The system was kept at room temperature 30°C with orbital shaking for 4 h. The bioadsorbent was removed from the solution by vacuum filtration and the resulting filtrate analyzed by PerkinElmer atomic absorption spectroscopy, using acetylene as an oxidizer at 2300°C and burning speed at 266 cm/s, using hollow cathode lamps (λ = 232.0nm for Ni; λ = 279.5nm for Mn). After analysis of atomic flame absorption, calculations were performed to determine the adsorption capacity and the efficiency of the bioadsorbent against metal ions, respectively, according to equations 1 and 2 :

$$Q_{eq} = \frac{Ci-Ceq}{M} \times V \quad \text{..... Eq -1}$$

$$\%\ Removal \ = \frac{Ci-Ceq}{Ci} \times 100 \quad \text{....Eq -2}$$

where Qeq is the adsorption capacity, Ci and Ceq the initial and final (equilibrium) concentrations of the solution, V the volume of the solution and M the mass of the bioadsorbent, and E_f its efficiency of removing these ions in the solution.

Analysis of Ni(II) and Mn(II): to determine the concentration of Ni(II) and Mn(II) present in the solutions that came into contact with the bioadsorbent, a calibration curve was prepared in the atomic absorption spectrophotometer with concentrations of 0.5 mg / L at 2.0 mg / L from a standard at 1000 mg / L of each metal, with deionized water as white. The Fig. 1 shows the profile of the calibration curves for both metals. After calibrating the equipment, Ni(II) and Mn(II) solutions were analyzed.

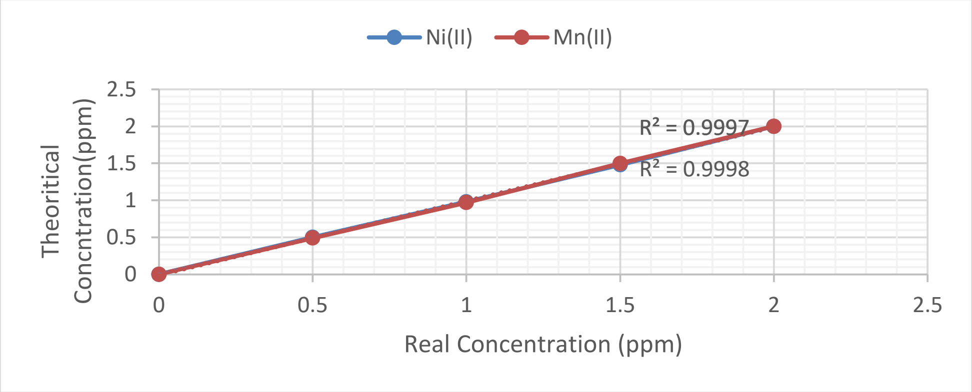

Figure 1 Calibration curve for Ni(II) and Mn(II

RESULTS AND DISCUSSION

Characterization of the bio adsorbent: according to the X-ray diffractogram (Fig. 2), the heat treatment of sugarcane bagasse ash at 700 ºC promoted the formation of silica with a hexagonal crystalline structure [14]. The ash also showed an amorphous structure due to a slight deviation from the baseline, which provides greater reactivity compared to crystalline materials .

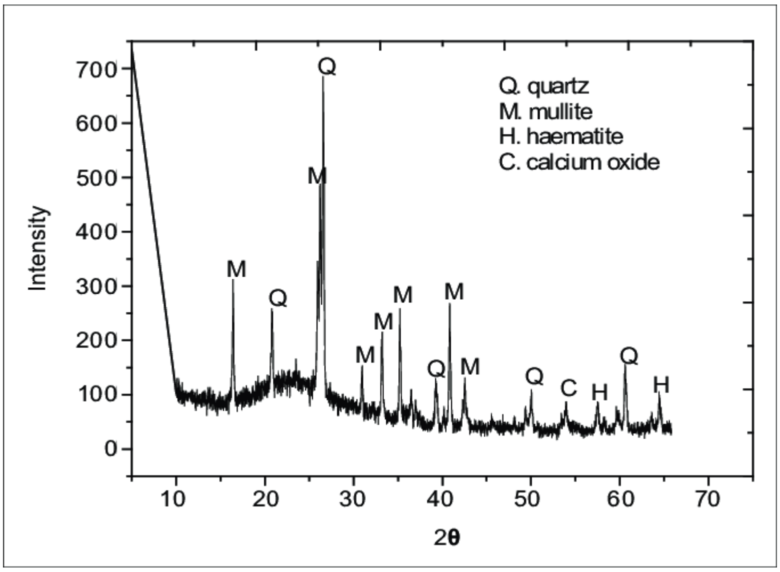

Figure 2 X-ray diffractogram of the CBA.

CBA showed 84.0% Quartz in its chemical composition. As a result of the chemical analysis in Table I, Mullite, Haematite & CaO were also identified, which represent about 13.8% of the chemical composition; other oxides and contaminants add up to 1.7% of CaO. The presence of Haematite, Mullite and Quartz is probably due to traces of fertilizers used in the cultivation of sugar cane, inorganic materials that after burning increase the ash yield. Natural factors such as climate, soil and water are also functions of the variation in the chemical composition of CBA,

Table 1:Chemical composition of CBA.

Chemical composition	Quartz	Mullite	Haematite	CaO
CBA	84.0	7.0	3.7	1.7

The result of the specific surface area of the bioadsorbent was 252.9 m^2/ g, a value considered relatively high when compared to other studies of CBA without any treatment (168.8 m^2/ g) , and pore diameter 44.7 Å, which is in the middle range characteristic of mesoporous materials (20 to 500 Å). The high specific area is an important factor for adsorption, however, it is not an exclusive criterion for the material to be considered a good adsorbent, as it requires sites that are active for its performance in relation to adsorbate.

The shape of the CBA showed a rough and massive appearance, with signs of rupture of the fibers due to the acid treatment, providing the presence of more defined and regular pores (Fig.3) possibly from the extraction process of inorganic minerals and organic compounds soluble by acid treatment (HCl). In addition, CBA has high porosity, as has been observed, this characteristic is associated with the release of organic matter during the bagasse burning process for energy generation in the sugar and alcohol industry.

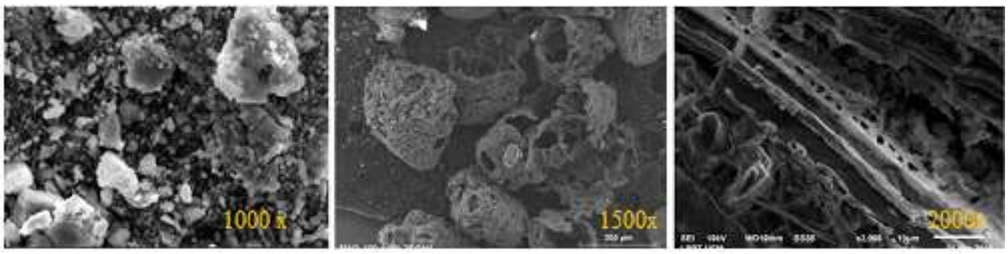

Figure 3 SEM Images of the CBA with (a) 1000x magnification; (b) 1500x and (c) 2000x

Adsorption isotherms: the adsorption isotherm models are fundamental to verify the efficiency of the adsorbents in relation to their adsorption capacity, through interactions with the adsorbate and thus be able to determine the best application of the adsorbent [15]. Isotherms were obtained by the relationship between the amount of adsorbed metal (Cs , mg / g) and the concentration at equilibrium (Ce , mg / L). The isotherm profile also provides data on the affinity between the adsorbent and the adsorbate and the probable adsorption mechanism. Several models have been proposed to describe the adsorption processes, including the Langmuir and Freundlich models. The Figs. 4 and 5 show the experimental results and models of the Langmuir and Freundlich isotherms for the adsorption of Nickel and Manganese using CBA as an adsorbent, respectively.

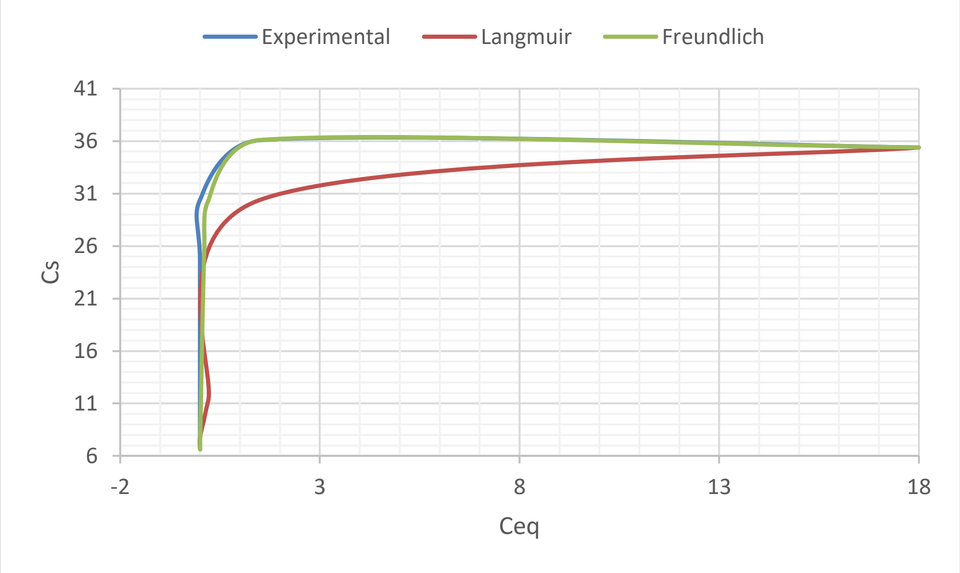

Figure 4 Adsorption isotherm for Nickel (II)

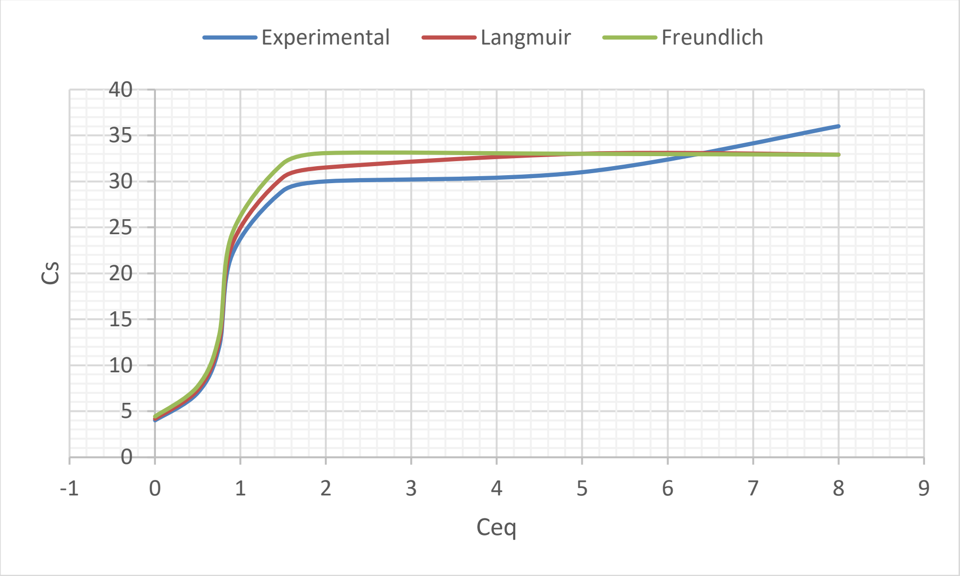

Figure 5 Adsorption isotherm for Mn(II)

In the Langmuir isotherm it is assumed that the adsorption process occurs in a monolayer of the substance on the surface of the solid particles outside the adsorbent, containing a finite number of identical sites. The model assumes uniform adsorption energies, without the migration of adsorbate on the plane of the adsorbent surface. The expression that represents the Langmuir model is given by equation 3:

$$C_s = \frac{K_L q_m C_e}{1+K_L C_e} \quad \text{Eq ..3}$$

where C_s is the amount of adsorbed metal at equilibrium (mg / g), $C_e$and the concentration of metal at equilibrium (mg / L), $K_L$the Langmuir adsorption constant (L / mg), related to energy of adsorption q_m the maximum adsorption capacity (mg / g). The Freundlich isotherm admits that the adsorptive process occurs on a heterogeneous surface, represented by the equation 4 :

$$C_s = K_f {C_e}^{1/n}$$

C_s and C_e and have the same meanings as the Langmuir model, K_f (L/g) is the Freundlich constant, related to the adsorption capacity and n is the heterogeneity factor. The Freundlich model reports the adsorption process on heterogeneous surfaces, considering that the adsorption sites have different adsorption energies, varying depending on the surface coverage. When the adsorption energies are equivalent at all sites, the adsorption is considered linear and the exponent value 1 / n is equal to 1 ; the lower the exponent value, the stronger the interaction of the adsorbent with the adsorbate . The values of $1/n$ are less than 1, indicating favorable adsorption, and sorption by heterogeneous high-energy sites being occupied first, followed by sorption in lower-energy sites . The adsorption processes showed n> 1 (n Ni= 5.26; n Mn = 3.56), which suggest heterogeneity related to the adsorbent adsorption sites [17]. The higher the value of n obtained, the more heterogeneous is the adsorption process, and the stronger the interaction between adsorbate and adsorbent [16]. The results of the adsorption isotherm and the parameters obtained (Table II) show that the Langmuir and Freundlich models present values close to those found in experimental isotherms, however, for Mn (II), the Langmuir isotherm is the most appropriate model, as it was the one that best suited the experimental data and presented the highest correlation factor (R^2 = 0.863), For Ni (II), the Freundlich model showed less variation with better adjustment to the experimental isotherm and a higher correlation factor.

Table II Langmuir and Freundlich isotherm parameters.

	Ni(II) ion			Mn(II) ion		
Model	R^2	Equation		R^2	Equation	
Langmuir	0.87	C_s =	126.4 (Ce)/1+3.48 (Ce)	0.93	C_s =	363.35(Ce)/1+0.88 (Ce)
		K_L	3.48, qm =36.92 mg/g)		K_L	0.88, qm =41.31 mg/g)
		R_L	0.0078		R_L	0.028
Freundlich	0.46	C_s =	21.07 Ce $^{(0.39)}$	0.85	C_s =	20.21 Ce $^{(0.28)}$
			(n=5.26; Kf=21.08			(n=3.36; Kf=20.91

In the adsorption process, several attractive forces (physisorption) are involved, such as ionic interaction, van der Waals forces and covalent bonds (chemisorption) [18]. In chemisorption, after the surface is covered by a monolayer of adsorbed molecules, it becomes saturated, as shown in the Ni(II) isotherm profile, in which the same adsorbed amounts (31.2 mg / g) are observed for different equilibrium concentrations (Ce) [19]. It can be said that the mechanism involved is of a physical-chemical or chemical nature. Langmuir isotherms have equilibrium parameter value, (R_L), between 0 and 1, showing that the adsorption of ions in the solutions (adsorbate) is favorable or extremely favorable by CBA (bioadsorbent), since large amounts adsorbed can be obtained with low concentrations of solute. The Table III shows the efficiency (%) removal of bioadsorbent (CBA) with respect to the adsorbed metal ions.

Table III Efficiency of the bio adsorbent (CBA), against metal ions Mn (II) and Ni(II)

Nickel (II)			Mn(II)		
C0 (mg/L)	Cf (mg/L)	Ef(%)	C0 (mg/L)	Cf (mg/L)	Ef(%)
10	0.003	99.97	10	0.13	98.6
20	0	100	20	0.09	99.64
30	0.57	98.64	30	0.185	99.53
40	1.68	97.67	40	0.402	99.32
60	4.01	94.67	60	0.9431	98.31
80	5.67	92.14	80	1.024	94.67
120	6.47	91.24	120	10.24	82.61

The efficiency calculation confirms the behavior of the graph, in which the isotherm curves have a certain proximity, and a better CBA performance in the adsorption of Manganese, since it has average efficiency (% Rem) = 97.28%, slightly higher when compared to Nickel, M = 96.4%. This result may be associated with the size difference between these elements, the Mn(II)has an ionic radius (0.61Å), smaller than Ni(II) (0.73Å), causing a better accommodation of the Manganese ions in the pores of the CBA, promoting greater adsorption efficiency of the bio adsorbent with the metal [20]. In the literature, the use of sugarcane bagasse as a bio adsorbent in the adsorption of heavy metals was presented, showing significant results, but with a more complex pre-treatment, in addition to the sugarcane bagasse being used in conjunction with passion fruit peel, while in this work, the objective was reached in a simpler way and without a joint action to achieve its good efficiency. Some authors treated the sugarcane bagasse ash using a mixture of acids (HCl and HNO_3) a concentration close to 2M for each acid), aiming at removing silicates, but leaving the treatment at a higher cost, and providing an adsorption efficiency of 91%, while the treatment presented here, with only a low concentration acid solution (0.25 M HCl), made the process less costly and more efficient when compared to other works in the literature [21-22]. Another study shows less than 80% arsenic removal using the sugarcane bagasse as a bio-absorbent, chemically impregnated with $ZnCl_2$ again, the present work showed greater efficiency in the adsorption of metal, without the need for a complex chemical treatment. The study carried out here presented an adsorption process using an abundant, natural adsorbent of renewable origin and of low cost, for the purposes of high efficiency adsorption for the studied ions.

CONCLUSION

CBA effectively presented itself as a bio adsorbent for both synthetic solutions, containing Ni(II) and Mn(II)ions, also present in the water produced in oil wells and other industrial effluents. The bio-adsorbent obtained adsorption efficiencies for the studied metals, however the applied isotherm models (Langmuir and Freundlich) showed that for the Nickel adsorption profile it was adapted to the Langmuir model; and for Manganese, the model that showed less variation compared to the experimental isotherm was the Freundlich model. The adsorption isotherms showed a convex profile, with parameters that indicate favourable adsorption for the ions analyzed. The bio adsorbent studied can be applied in several liquid effluents, such as water produced in oil wells, improving its quality, for its disposal or reuse, with a greater cost benefit for the industry.

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