FERROMAGNETIC NANOPARTICLES BASED ON CARNAUBA STRAW (COPERNICIA PRUNIFERA) FOR METAL REMOVAL

Bruno Rodrigues de Freitas[a], Second Author[b], Third Author[a,b,*]

[a] *Federal University of Ceará, Fortaleza, 60455-760, Brazil*

[b] *Second affiliation, Address, City and Postcode, Country*

Abstract

In recent years, awareness of the need for the rational use of natural resources and the development of technologies that minimize environmental impacts has become more evident Given this context, it is necessary to treat these effluents to environmentally acceptable levels before releasing them into the environment.. From this perspective, this work sought to analyze the feasibility of using powder from the fresh leaves of the red cashew tree carnauba (Copernicia prunifera) and magnetic nanoparticles ($Fe3O4$) for the synthesis of nanostructured composite with paramagnetic capacity to be used in the removal of heavy metals in aqueous solution. The experimental procedures allowed the synthesis of 10.0g of nanostructured composite of magnetite and carnauba straw with high paramagnetic capacity, presenting a particle size of 0.106mm. The yield was 92%.

Keywords: adsorption; carnauba straw; copper; zinc; cadmium.

1 Introduction

In recent years, awareness of the need for the rational use of natural resources and the development of technologies that minimize environmental impacts has become more evident, as a result of the growing concern of the world population with the damage caused to the environment. Among the environmental components, water bodies are the most affected by pollution in Brazil, as a result of their effective participation in the economic and biological processes that structure society [1],[2]. In this context, the release of effluents contaminated with metal ions into receiving bodies, such as rivers and lakes, represents a serious environmental problem experienced by contemporary society. In the northeast region, mainly in the states of Rio Grande do Norte, Ceará and Piauí, carnaúba (Copernicia prunifera) stands out as a biomass with great potential for use. Carnauba, popularly known as the tree of life, due to its countless uses, was once one of the main sources of income in some states.

1.1 General objective

Synthesize nanocomposite with adsorbent properties.

1.2 Specific objectives

I. Synthesize the nanocomposite
II. Characterize the nanocomposite

2 Materials and methods

In the adsorption tests, biomass from carnauba straw was used, supplied by the community industry of Canafistula, district of Caio Prado, in the municipality of Itapiúna-CE. The material was milled using a knife mill and as the particle size was still high, it was decided to pass the material through a ball mill, aiming to obtain even smaller particle sizes, and consequently a larger surface area. The two larger fractions remained in the mill for 15 minutes, while the two smaller fractions remained for 10 minutes, always with aliquots of 10 g for each procedure. After grinding in the ball mill, 100 g of the material was placed on the sieve, obtaining the following fractions in each plate:The fraction retained on the sieve with an opening of 0.106

2.1 *Chemical treatment*

Alkaline treatment was carried out with 0.05 M NaOH, placing the biomass in contact with the basic solution for 1 hour, heating between 70 and 80 °C and constant stirring. The proportion used was 5 g of biomass for every 100 ml of solution. 1 500 ml Becker, 1 200 ml Becker, 1 thermometer and 1 magnetic stirrer with heating were used. The pH of the prepared solution was determined using the appropriate equipment, reaching a value of 12.88. After the procedure, the biomass was washed with distilled water until a pH close to 7, which could vary between 6.7 and 7.3. The modified material was placed to dry in an oven at a temperature of 80°C for 12 hours.

After the alkaline treatment and proper drying, treatment was started with 0.01 M oxalic acid for 1 hour under heating between 70 and 80 and constant stirring. The proportion used was 5 g of biomass for every 100 ml of solution. 1 500 ml Becker, 1 200 ml Becker, 1 thermometer and 1 magnetic stirrer with heating were used. The pH of the solution was determined using the appropriate equipment, reaching a value of 1.63. After the procedure, the biomass was washed with distilled water until a pH close to 7, which could vary between 6.7 and 7.3. The modified material was placed to dry in an oven at a temperature of 80°C for 12 hours. This provided solubilization of hemicellulose in an acidic medium [4].

2.2 *Preparation of magnetite nanocomposites*

The nanomagnetized biomass was obtained from the methodology proposed by Barreto et al., 2012 [5] The synthesis followed through the co-precipitation of the Fe^{2+} (2.1 g) and Fe^{3+} (4.2 g) salts ($FeSO_4$ II and $FeCl_3$ III). The aqueous solution containing the salts was under constant stirring and at a temperature of 70ºC for 20 minutes (figure 3), after which interval, 35 ml of ammonium hydroxide P.A (38%) of Dinâmica was added slowly (for 30 minutes), through a burette, to the system (figure 4), after the end of the ammonia addition, 10 g of the biomass (colocar a granulometria aqui) was slowly added, leaving the system under agitation and constant temperature for another 30 minutes. At the end of the interval mentioned above, the solution was allowed to cool and the solution was washed with distilled water until the pH of the solution decreased to approximately 7. After washing, the nanomagnetized biomass was placed to dry in an oven at a temperature of 60ºC. for 72 hours to eliminate moisture. Finally, the material was reserved in a plastic container.

2.3 *The pH_{PZC} of the adsorbent materials*

To determine the zero charge point (pHPZC), 50 mg of carnauba straw adsorbent and 10 mL of 1 mol/L sodium chloride solution were used, in the pH range 2,15-11,89The system was kept in AC for 24 hours, after which the final pH of each solution was measured.

3 Results and discussion

3.1 *Granulometry of the studied material.*

After the grinding process, using the knife mill and the proposed methodology, the fresh biomass fractions were sieved and the retained fractions were weighed. This step was important to develop the study on the particle size of the material, and the results can be seen in Table 1 and Figure 1:

Table 1. Granulometric sieve and retained mass.

Opening (mm)	Retained mass (g)
0,250	10,280
0,150	20,730
0,106	25,030
0,074	28,200
Bottom	13,070

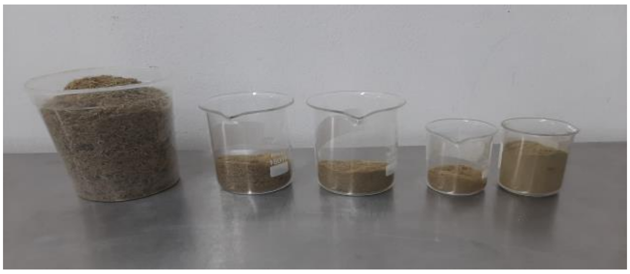

Figure 1. From right to left we have the fractions retained on the sieve plates, 0.250 mm, 0.150 mm, 0.106 mm, 0.074 mm and the bottom.

3.2 Chemical treatment

The alkaline and acid treatments was carried out at the specified time and temperature and stirring. In Figure 2 it is possible to observe the biomass after the alkaline treatment, before washing and after, when the pH was already close to neutral. The main effect of alkaline pretreatment consists of removing lignin from the biomass, promoting greater fiber reactivity [3].

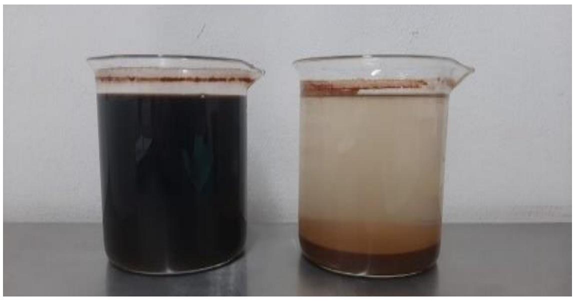

Figure 2. From left to right we have the biomass after alkaline treatment and at basic pH, and on the right the material at neutral pH. .

3.3 Magnetite nanocomposites

The experimental procedures allowed the synthesis of 10.0 g of nanostructured composite of magnetite and carnauba straw with high paramagnetic capacity, presenting a particle size of 0.106 mm. The yield was 92%. The use of magnetic nanoparticles ($Fe3O4$) for complexation with biomass results in a hybrid material that presents the amorphous and organic character of biomass associated with the cubic and crystalline structure of magntite, which has a high inverted polarity, which gives it the highest magnetic values. The new material formed, which is called composite, has paramagnetic properties as it is composed of magnetite. The ferromagnetic potential allows the composite to be easily removed from the aqueous medium by applying a magnetic field (such as a Neodymium magnet)., as can be seen in Figure 3:

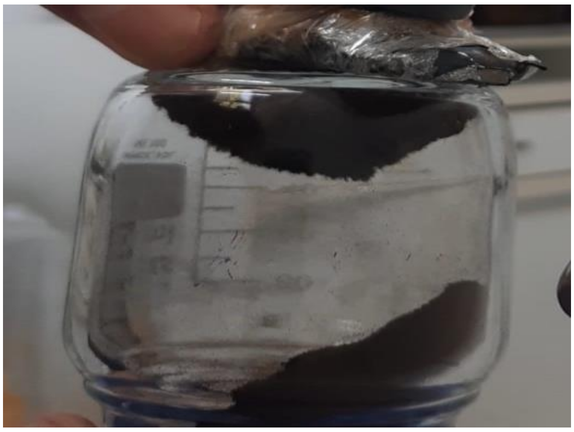

Figure 3. Magnetized biomass produced from carnauba straw and interacting with a neodymium magnet.

3.4 The pH_{PZC} of the adsorbent materials

pHPCZ was obtained for both fresh biomass and nanocomposite, and the results can be seen below in Figure 4 and Figure 5.

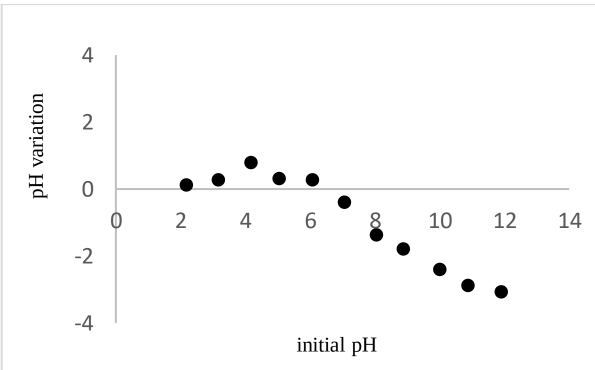

Figure 4. The pH at the point of zero charge (pH_{PZC}) to biomass *in natura*.

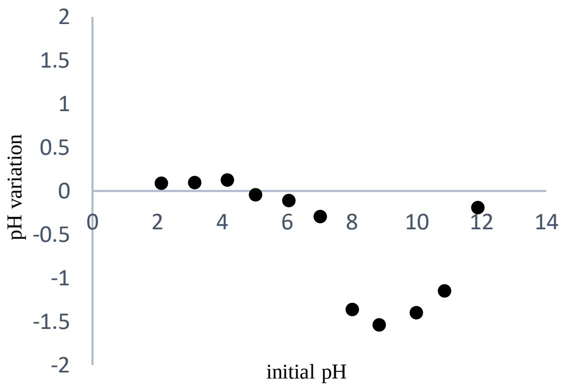

Figure 5. The pH at the point of zero charge (pHPZC) for biomass after chemical treatment and nanomagnetization.

3.5 Conclusions

The experimental procedures allowed the synthesis of 9.2 g of nanostructured compound of magnetite and carnauba straw with high paramagnetic capacity, with a particle size of 0.106 mm. The yield was 92%. The results indicated that the chemical treatment followed by nanomagnetization of the material lowered the pH_{PCZ}, providing greater safety for adsorption processes of toxic metals in acidic media. Therefore, the present work revealed that the use of a carnauba straw has the potential to be used as a as raw material for the production of paramagnetic biocomposite, being a promising technology as it is an abundant, renewable and low-cost biomass. Furthermore, it is a perennial plant, with good productivity and does not require replanting, and can also be used in association with the carnauba wax extraction chain.

5 Acknowledgment

We acknowledge the support of the Trace Analysis Laboratory (LAT), which is linked to the Department of Analytical and Physical Chemistry of the Federal University of Ceará (UFC) and the Coordination for the Improvement of Higher Education Personnel (CAPES) for funding the research.

6. References

[1] GÓMEZ, D. N. Potential of shrimp shell for remediation of waters contaminated with acid mineral drainage aiming at its secondary non-potable reuse. 2014. 151f. Dissertation (Master's in Environmental Engineering) – Department of sanitary and environmental engineering, Federal University of Santa Catarina, Florianópolis

[2] PINO, G. A. H. Biosorption of heavy metals using green coconut shell powder (Cocos nucifera). 2005. 113f. Dissertation (Master's in Chemistry) – Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro.

[3] BAUDEL, H. M. 2006. Pretreatment and hydrolysis. III Technological workshop on hydrolysis for ethanol production. Public Policy Research Program Project – Ethanol, São Paulo.

[4] NASCIMENTO, V. M., ROCHA, G. J. M., GIORDANO, R. C., CRUZ, A. J. G. 2011. Optimization of alkaline (NaOH) pretreatment of sugarcane bagasse for production of second generation bioethanol. In: Society for Industrial Microbiology.

[5] BARRETO, A. C. H. et al. Novel ferrofluids coated with a renewable material. Microfluid. Nanofluidics., v. 12, n. 5, p. 677–686, 19 Mar. 2012