

# Synthesis, characterization, and use of nanomodified sugarcane bagasse for the sorption of hexavalent chromium

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## Introduction

Decontamination of potentially toxic metals in aquatic environments has always been a challenge. Hexavalent chromium is one of the most common environmental contaminant due to its industrial applications (JOBBY et al., 2018). It is highly soluble in water and carcinogenic to humans (CONGEEVARAM et al., 2007), and due to its adverse effects and the high amount of industrial Cr(VI)-containing residues, new techniques employing biological materials have been proposed for its removal and recovery from the environment. The biosorption process has become an economic and eco-friendly alternative treatment to water decontamination. Associated with this process, the use of ferromagnetic nanoparticles has been proposed to improve the sorption properties by potentializing the biosorption process (DEBS et al., 2019). Sugarcane bagasse is generated as a waste in large amounts by the alcohol agroindustry (MILANI et al., 2018), and it is of great relevance to find ways to its efficient use in order to reduce costs and environmental impacts. This work proposes to evaluate the potential of a nanomodified biosorbent prepared from sugarcane bagasse and magnetite to be used in the removal of Cr(VI) from contaminated aquatic environments.

## Methods

**Preparation of the biomass:** Sugarcane bagasse biomass was washed with distilled and deionized water (Milli-Q<sup>®</sup> system, Millipore – USA) and oven-dried at 50 °C for approximately 6 h. For the chemical modification 1.5 g of biomass was weighed and treated with 1 mol/L HCl solution and KCH<sub>3</sub>COO/CH<sub>3</sub>COOH buffer. The mixtures were agitated, centrifuged, and dried at 50 °C for approximately 4 hours.

**Preparation of magnetite nanoparticles (NP) and sugarcane bagasse magnetic nanocomposites (SB-NP and MSB-NP):** Magnetite nanoparticles (NP) were synthesized employing the coprecipitation method (DEBS et al., 2019; Panneerselvam et al., 2011). Solutions of Fe(II) and Fe(III) salts were mixed in a 1:2 molar proportion in HCl 1.0 mol/L medium. To this mixture, 0.7 mol/L NH<sub>4</sub>OH was slowly added and continuously stirred for 30 min. The synthesis of the nanocomposites SB-NP and MSB-NP was performed by adding sugarcane bagasse (SB) into the NP-containing suspension at 5:1 SB:NP proportion, under heating at 80 °C for 30 min. The resulting magnetic nanocomposites (SB-NP and SB-MNP) were washed with ethanol to remove remaining reagents and to improve the drying process of the materials. All reagents (FeCl<sub>3</sub>·6H<sub>2</sub>O, FeSO<sub>4</sub>·4H<sub>2</sub>O, HCl, NH<sub>4</sub>OH, and C<sub>2</sub>H<sub>6</sub>O) were P.A. grade (LabSynth, São Paulo, Brazil).

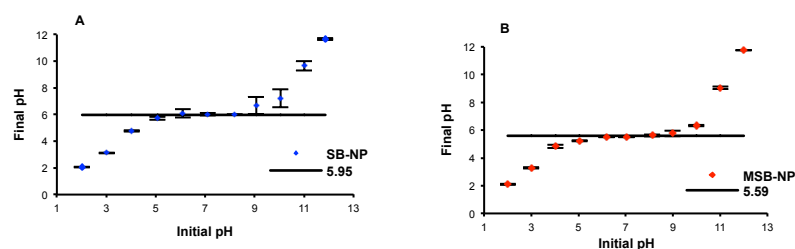
**Point of zero charge (pH<sub>PZC</sub>) and pH assessment:** The preliminary study of the surface characterization of the biomass was determined by the pH at the point of zero charge (pH<sub>PZC</sub>). This test was carried out by using 10 mL of 0.1 mol/L NaCl solution at initial pH values ranging from (2-12) adjusted with 0.1 mol/L HCl or NaOH. This saline solution containing 10 mg of *in natura* and acid washed nanomodified biomass was shaken for 24 h in a shaker incubator at 185 rpm. After determining the pH<sub>PZC</sub>, sorption of chromium (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, LabSynth, São Paulo, Brazil) at pH values higher than the pH<sub>PZC</sub> was evaluated by mixing 0.250 g of SB-NP or SB-MNP with 10 mL of 10 mg/L Cr(VI) solution. The mixtures were kept under stirring at 185 rpm for 10 min and the supernatants were analyzed by Flame Atomic Absorption Spectroscopy (FAAS, AAnalyst 400, PerkinElmer, USA) for Cr determination. These assays were performed in triplicate.

**Kinetics of sorption:** The kinetics of Cr(VI) sorption was assessed by mixing 0.750 g of SB-NP or SB-MNP and 30 mL of 10 mg/L Cr(VI) solution, at pH 1.0, under constant stirring. Aliquots of 5 mL were taken at intervals time of 10, 30, 60, 90, and 120 min and analyzed by FAAS for Cr determination. These assays were performed in triplicate.

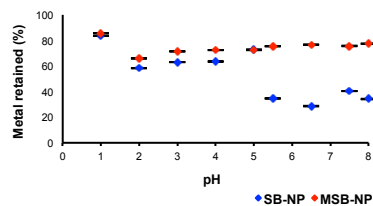
## Results and discussion

The pH<sub>PZC</sub> for SB-NP and SB-MNP was 5.95 and 5.59, respectively (Fig. 1). Below these pH values the surface of the biosorbents shows positive charges, which would favor chromium sorption mainly as HCrO<sub>4</sub><sup>-</sup> ions. At higher pH (above the pH<sub>pzc</sub>) the surface of the material is negatively charged, and is attracted by chromium as cations. The assessment of pH effect in the sorption process was carried out at 1-8 pH range and the results are shown in Fig. 2. The results show that sorption of Cr(VI) by SB-NP and SB-MNP was favorable for most of the pH values tested. On the other hands, above pH 5.0 chromium sorption by SB-NP was drastically reduced. At the lowest value, pH 1.0, both materials presented maximum chromium removal efficiency (approximately 84 and 86% for *in natura* and acid washed

biosorbent, respectively). This occurred due to the attraction of positively charged functional groups on the surface of the biosorbents for  $\text{HCrO}_4^-$  ions.

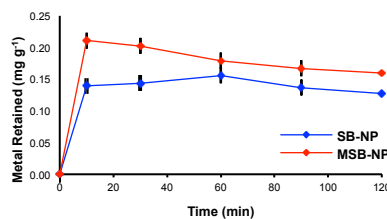


**Figure 1.** Point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of *in natura*, SB-NP (A) and acid washed, MSB-NP (B) nanommodified sugarcane bagasse. Biomass (10 mg) was mixed with 10 mL of 0.1 mol/L NaCl at 2-12 pH range.



**Figure 2.** Effect of pH increase on the removal capacity of Cr(VI) by *in natura* (SB-NP) and acid washed (MSB-NP) nanommodified sugarcane bagasse.  $n = 3$

Figure 3 shows the retention of Cr(VI) in function of the contact time of biosorbent and metal ion solution, at pH 1.0. The maximum chromium removal was reached in the first 10 and 60 min for MSB-NP and SB-NP, respectively.



**Figure 3.** Kinetics of Cr(VI) sorption by *in natura* (SB-NP) and acid washed (MSB-NP) nanommodified sugarcane bagasse; 30 mL of 10 mg/L Cr(VI) at pH 1.0, and 750 mg of biosorbent.  $n = 3$ .

### Conclusion

Nanommodified sugarcane bagasse showed a great potential to uptake Cr(VI) in aqueous medium. It was observed that Cr(VI) sorption by SB-NP was improved at lower pH, and at pH 1.0 both materials showed higher sorption efficiency. In addition, chemical modification increased the sorption efficiency, demonstrated by the removal of higher amounts of chromium by MSB-NP, at a lower contact time (the first 10 min). Therefore, SB-NP and SB-MNP seems to be an efficient, abundant, and low cost material for the removal of Cr(VI) from aqueous medium.

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### References

Congeevaram, S.; Dhanarani, S.; Park, J.; Dexilin, M.; Thamaraiselvi, K. Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. *J. Hazard. Mater.*, 146:270-277, 2007.

Debs, K. B.; Cardona, D. S.; Silva, H. D. T.; Nassar, N.; Carrilho, E. N. V. M.; Haddas, P. S.; Labuto, G. Oil spill cleanup employing magnetite nanoparticles and yeast-based magnetic bionanocomposite. *J. Environ. Manage.*, 230:405-412, 2019.

Jobby, R.; Jha, P.; Kumar, A.; Desai, Y. N. Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: A comprehensive review. *Chemosphere*, 207:255-266, 2018.

Milani, P. A.; Debs, K. B.; Labuto, G.; Carrilho, E. N. V. M. Agricultural solid waste for sorption of metal ions: part I – characterization and use of lettuce roots and sugarcane bagasse for Cu(II), Fe(II), Zn(II), and Mn(II) sorption from aqueous medium. *Environ. Sci. Pollut. Res.*, 25:35895–35905, 2018.

Panneerselvam, P.; Morad, N.; Tan, K. Magnetic nanoparticle ( $\text{Fe}_3\text{O}_4$ ) impregnated onto tea waste for the removal of nickel(II) from aqueous solution. *J. Hazard. Mater.*, 186:160-168, 2011.