Sorption of Cu(II), Fe(II), Zn(II) and Mn(II) from aqueous medium using lettuce roots and sugarcane bagasse

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The impact caused by human activities in the environment is not a recent phenomenon. Due to the demographic and industrial growth, there is the generation of toxic wastes, which are related to the consumption and exploitation of raw materials (Santos *et al*, 2011). Biosorption stands out as a water treatment, using widely available biomasses, especially residues such as sugarcane bagasse and lettuce roots, which are daily discarded in tons in Brazil. It is an efficient process due to the high rate of renewal in nature, its low costs, and the high capacity of potentially toxic metals removal from aqueous solution and, consequently, great possibility of the recovery of the contaminants through desorption (Labuto and Carrilho, 2016). Most potentially toxic metal ions are highly dangerous to living things, and can contribute to environmental destruction when discharged without previous treatment.

The biomasses used in this research, sugarcane bagasse and lettuce roots, present cellulose, hemicellulose and lignin in their composition, which are able to adsorb metal ions by their functional groups such as carboxylic acids, alcohols, amines, and others (Verma *et al,* 2012). This work aimed to evaluate the efficiency of these biomasses in the sorption of Cu(II), Zn(II), Fe(II), and Mn(II) from multielement solution, in order to be used in waste water decontamination.

The biomasses of sugarcane bagasse and lettuce roots (1.5g) were washed with distilled and deionized water and dried in oven at 50ºC for 24 hours. Dried samples were ground and used *in natura* or after being washed with 240mL of HNO_3 1mol L^{-1} for chemical modification of the biomass. After centrifugation at 3500 rpm for 15 min, the supernatants were discarded and the biosorbents conditioned with potassium acetate buffer at pH 5.5 (Carrilho *et al* 2003). After treatment, the biomasses were placed in contact with a multielement solution containing 10mg L^{-1} of Fe (II), Cu (II), Mn (II), and Zn (II), at pH 5.5. The mixture was stirred manually for 1 min and then centrifuged at 10,000 rpm for 25 min. This procedure was repeated 6 times, all performed in triplicate, to evaluate the sorption of these metal ions by the biomasses, which were quantified by atomic absorption spectrometry (AAnalyst 400, PerkinElmer).

The results obtained in the sorption tests of 10mg L^{-1} Cu (II), Fe (II), Zn (II) and Mn (II) in multielement solutions are presented in Figures 1 and 2 for *in natura* and modified biomasses, respectively, and the percentage of metal uptake is compared. For Cu (II) sorption, it can be observed that there was an efficient accumulation of this ion in the two modified biomasses, in which after the addition of aliquot 6 of the multielement solution, the sorption remained around 82%, with variability less than 1% among the replicates.

The sorption of Cu(II) by *in natura* and modified lettuce roots (Figures 1A and 2A) showed similar retention of Cu (II), around 82%. Same results were found for modified sugarcane bagasse (Figure 2B). Eventhough, modification of the biomass is known to improve sorption efficiency (Moreira *et al*, 2011; Santos *et al*, 2011), Cu (II) sorption was efficient by both treated or *in natura* lettuce roots. On the other, Cu (II) uptake by *in natura* sugarcane bagasse (Figure 1B) was drastically decreased, indicating the importance of acid treatment of this biomass. Regarding to Fe (II), modified lettuce roots (Figure 2A) and sugarcane bagasse (Figure 2B) showed a total retention around 77% and 55%, respectively. As for *in natura* lettuce roots (Figure 1A), great retention efficiency was achieved, reaching up to 100%. As for *in natura* sugarcane bagasse, lower retention was observed for Fe(II), around 40%. The adsorption of Zn (II) by lettuce roots, as observed in Figures 1A-2A, shows excellent retention (80-100%), while lower efficiency was found for bagasse biomass. At last, the adsorption of Mn (II) was very efficient in the assays with lettuce roots (Figures 1A-2A) and modified sugarcane bagasse (Figure 2B), reaching retention of almost 100%. Among the other ions studied, Mn (II) was more efficiently sorbed by the biomasses. Compared to these adsorption results, Mn (II) retention by *in natura* sugarcane bagasse was extremely low, around 5%.

Since the results of modified biomasses were more satisfatory, the sorption kinetic experiments were carried out under this condition. Figure 3 shows the accumulation of Cu (II), Fe (II), Mn (II), and Zn (II) in function of time. Lettuce roots showed great retention in the first 5 minutes of contact time, while bagasse was not efficient for most of the metal ions, except for Cu(II), which showed similar retention efficency as for the roots.

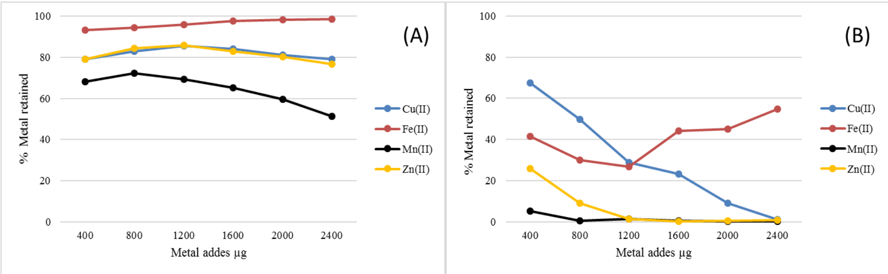

Figure 1. Sorption curves of Cu, Fe, Mn and Zn in (A) *in natura* lettuce roots and (B) *in natura* sugarcane. The concentration of each aliquot (40 mL) of the metals was 10mg L^{-1} (pH 5.5).

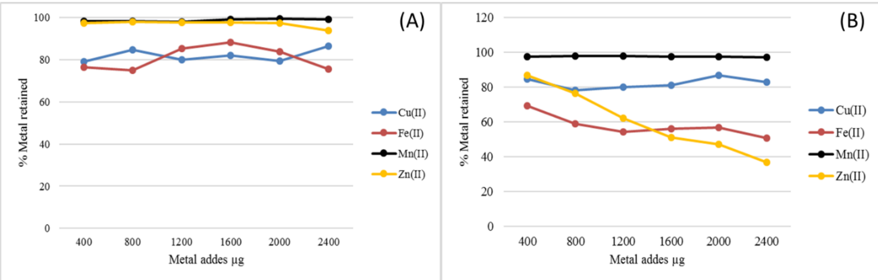

Figure 2. Sorption curves of Cu, Fe, Mn and Zn in (A) modified lettuce root and (B) modified sugarcane bagasse. The concentration of the aliquots (40 mL) of the metals was 10mg L^{-1} (pH 5.5).

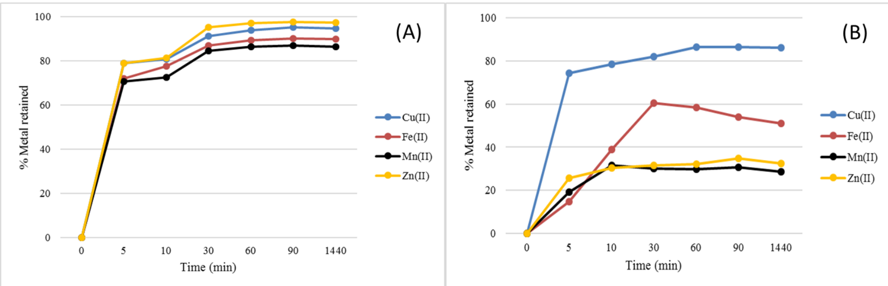

Figure 3. Sorption kinetics of the metals by modified lettuce root (A) and sugarcane bagasse (B). The concentration of the volume (500 mL) of the metals was from 10mg L^{-1} (pH 5.5) to 1.5g of biomass.

According to these results, *in natura* and modified lettuce roots as well as modified sugarcane bagasse showed great potential in the sorption of Cu (II), Fe (II), Mn (II), and Zn (II) from aqueous solutions. In general, the chemically modified biomasses tested presented higher affinity for most of the metal ions (except for Zn). On the other hands *in natura* lettuce roots retention was as efficient as the modified roots, indicating that this biomass is capable of removing metal ions from contaminated water by the biosorption process with no previous treatment. Thus, these are promising biosorbents, which also present low costs and easy accessibility.

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