

Agricultural solid waste for sorption of metal ions, Part II: Competitive assessment in lake water

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Abstract

Sugarcane bagasse and hydroponic lettuce roots were used as biosorbents for removal of Cu(II), Fe(II), Mn(II), and Zn(II) from multielement solutions, as well as from lake water, at pH 5.5, in batch processes. These biomasses were studied *in natura* (lettuce roots, NLR, and sugarcane bagasse, NSB) and chemically modified with HNO₃ (lettuce roots, MLR, and sugarcane bagasse, MSB). The results showed that higher adsorption efficiency was achieved with the modified biomass, with the exception of lettuce roots, which also presented similar efficiency when used *in natura*. The maximum adsorption capacities (q_{max}) in multielement solution for Cu(II), Fe(II), Mn(II), and Zn(II) were 35.86, 31.42, 3.33, and 24.07 mg/g for NLR, 25.36, 27.95, 14.06, and 6.43 mg/g for MLR, 0.92, 3.94, 0.03, and 0.18 mg/g for NSB, and 54.11, 6.52, 16.7, and 1.26 mg/g for MSB, respectively. In kinetic studies with modified biomasses, sorption was achieved in the first 5 min and reached equilibrium in 30 min. Modified biomasses were used in the adsorption of Cu(II), Fe(II), Mn(II), and Zn(II) in lake water, in which retention of 24.31, 14.50, 8.03, and 8.21 mg/g by MLR, and 13.15, 10.50, 6.10, and 5.14 mg/g by MSB was found, respectively. These biosorbents are promising and low costs agricultural residues, and lettuce roots showed great potential even in its *in natura* form, avoiding the costs with reagents for chemical modification. The ability of these biomasses to efficiently adsorb metal ions in solution indicates that these materials can be used to recover and cleanup contaminated water.

Keywords: sugarcane bagasse, lettuce roots, biosorption, isotherms, matrix influences, water decontamination

1. Introduction

Water contamination by inorganic and organic species is a global concern and strategies to proceed the efficient and inexpensive decontamination is an important research subject [1]. Methods employing biosorbents have been reported as an efficient option to remove metals from aqueous medium. The use of agricultural wastes can be an alternative to boost up bioeconomy since these materials are cost-effective and present a high capacity for the removal of potentially toxic substances [2]. Vegetal biomasses present structures such as cellulose, hemicellulose, and lignin, which contain functional groups such as carboxylic acids, alcohols, and amines with high affinity for metal ions [3].

On the other hand, water matrices can present constituents that can favor or difficult the interaction between such biosorbents and the substance of interest, such as organic and inorganic anionic and cationic species, which can compete by the sorption sites, form complexes, or precipitate with the analyte. These species in the water matrix may also change the chemical form of the ion of interest, making it unavailable for sorption, or can modify the pH of the medium affecting the availability of the sorption sites [4,5]. However, the majority of the approaches report sorption studies in synthetic samples prepared with distilled water.

In this work, we evaluated the competitive sorption among the metal ions, Cu(II), Fe(II), Mn(II), and Zn(II) by *in natura* (NSB) and modified (MSB) sugarcane bagasse, and *in natura* (NLR) and modified (MLR) hydroponic lettuce roots. Competitive isotherms and kinetics were obtained to describe the behavior of sorption phenomena. In addition, the most efficient adsorbents were used to evaluate water matrix influences on the metal ions removed.

2. Methods

2.1. Materials

All glassware and plasticware were washed with neutral detergent, decontaminated with HNO₃ 1% (v/v), and rinsed with distilled and deionized H₂O. All solutions were prepared using purified water from a Direct-Q 3 System (Merck Millipore – Germany) at 25 °C and 18.2 MΩ.cm resistivity. Nitric acid solutions used for biomasses leaching were prepared from concentrated HNO₃ 65% (m/v). Buffer solution 0.005 mol/L KCH₃COO/CH₃COOH, at pH 5,5, prepared from 100% glacial acetic acid and potassium acetate was used to condition the biomasses prior metal sorption and also to prepare Cu(II), Fe(II), Mn(II), and Zn(II) solutions. All chemicals used were of analytical grade. Stock solutions of metal ions used to prepare the work solutions and analytical curves were prepared by appropriate dilutions of their respective salts CuSO₄.5H₂O, FeSO₄.7H₂O, MnSO₄.H₂O, and ZnSO₄.7H₂O (purity higher than 99%, Merck).

2.2. Preparation and elemental analysis of biomasses and lake water

The biomasses of sugarcane bagasse (NSB) and lettuce roots (NLR) (1.5g), collected from an university farm in the southeast of Brazil, were washed with distilled and deionized water, and dried at 50 °C for 24 h. These biomasses were then ground in analytical mill (IKA, Staufen-Germany) to particle sizes from 0.5 to 1 mm, and used *in natura* or after being leached with 200 mL of HNO₃ 1 mol/L for chemical modification. After centrifugation at 10,000 rpm for 5 min, the supernatants were discarded and

the biosorbents were conditioned with 200 mL of 0.005 mol/L $\text{KCH}_3\text{COO}/\text{CH}_3\text{COOH}$ buffer at pH 5.5 [6]. The biomasses were oven dried at 50 °C for 3 h and stored in decontaminated vials.

In order to determine elemental contents in the biomasses used, around 250 mg of *in natura* (NLR and NSB) and modified lettuce roots (MLR) and sugarcane bagasse (MSB) were weighted and digested in a closed microwave oven (Multiwave, Anton Paar, Germany) with 3 mL HNO_3 and 1 mL H_2O_2 33% v/v [7]. The heating program was performed in 3 steps: A) Power of 250W (ramp, 5 min and slope, 3 min); B) 650W (ramp 7 min and slope, 10 min); C) followed by cooling for 20 min. After digestion, samples and blank solutions were diluted to 50 ml in volumetric flasks for elemental analysis.

Lake water was sampled and brought to the lab for homogenization and vacuum filtration. Temperature (28 °C) and pH (6.4) were measured and then, the samples were stored under refrigeration.

The elemental determination from the biomasses digests and from the lake water samples was carried out by inductively couple plasma optical emission spectrometry (ICP OES), employing a concentric nebulizer, using the following parameters: power supply (1.10 kW), flow rates for plasma gas (15.0 L/min), auxiliary gas (1.5 L/min), and nebulizer gas (0.65 L/min), observation height (8 mm), sampling rate (1 mL/min). The wavelengths selected for all elements investigated were: Ca 393.366, Cu 324.754, Fe 238.204, K 766.490, Mg 280.271, Mn 259.372, Na 589.592, P 213.617, S 180.669, and Zn 213.857 nm. The analytical curves for all species were prepared from either 0.1 – 5.0 mg/L or 10 – 100 mg/L.

2.3. *Competitive sorption isotherms studies employing standard solutions*

Around 1.5 g of NLR, MLR, NSB or MSB were weighted and suspended in 40 mL of solutions containing 10 mg/L of each studied metal ions, namely Cu(II), Fe(II), Mn(II), and Zn(II) in $\text{KCH}_3\text{COO}/\text{CH}_3\text{COOH}$ buffer (0.005 mol/L at pH 5.5). The suspensions were stirred for 1 min at 400 rpm and 25 °C, and then centrifuged for 25 min at 10,000 rpm. After this process, the supernatants were separated for determination of the remaining metal in solution and a new aliquot of 40 mL of the multielement solution was added to the same biomasses. This procedure was repeated six times, originating six aliquots of sequential additions of the multielement solution over a same mass of biosorbent. All procedures were made in triplicates.

2.4. *Kinetics of sorption employing multielemental standard solution*

The adsorption kinetics of Cu(II), Fe(II), Mn(II) and Zn(II), in a multielement solution, by MSB and MLR were based on the approaches carried out by [8]. Around 1.5 g of MSB or MLR were suspended in 500 mL of 10 mg/L multielement solution containing Cu(II), Fe(II), Mn(II) and Zn(II) buffered with 0.005 mol/L $\text{KCH}_3\text{COO}/\text{CH}_3\text{COOH}$ (pH 5.5) were placed in an Erlenmeyer flask under stirring. Aliquots of 20 mL were collected at 5, 10, 30, 60, 90, and 1440 min, and filtered for further element determination. This experiment was performed in triplicate.

2.5. *Influence of matrix on total metals adsorption employing multielemental solutions*

The competitive studies were conducted weighting around 0.5 g of MLR or MSB, which were suspended in 1 L of two different mediums: A) standard solution containing 10 mg/L of each studied

metal ion, Cu(II), Fe(II), Mn(II), and Zn(II) at pH 5.5 in 0.005 mol/L KCH₃COO/CH₃COOH at pH 5.5 and, B) lake water previously conditioned at pH 5.5 with HNO₃ 0.1 mol/L and containing known quantities of Cu(II), Fe(II), Mn(II), and Zn(II), previously determined by ICP OES.

The suspensions were kept under stirring at 400 rpm and 25 °C and aliquots of 20 mL were taken at 10, 30, 60, 90, and 1440 min. The aliquots were filtered and analyzed by ICP OES to determine the remaining quantities of metal ions in solution. All experiment was carried out in triplicate.

3. Results and discussion

3.1. Competitive sorption isotherms studies employing standard solutions

The behavior of the experimental data obtained from isotherms was evaluated employing the Langmuir multielemental models [9] and the respective theoretical parameters are presented in Table 1. Langmuir model assumes that sorption of the analyte occurs at defined and localized sites, each sorption site may retain only one molecule or ion adsorbed; All active sites of the biosorbent have the same sorption energy and are homogeneously distributed; The sorption at one site does not affect the energy or the sorption availability in a neighboring site; And the analyte activity is directly proportional to its concentration, not having interaction with the adsorbed analytes [9, 10]. When the system has more than one analyte the Langmuir equation can be extended, and written as in equation 1, where q_{max} = experimental specie removed (mg/g) in multielement experiment; q_i , b_i , and b_k are the Langmuir constants obtained from monoelement studies for the specie i , and for the concomitant specie k present in solution, C_i is the equilibrium concentration of specie i in the multielement medium and C_k ($k = 1, 2, \dots; N$ is the number of components) is the concentration of each concomitant specie present in solution in equilibrium [11,12]. The individual constants were obtained from sorption studies employing monoelement solutions.

$$q_{max} = \frac{q_i^0 b_i C_i}{1 + \sum_{k=1}^N b_k C_k} \quad (\text{Equation 1})$$

In Table 1, it is possible to observe that Langmuir isotherm presented a good adjustment (r^2) and small values of nonlinear Chi-square test (χ^2) for most of the metal ions sorption by NSB and MSB, regardless the modifying treatment (italic values). The r^2 values were obtained plotting experimental metal ion removal (q_{exp}) \times predicted metal ion removal (q_{calc}) by model for each experimental C_i and performing a linear fitting. Nonlinear chi-square test has been employed as a statistical tool for the best fit of an adsorption system and small values indicates a huge similarity between the experimental data (q_{calc}) and predict values by the employed model (q_{calc}) [13]. Analyzing both, r^2 and χ^2 , it is possible to present a better vision about the model adjustment to the experimental data and have a higher confidence in the isotherms parameters provided by the employed model.

For NSB and MSB, good fitting of data was not obtained for Fe(II) and Mn(II), the similar behavior for both materials denotes that the competitive Langmuir model does not describe the experimental data for these metal ions in these employed biosorbents. It is important to emphasize that Cu(II) and Fe(II) can complex with H₃CCOO⁻ ions producing CuCH₃COO_(aq) (log K_f = -4.4274), CuCH₃COO⁺ (-log K_f = 2.5252) and FeCH₃COO²⁺ (-log K_f = 3.88) [14]. This fact can promote a

competition between the equilibrium of complex formation and the metal ion uptake on the biosorbent surfaces sorption sites, or can improve adsorption as long as the complex formed shows affinity for those [15].

Table 1. Error analysis and competitive Langmuir calculated isotherm parameter for Cu (II), Fe(II), Zn(II), and Mn (II) sorption on NSB, MSB, NLR and MLR employing a multielemental standard solution containing 10 mg/L of each studied metal ion in 0.005 mol/L KCH₃COO/CH₃COOH buffer solution pH 5.5. Degrees of freedom N = 5, $\alpha = 0.10$.

| Parameters | NSB | | | | MSB | | | |
|-------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| | Cu(II) | Fe(II) | Mn(II) | Zn(II) | Cu(II) | Fe(II) | Mn(II) | Zn(II) |
| q_{\max} (mg/g) | 0.92 | 3.94 | 0.03 | 0.18 | 54.11 | 6.52 | 16.7 | 1.26 |
| b (L/mg) | 0.1414 | 0.02 | 0.16 | 0.3271 | 0.0022 | 0.009 | 0.075 | 0.153 |
| χ^2 | 0.0024 | 0.400 | 0.0001 | 0.0002 | 0.0100 | 0.0030 | 0.0200 | 0.0090 |
| $r^{2(*)}$ | 0.9964 | 0.1485 | 0.9999 | 0.9987 | 0.9895 | 0.9982 | 0.9973 | 0.9921 |
| Parameters | NLR | | | | MLR | | | |
| | Cu(II) | Fe(II) | Mn(II) | Zn(II) | Cu(II) | Fe(II) | Mn(II) | Zn(II) |
| q_{\max} (mg/g) | 35.86 | 31.42 | 3.33 | 24.07 | 25.36 | 27.95 | 14.06 | 6.43 |
| b (L/mg) | 0.0194 | 0.0801 | 0.1111 | 0.0063 | 0.0047 | 0.0041 | 0.1390 | 0.2060 |
| χ^2 | 0.60 | 1.37 | 0.65 | 0.03 | 0.01 | 0.06 | 0.15 | 0.03 |
| $r^{2(*)}$ | 0.9323 | 0.0242 | 0.9737 | 0.9953 | 0.9959 | 0.9789 | 0.9354 | 0.9998 |

(*) corresponds to the linear fitting by plotting $q_{\text{exp}} \times q_{\text{calc}}$ obtained from the model adjustment.

3.2. Kinetics of sorption employing multielement standard solution

The kinetic models are represented by mathematical equations used to describe the adsorption profile of solutes by solids, which allow knowing more about the adsorption process. Table 2 presents the adjustment equations for pseudo 1st order and pseudo 2nd order kinetics studies [16]. For all metal ions and materials, the kinetics studies revealed that the pseudo 2nd order equation provided the best adjustments of the experimental data being the most adequate to represent the studied sorption phenomenon. This means that the amount of adsorbed ions at equilibrium is a function of temperature, initial concentration of the metal ions of the biosorbent, and the nature of the interaction between them. Also there is more than one type of sorption site available for the removal of the studied chemical species [17].

Table 2. Equations and respective correlation coefficients for kinetics sorption of multielemental standard solution studies at 25 °C. For pseudo 1st order the slope = k_1 (min^{-1}). For pseudo 2nd order the angular parameter = k_2 ($\text{g mg}^{-1} \text{min}^{-1}$), $n = 3$.

| | MSB | | MLR | |
|---------------|---|--|--|--|
| | pseudo 1 st order | pseudo 2 nd order | pseudo 1 st order | pseudo 2 nd order |
| Cu(II) | $y = -1.6132x + 2.4689$ $r^2 = 0.8936$ $k_1 = 0.16$ | $y = 0.1426x + 0.1796$ $r^2 = 0.9998$ $k_2 = 1.56$ | $y = -0.0502x + 0.5011$ $r^2 = 0.9850$ $k_1 = 0.006$ | $y = 0.1292x + 0.2108$ $r^2 = 0.9999$ $k_1 = 0.98$ |
| Fe(II) | $y = -2.6053x + 5.0601$ $r^2 = 0.8227$ $k_1 = 0.08$ | $y = 0.1814x + 1.5368$ $r^2 = 0.9971$ $k_2 = 1.02$ | $y = -0.0774x + 0.8406$ $r^2 = 0.9999$ $k_1 = 0.60$ | $y = 0.1219x + 0.1977$ $r^2 = 1.000$ $k_2 = 0.41$ |
| Zn(II) | $y = -0.7672x - 0.02$ $r^2 = 0.9703$ $k_1 = 0.07$ | $y = 0.3922x + 0.9451$ $r^2 = 0.9975$ $k_2 = 1.51$ | $y = -0.0917x + 0.8823$ $r^2 = 0.9965$ $k_1 = 0.01$ | $y = 0.1374x + 0.2284$ $r^2 = 0.9999$ $k_2 = 0.83$ |
| Mn(II) | $y = 0.0279x - 0.1184$ $r^2 = 0.5333$ $k_1 = 0.32$ | $y = 0.4092x + 0.3917$ $r^2 = 0.9985$ $k_2 = 1.41$ | $y = -0.9895x + 1.5884$ $r^2 = 0.9485$ $k_1 = 0.005$ | $y = 0.1409x + 0.2304$ $r^2 = 0.9999$ $k_2 = 1.12$ |

According to Figure 1, it is possible to verify that the maximum efficiency of sorption was achieved in the first 5 min and the equilibrium was completed at 90 and 60 min for MSB and MLR, respectively. The fast adsorption of metal ions by biological materials, specially roots and sugar cane bagasse, have been reported by other authors as advantage of the employment of this kind of material for water treatment [15, 18].

The choice of a biosorbent depends not only on its adsorption capacity but also on adsorption kinetics, since it is an important factor in the rapid removal of pollutants in wastewater, since most treatments are carried out in flow systems [19].

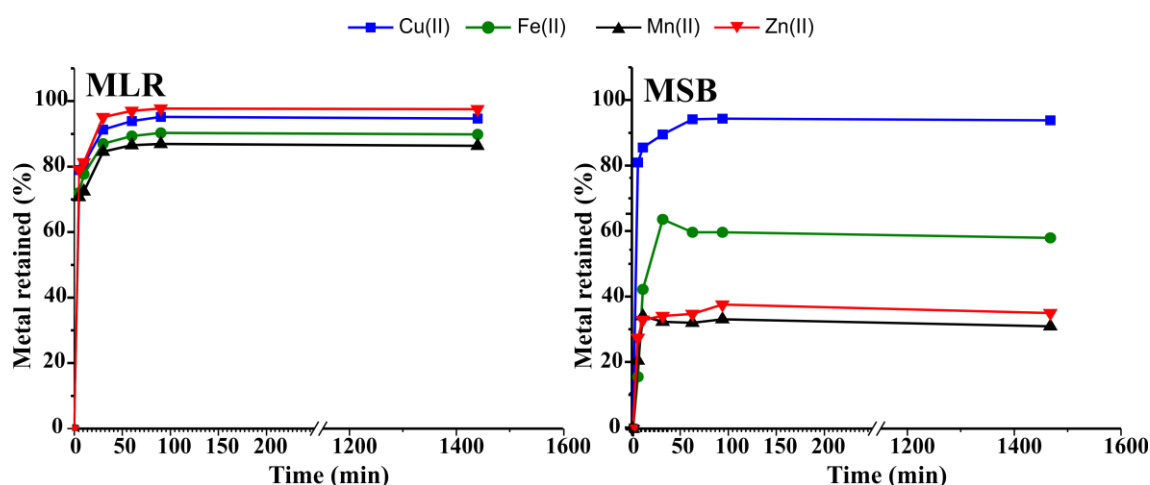


Figure 1. Adsorption kinetics of Cu, Fe, Mn, and Zn in modified lettuce roots (MLR) and modified sugarcane bagasse (MSB). The metals concentration was 10 mg/L in 500 mL (pH 5.5), $n = 3$.

3.3. Influence of matrix on total metals adsorption employing multielemental solutions

Real samples of water present a diversity of organic and inorganic components that can interfere in sorption processes, both by the competition of such components by the sorption sites and by the species of interest through association, complexation, or promotion of the precipitation of species [4]. Changes in the chemical form of the analyte or the pH of the medium compared to the studies performed with standard solutions can also lead to different behaviors when a study is conducted using synthetic and real samples [5].

In the case of lake water used, the following concentrations of metal ions studied and other species generally present in high concentrations in natural waters were found: 0.01 ± 0.003 mg/L (Cu), 1.08 ± 0.014 mg/L (Fe), 0.004 ± 0.001 mg/L (Zn), 0.02 ± 0.003 mg/L (Mn), 0.01 ± 0.00 mg/L (P), 2.54 ± 0.19 mg/L (K), 0.84 ± 0.12 mg/L (S), 2.07 ± 0.18 mg/L (Ca), 1.31 ± 0.14 mg/L (Mg).

Table 3 presents the removal of Cu(II), Fe(II), Zn(II), and Mn(II) using MSB and MLR in known concentration solutions of metal ions prepared with distilled deionized water and in the lake water. Modified lettuce roots showed higher metal ion removal than MSB, with greater affinity for Cu(II), Fe(II), and Mn(II). These results, in addition to the low cost of the biomasses employed, leads to a safe and efficient use of these materials for metal ion uptake from water for human consumption since chronic exposure to Cu and Mn has been associated to Alzheimer's disease, early childhood liver cirrhosis, brain inflammation, intellectual impairment in children, as well as motor neuron disease. The permitted limits in established for drinking water are 1.0 mg/L (Cu) and 0.05 mg/L (Mn) [20-24].

Probably, the root structure that makes up the MLR presents a higher availability of sorption sites able to retain metal ions such as macro and micronutrients necessary for the development of the plant [25]. On the other hand, the sugarcane bagasse is basically formed from the stem, a segmented organ constituted by apical bud, axillary buds, nodes and internodes, which is responsible for conducting the crude sap to the foliar part, where it will be elaborated and redistributed to the plant [26].

It can also be observed that, in general, for MSB, there were gains in the removal of all metal ions studied when the studies were conducted with lake water. The same behavior can be observed for Cu(II) and Fe(II) sorption of lake water using MLR. Possibly, the absence of acetate ions complexing with Cu(II) and Fe(II) allowed their more efficient removal from samples of lake water [15].

Table 3. The effect of different water matrix (Standard Solution or Lake water) on metal ions sorption by MSB (Modifiend Sugarcane Bagasse) and MLR (modified Lettuce Roots). (n=3).

| Metal ion | MSB | | MLR | |
|---------------|-----------------------------|-------------------------|-----------------------------|-------------------------|
| | Standard solution (mg/g) | Lake water (mg/g) | Standard solution (mg/g) | Lake water (mg/g) |
| Cu(II) | 5.00 ± 0.2 (22.9%) | 13.15 ± 0.05 (42.9%) | 15.72 ± 0.07 (71.8%) | 24.31 ± 0.02 (79.2%) |
| Fe(II) | 7.19 ± 0.32 (33.1%) | 10.50 ± 0.01 (50.5%) | 14.17 ± 0.21 (65.2%) | 14.50 ± 0.05 (69.8%) |
| Mn(II) | 5.01 ± 0.09 (11.3%) | 6.10 ± 0.08 (23.1%) | 2.50 ± 0.35 (22.6%) | 8.03 ± 0.16 (31.3%) |
| Zn(II) | 4.80 ± 0.14 (21.8%) | 5.14 ± 0.25 (20.3%) | 10.08 ± 0.09 (45.8%) | 8.21 ± 0.25 (32.5%) |

4. Conclusions

The investigated biomasses, lettuce roots and sugarcane bagasse, show high adsorption potential of Cu(II), Fe(II), Mn(II), and Zn(II) from aqueous medium as well as from lake water. This suggests that these biosorbents can efficiently remove metal ions from contaminated waters by a biosorption process.

The chemical modification of the biomass was efficient to increase the maximum capacity of multielement adsorption of all the elements for MSB, however for MLR, there was an increase of the adsorption capacity of Mn(II). Therefore, the modification promoted a significant increase of the sorption efficiency of the sugarcane bagasse, unlike that of the lettuce roots, which, even without the treatment, showed an excellent adsorption capacity.

A better adsorption efficiency for the removal of Cu(II), Fe(II), Mn(II), and Zn(II) was obtained in lake water than in a standard buffered model.

The ability of these biomasses to efficiently adsorb metal ions in solution indicates that these materials can be used to recover and cleanup water contaminated with them. In the tests developed, 1.5 g of biomass was able to remove contents above the limits allowed by EPA. In this way, these biosorbents are promising and, in addition to low maintenance costs of agricultural residues.

On an industrial scale, we believe that the biomass from lettuce roots is a more promising biosorbent due to their great potential in the *in natura* form, avoiding the costs with reagents for chemical modification.

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