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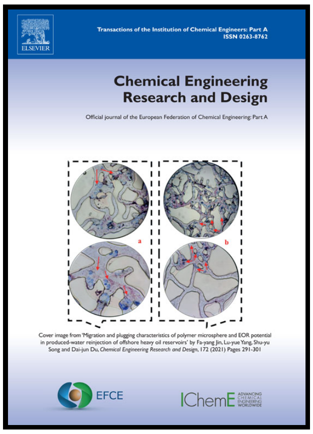

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PII: S0263-8762(23)00159-4

DOI: https://doi.org/10.1016/j.cherd.2023.03.013

Reference: CHERD5499

To appear in: *Chemical Engineering Research and Design*

Received date: 28 December 2022
Revised date: 3 March 2023
Accepted date: 6 March 2023

Sorption as a pre-concentration step for metal ions recovery in multi-elemental systems

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Abstract

Sorption is here proposed as a promising approach for metal pre-concentration and recovery from wastewater. A study was carried out on the simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} on macroalgae, microalgae and cyanobacteria. The effect of pH, initial metal concentration, metal competition and time of contact on metal sorption were evaluated. Metal competition hampers sorption at the studied metal concentration ranges. The metal counterion (sulfate, chloride or acetate) did not influence metal sorption. The brown algae *Sargassum sp*. was the most promising sorbent (q_{max} = 0.66 ± 0.03 mmol·g^{-1}), followed by the microalgae *Phaeodactylum tricornutum* (q_{max} = 0.36 ± 0.02 mmol·g^{-1}) and the cyanobacteria *Spirulina sp.* (q_{max} = 0.216 ± 0.007 mmol·g^{-1}). All biomass samples showed preferential sorption of Cu^{2+}. The experimental kinetic data were well described by Ho's model, showing chemisorption to be the main sorption mechanism. Ion-exchange of Ca^{2+}, K^{+} and H^{+} also played a significant role in metal sorption. After sorption, metal recovery was achieved resorting to incineration. The metal content of the obtained biochar was 4639-fold higher when compared to the initial aqueous solution concentration.

Keywords: Macroalgae, microalgae, cyanobacteria, sorption mechanism, incineration, biochar.

Introduction

Increased investment in digitalization, renewable energies and low-carbon technologies is fostering the demand for metal commodities and boosting metal scarcity in spite of the ongoing extensive metal ore exploration.[1] Within the circular economy framework, secondary metal sources can be an integrative solution for the low concentration and limited ore supply.[2] Electrical and electronic waste, conventional scrap and wastewater are some of the available secondary metal sources.[3–5] Concerning wastewaters, metal concentration may be challenging as large volumes of effluents are produced. For this reason, a pre-concentration step may be required to develop a cost-effective process. Among the possible methodologies for metal recovery from wastewaters, (bio)sorption has been proposed as a promising candidate for simultaneous metal pre-concentration and recovery.[6–8]

Biosorption is a passive process involving the interaction of metal ions with the biomass surface.[9] This process can occur in living and non-living biomass. The use of non-living biomass is convenient since it requires no substrate, copes with wide pH and concentration ranges, has rapid kinetics, enables easier metal recovery compared to living biomass and is cost-effective.[10] There is also a wide array of non-living biomass suitable for metal sorption, such as biochar,[11,12] paper by-products, wheat, fruit and agricultural wastes,[13–15] shells[16] and leaves.[17] Macroalgae,[18,19] microalgae[20] and cyanobacteria[21] are also popular metal biosorbents. This is mainly due to their availability and cost-effective metal removal.[22] Metal sorption efficiency will depend on the biomass functional groups and their bioavailability to interact with metals. Carboxylic groups were identified as the most relevant functional groups for metal sorption.[22] Hydroxyl, phosphoryl, sulfonate and amino groups may also be involved in metal sorption, but to a lower degree than carboxylic groups. Despite the importance of carboxylic groups for metal sorption, the oxygen content of algae and cyanobacteria does not seem to correlate with better metal sorption efficiencies. In the case of divalent metal ions (M^{2+}), oxygenated groups must be adequately spaced to enable the formation of a bidentate complex.[22]

Metal sorption may occur through different pathways, including complexation, chemisorption, physisorption, microprecipitation and ion-exchange.[23] Multiple metal sorption mechanisms can occur within the same system.[24] Several parameters, such as temperature, pH, initial metal concentration, biomass concentration, ion competition, contact time and biomass nature can influence the efficiency of metal sorption.[25–27] The temperature effect is still ambiguous, with reports showing conflicting results, and most studies being performed at room temperature.[28–32] Among the mentioned parameters, pH is deemed to have a key role in metal sorption. The pH will directly affect the protonation of the binding sites of the sorbent.[20] Lower pH values result in a positive surface charge, suitable for the sorption of anionic species. Yet, pH values above 7 tend to prompt the formation of metal hydroxides, leading to their precipitation and limiting their availability for sorption. Finding a suitable metal:sorbent ratio is of utmost importance concerning metal pre-concentration. If this ratio is too low, many binding sites will be unoccupied, failing to achieve optimal pre-concentration. In contrast, an unreasonably high ratio can hinder mass transfer and compromise the efficiency of the process. Despite its relevance, metal ion competition is often disregarded in sorption studies with more simplistic mono-element assays being conducted.[18,19,33,34] Studies based in single metal solution are inadequate portraits of wastewater, preventing the transition of this process to real matrices.[35]

Sorption is usually employed for water decontamination, with no emphasis on metal recovery. Since the scope is mainly environmental, metals are perceived as contaminants instead of potential valuable elements.[19,20,36] These studies focus on achieving high metal removal percentages, usually at the expense of larger solid:liquid ratios. This affords complete metal removal but poor metal pre-concentration onto the biomass surface. It is also common for sorption studies to overlook the metal recovery prospect once adsorbed onto the biomass. When considered, metal recovery is usually accomplished by applying eluents such as acid or alkaline solutions.[37] This will dilute metals again, overriding the potential of biomass as metal pre-concentrators from wastewater. It also promotes the formation of biomass-derived and hazardous solvent wastes requiring appropriate disposal. Biomass incineration may overturn this problem.[38] Incineration spares the use of additional solvents, minimizing the waste volume and further promoting metal concentration.[39] Moreover, decreasing the generated biomass waste volume reduces the transport and treatment costs of the metal-loaded biomass. This methodology has the drawback of being energy-intensive. Yet, coupling incineration with energy recovery strategies enables to decrease its environmental impact.[39]

Our group previously reported a biomass screening for metal sorption in multi-metal Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} solutions.[40] The most promising non-living macroalga (*Sargassum sp.*), microalga (*Phaeodactylum tricornutum*) and cyanobacterium (*Spirulina sp.*) were herein selected for an in-depth sorption study, focused on metal recovery. The influence of pH, metal concentration in mono- and multi-elemental systems, metal counterion and sorption time was evaluated and optimized. To better understand the sorption mechanism, ion-exchange was assessed in the kinetic assay by tracking the release of Ca^{2+}, K^+ and H^+ from the biomass over time. The sorption mechanism was further explored by fitting Lagergren's pseudo-first order model[41] and Ho's pseudo-second order model[42] to the obtained data. The most promising biomass was incinerated post-sorption for metal recovery. The biomass char composition was determined using total reflection X-ray fluorescence spectrometer (TXRF).

Materials and Methods

Biomass

Metal sorption by the brown macroalga *Sargassum sp*., the microalga *Phaeodactylum tricornutum* and the cyanobacterium *Spirulina sp*. was optimized by studying the influence of pH, initial metal concentration, counterion and contact time. *Sargassum sp*. was kindly supplied by ALGAplus Lda. This macroalga was received dry and frozen with liquid nitrogen followed by its immediate griding in a coffee grinder. The obtained particles were mechanically sieved (< 200 μm). *Spirulina sp*. was acquired dry from Shine Superfoods – Alma & Valor and used as received. Lastly, *P. tricornutum* was purchased dry from Necton S.A. and used as received. The biomass samples were stored in a dry cabinet at room temperature.

Materials and reagents

The metal salts $CoSO_4 \cdot 7H_2O$ (> 99 wt %), $Cu(CH_3CO_2)_2$ (> 99 wt %), $CuSO_4 \cdot 5H_2O$ (> 99 wt %) and $ZnSO_4 \cdot 7H_2O$ (> 99 wt %) were acquired from Merck. $NiSO_4 \cdot 6H_2O$ (> 99 wt %) and $CuCl_2 \cdot 2H_2O$ (> 98 wt %) were purchased from Riedel de Haen and Analar, respectively. Yttrium standard (1000 $mg \cdot L^{-1}$ in 2 wt % nitric acid), Triton® X-100 (for analysis) and poly(vinyl alcohol) (> 99 wt %) were acquired from Sigma Aldrich. The metal solutions were prepared by weighing ($\pm 10^{-4}$ g) each metal salt and adding the appropriate volume of ultra-pure water. The ultra-pure water was obtained through a Millipore filter system MilliQ®. All multi-metallic solutions were prepared using equal concentrations of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}. The used glassware material was previously washed with nitric acid (20 v/v %) for at least 24 h and thoroughly rinsed with ultra-pure water.

Metal quantification

All the evaluated metals (Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) were quantified by total reflection X-ray fluorescence spectrometer (TXRF) using a Picofox S2 (Bruker Nano) with a molybdenum X-ray source. Briefly, sample carriers were pretreated with 10 µL of silicon in isopropanol solution and dried at (353 ± 1) K for at least 15 min. Afterward, 10 µL of the diluted sample with a known yttrium concentration was added to the sample carrier and dried in a hot plate at (353 ± 1) K for at least 30 min. The sorption capacity (q, mmol·g^{-1}) of the biomass at time t was calculated according to Equation 1:

$$q = \frac{V\,(C_0 - C_t)}{m} \#\#1$$

where V (L) is the volume of the solution, C_0 (mmol·g^{-1}) is the initial metal concentration, C_t (mmol·g^{-1}) is the metal concentration at that time (t) and m (g) is the dry biomass mass.

Sorption assays

All sorption batch studies were performed in an orbital shaker (IKA KS4000 ic control) with temperature fixed at (303 ± 1) K and 200 rpm rotation speed. Schott Duran® glassware (100 mL) was used throughout the experiments. The biomass dosage was maintained at 500 ppm for all assays.[40] This dosage is expected to afford high metal sorption capacity values and to promote good metal pre-concentration in the biomass surface.[33] Control solutions with no biomass were used to ensure no metal losses occurred during the assays. Contact time was set to 6 h, unless otherwise stated. At the desired time of contact, samples of the sorbent suspension (1.5 mL) were collected. Residual biomass was removed by centrifuging the samples at 12000 rpm for 2 min. Then, the liquid phase was collected and analyzed. The same procedure was applied to the control solutions. All assays were performed in triplicate. The optimization studies were conducted in multi-metal aqueous solutions. Mono-elemental assays were conducted to better understand the competition between the metal ions and the metal counterion effect.

pH optimization

The influence of the pH on metal sorption was studied by fixating the initial metal concentration, biomass dosage, temperature and contact time. Briefly, quaternary metal solutions of $CoSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 4H_2O$ with a metal concentration of 10 ppm each were placed in contact with 500 ppm of biomass at (303 ± 1) K. The pH of the solutions was adjusted to 3, 4, 5 or 6 by adding diluted H_2SO_4 or NaOH and determined using a Mettler Toledo SevenMultiTMdual pH meter (± 0.02).

Initial metal concentration and metal competition

The impact of the initial metal concentration was evaluated by preparing quaternary metal solutions with a total metal concentration ranging from ≈ 8 to 100 ppm. All assays were performed at pH = 5 and the biomass dosage, temperature and contact time were fixated as previously mentioned. All the presented concentrations refer to the metal ion concentration and not to the metal salt concentration. Mono-elemental solutions of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} with initial metal concentrations ranging from ≈ 8 to 100 ppm and pH = 5 were also prepared and placed in contact with 500 ppm of *Sargassum sp*. to assess the impact of metal competition.

Metal counterion influence

The effect of the metal counterion was evaluated by placing the brown macroalga *Sargassum sp*. in contact with mono-elemental solutions of $CuSO_4$, $Cu(CH_3CO_2)_2$ or $CuCl_2$ at pH = 5. The initial metal concentration was set to 60 ppm.

Sorption kinetics

The kinetics of metal sorption was evaluated in the macroalga *Sargassum sp*. by exposing it to a quaternary metal solution with pH = 5 and an initial total metal concentration of 70 ppm. Samples were collected at a contact time of 5, 15, 30, 60, 120, 240 and 360 min. Two non-linearized kinetic models were adjusted to the experimental data obtained from the multi-metal kinetic study of *Sargassum sp*., Lagergren's pseudo-first order model (Equation 2)[41]

$$q_t = q_e(1 - e^{-k_1 t}) \#2$$

and Ho's pseudo-second order model (Equation 3)[42]

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \#3$$

where q_t ($mmol\cdot g^{-1}$) is the sorption capacity of the *Sargassum sp*. at that time (t), q_e ($mmol\cdot g^{-1}$) is the sorption capacity of the biomass at equilibrium, k_1 (h^{-1}) is the rate constant of pseudo-first order and k_2 ($g\cdot mmol\cdot h^{-1}$) is the rate constant of pseudo-second order.

Metal recovery

The alga *Sargassum sp.* was metal loaded at the optimal condition. Afterward, the solution was filtered to recover *Sargassum sp.*, which was dried overnight in the oven at (303 ± 1) K. The metal-loaded sample was placed in a combustion furnace at (798 ± 1) K for 12 h. The biomass char (≈ 2 mg) was suspended in 0.8 g of poly(vinyl alcohol) (1 wt %) and 0.2 g of Triton® X-100 (1 wt %), with a known concentration of the internal yttrium standard. The remaining sample preparation was performed as previously described and samples were subsequently analyzed by TXRF. The assay was performed in duplicate. The enrichment factor (EF) was calculated according to Equation 4:

$$EF = \frac{C_{i,biochar}}{C_{i,aq}} \#4$$

where $C_{i,biochar}$ is the metal concentration (mmol·g^{-1}) quantified in the biochar and $C_{i,aq}$ is the initial metal concentration (mmol·g^{-1}) in the aqueous solution.

Results and Discussion

Influence of the pH

The influence of pH on metal sorption by the non-living biomass was evaluated in multi-metal aqueous solutions, as depicted in Figure 1.

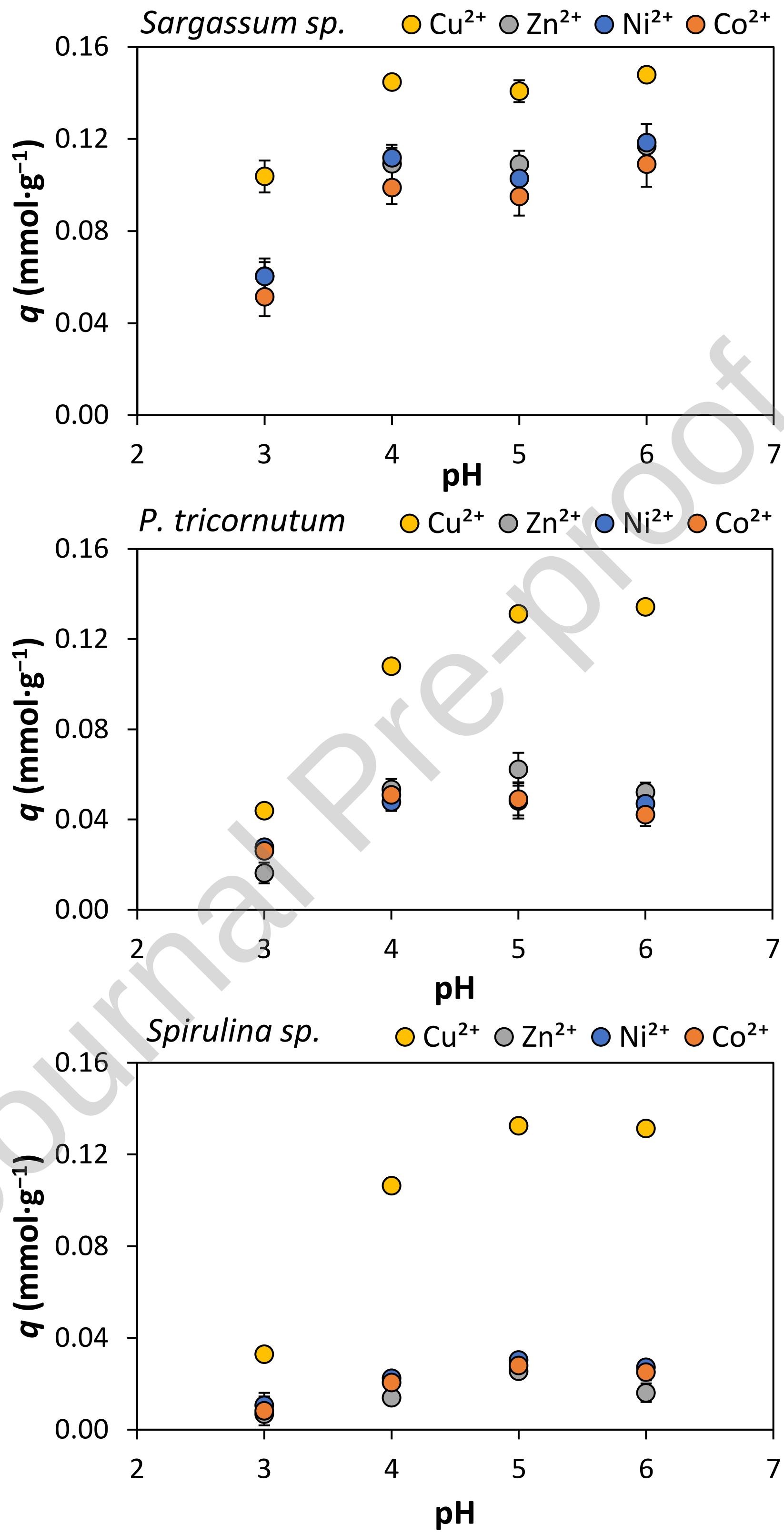
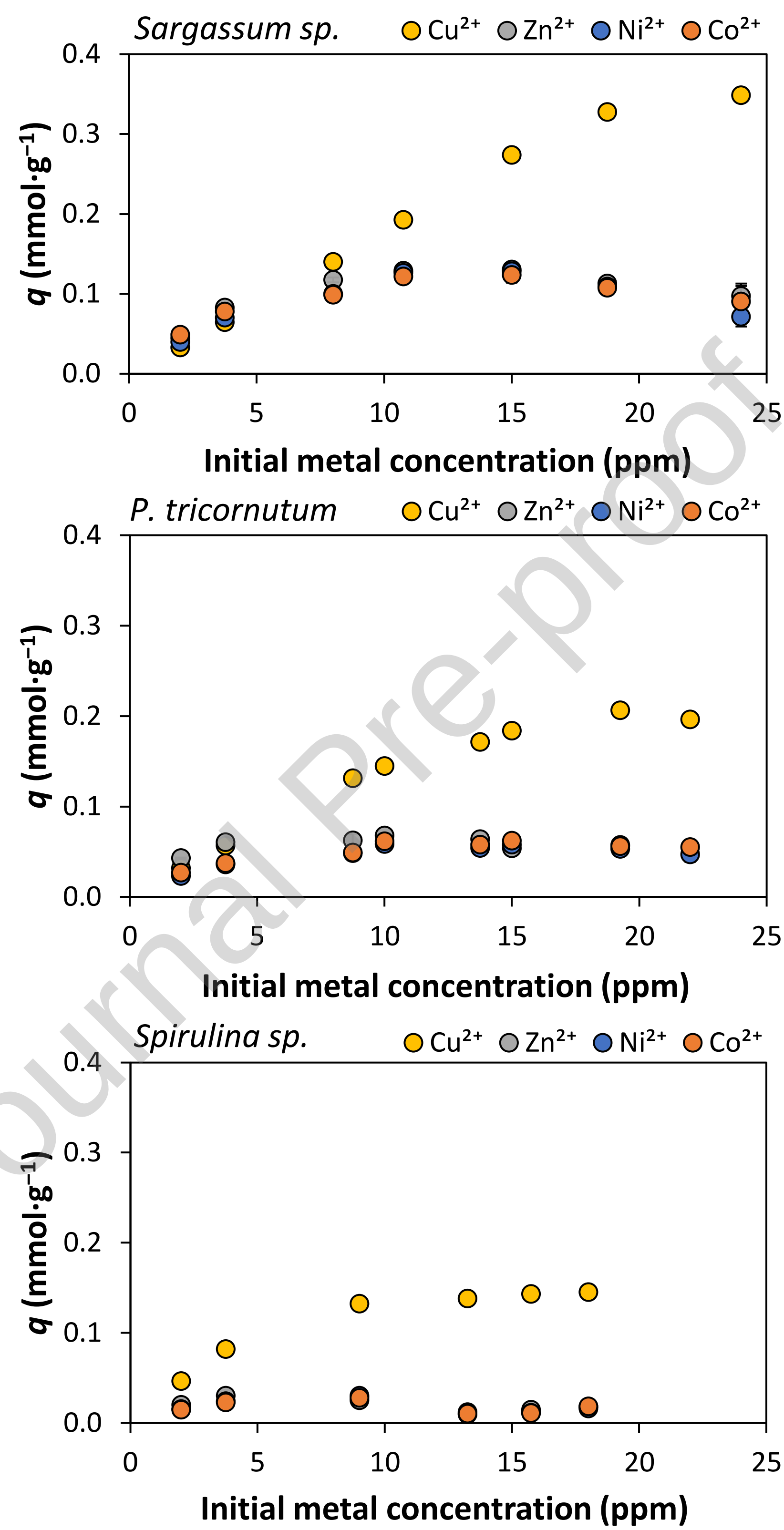

Sargassum sp.
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
0.16
0.12
0.08
0.04
0.00
2
3
4
5
6
7
pH
P. tricornutum
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
pH
Spirulina sp.
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
pH

Figure 1. Influence of pH on the simultaneous sorption capacity of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by *Sargassum sp*., *P. tricornutum* or *Spirulina sp*. at a total initial metal concentration of 40 ppm, 500 ppm of biomass and T = (303 ± 1) K.

All biomass samples show sorption improvements as the pH increases from 3 to 5. Sorption equilibrium was reached at pH = 5, with the sorption and desorption rate being equal. Throughout the evaluated pH range, the biomass samples consistently presented a better affinity to Cu^{2+}. This can be linked to the complexation constant of each metal with relevant functional groups and the Irving-Williams series.[40] For instance, Cu^{2+} has a higher complexation constant than the remaining metals for the same functional groups, causing its preferable sorption.[43] Moreover, according to the Irving-Williams series, octahedral complexes of Cu^{2+} have better stability than Co^{2+}, Ni^{2+} and Zn^{2+} complexes, irrespective of the ligand, due to the Jahn–Teller effect experienced in Cu^{2+} complexes.[44] The sorption capacity of the biomass is hampered at lower pH values. This is mainly due to the higher competition between H^+ and metals for the available binding sites. Also, pH influences the protonation and dissociation degree of the biomass functional groups, affecting their availability for metal interaction. Most functional groups are protonated at lower pH values, leading to a more positive surface charge on the biomass. This causes electrostatic repulsion of the metals and lowers the metal sorption capacity values. In a previous work we showed that carboxyl groups are significantly involved in metal sorption in the studied biomass samples.[40] Considering that carboxyl groups have a pK_a ranging from 1.7 to 4.7,[45] optimal sorption capacity is expected at pH values closer to the upper limit of this interval. Similar trends were reported in mono-elemental studies.[19,33,46] Karthikeyan *et al*.[46] showed that *Sargassum sp*. achieved a maximum sorption capacity of Cu^{2+} at pH = 5.5 ± 0.5, which is in close agreement with the results obtained here. Still, the sorption capacity of *Sargassum sp*. in that mono-elemental assay is 1.2 mmol·g^{-1}, whereas herein the total sorption capacity of *Sargassum sp*. in multi-elemental assays is 0.5 mmol·g^{-1}. This is probably related to metal competition, as discussed in the following sub-section.

Initial metal concentration in mono- and multi-metal assays

The sorption capacity of all biomass samples in multi-elemental aqueous solutions was evaluated at optimum pH value (pH = 5) and initial individual metal concentration ranging from 2 to 25 ppm, affording a total initial metal concentration ranging from 8 to 100 ppm, as depicted in Figure 2. The effect of metal concentration in mono-metal solutions was assessed in *Sargassum sp*. with initial metal concentrations ranging from 8 to 100 ppm (Figure 3) to mimic the total initial metal concentration in the multi-elemental assays.



Sargassum sp.
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
Initial metal concentration (ppm)
P. tricornutum
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
Initial metal concentration (ppm)
Spirulina sp.
Cu²⁺ Zn²⁺ Ni²⁺ Co²⁺
q (mmol·g⁻¹)
Initial metal concentration (ppm)

Figure 2. Initial metal concentration influence on the sorption capacity of *Sargassum sp.*, *P. tricornutum* or *Spirulina sp.* in multi-elemental aqueous solutions of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} at pH = 5, biomass dosage of 500 ppm and T = (303 ± 1) K.

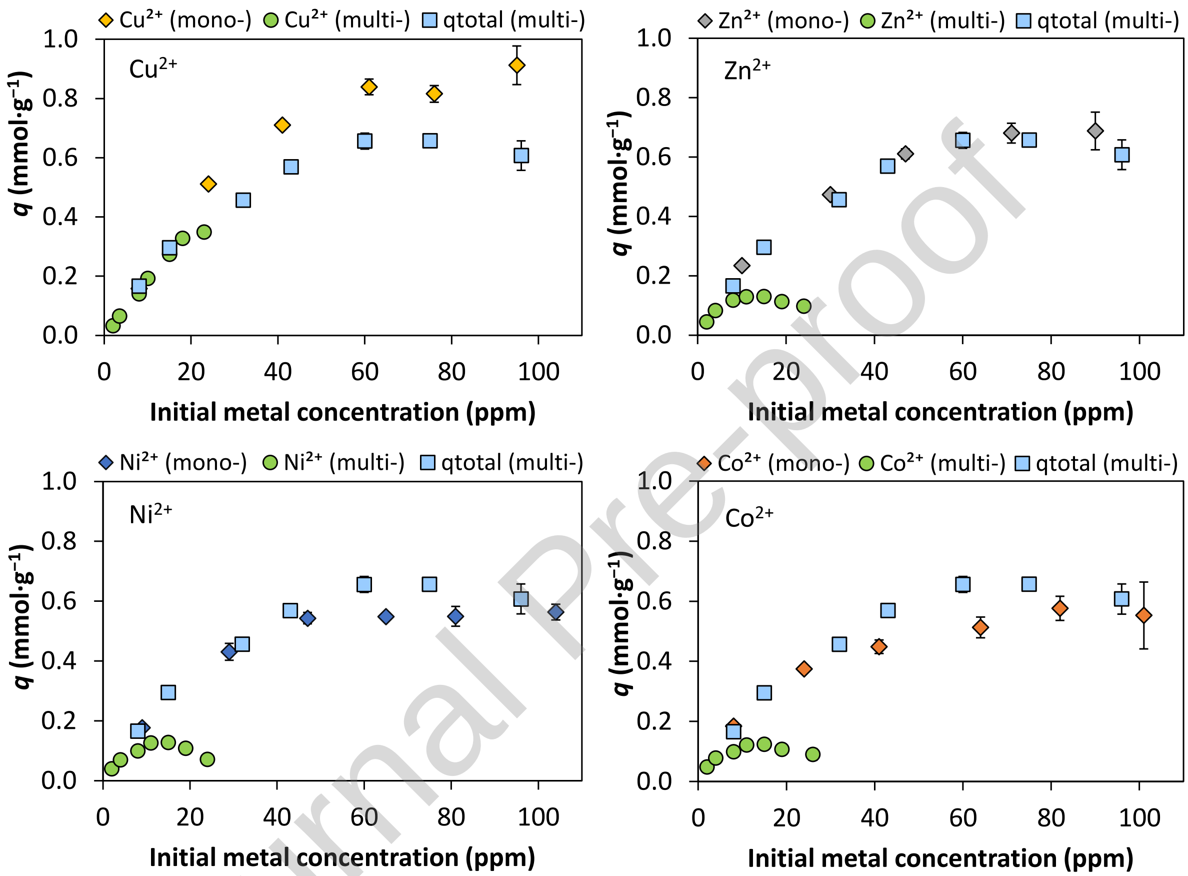


Figure 3. Influence of the initial metal concentration on the sorption capacity of *Sargassum sp.* in mono-metal aqueous solutions of Co^{2+}, Cu^{2+}, Ni^{2+} or Zn^{2+} at pH = 5, 500 ppm of biomass and T = (303 ± 1) K.

When in contact with multi-metal aqueous solutions, all biomass samples behaved differently – *cf.* Figure 2. Sargassum sp. shows a better Cu^{2+} sorption capacity as the initial metal concentration increases. The sorption capacity of the remaining metals improves until 10 ppm of each metal (40 ppm total) and decreases after 15 ppm of each metal. This prompts a better relative Cu^{2+} selectivity as the initial metal concentration increases. Concerning *P. tricornutum*, its Cu^{2+} sorption capacity improves as the initial concentration of each metal increases up to 20 ppm (80 ppm total) and then reaches equilibrium. The sorption capacity of the remaining metals reaches equilibrium around 10 ppm of each metal. Ultimately, *Spirulina sp.* is the biomass that reaches equilibrium at the lowest initial metal concentration, with all metals being at equilibrium after 8 ppm of each metal. At optimum conditions the maximum total sorption capacity of each biomass is as follows: 0.66 $mmol \cdot g^{-1}$ *Sargassum sp.*, 0.36 $mmol \cdot g^{-1}$ *P. tricornutum* and 0.22 $mmol \cdot g^{-1}$ *Spirulina sp.* (Figure S1). Overall, increasing the initial metal concentration promotes ligand-metal interaction. After a certain metal concentration threshold, the biomass functional groups reach saturation causing the sorption to plateau. This is more straightforward for non-living biomass since metal toxicity has no role here. The obtained results are in agreement with the literature,[19,33,46] with the optimal initial concentration being dependent on the metal:sorbent ratio and the sorption potential of each biomass.

The sorption performance was also studied in mono-elemental assays (Figure 3). Comparison of the results obtained in mono- and multi-elemental assays enable a better understanding of the metal competition effect on the biomass sorption capacity. In the quaternary systems, the sorption capacity of the individual metal is lower than in the mono-elemental assays. Metals compete for the biomass binding sites causing lower sorption capacity values in multi-metallic assays.[47] This underlines the occurrence of destructive metal competition, showing that mono-elemental assays may be redundant when targeting wastewaters for metal recovery. The antagonistic effect of metal competition in multi-elemental systems is in agreement with the literature.[48,49] The comparison of the sum of the sorption capacity of each metal (total sorption capacity, q_{total}) in the quaternary systems with the sorption capacity in mono-elemental assays is also noteworthy since both account for the total occupied binding sites. The relationship between the sorption capacity in mono-elemental studies and the q_{total} in multi-elemental studies is as follows: q Cu^{2+} mono $\geq q_{total}$ multi, q Zn^{2+} mono $\approx q_{total}$ multi, q Ni^{2+} mono $\leq q_{total}$ multi and q Co^{2+} mono $\leq q_{total}$ multi. The sorption of Cu^{2+} in mono-elemental studies exceeds the sum of the sorption capacity of all metals in the multi-metal assay. The higher Cu^{2+} sorption in mono-elemental studies discloses the enhanced affinity of this metal for the biomass binding sites, as previously discussed, based on the Irving-Williams series and the complexation constant of each metal. These results also suggest that some binding sites are still available in the multi-metal assay. Still, metal competition hampers their interaction with more metal moieties, preventing a better total sorption capacity. For the remaining metals, the sorption capacity in mono-elemental assays is similar to the q_{total} in multi-elemental assays. Without competing species, the individual metals distribute onto the available binding sites, attaining a sorption capacity similar to the q_{total} in multi-elemental assays.

Metal counterion effect

The metal counterion effect on sorption capacity was evaluated by preparing mono-elemental solutions of $CuSO_4$, $Cu(CH_3CO_2)_2$ and $CuCl_2$, each solution containing 60 ppm of Cu^{2+} and 500 ppm of *Sargassum sp.* at pH = 5 and T = (303 ± 1) K (Figure 4).

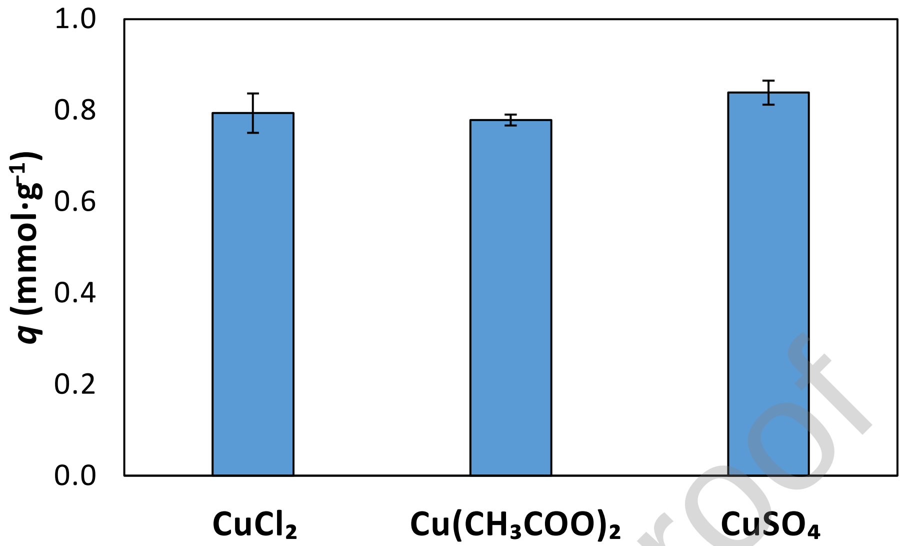


Figure 4. Sorption capacity of *Sargassum sp.* in mono-elemental aqueous solution of $CuCl_2$, $Cu(CH_3CO_2)_2$ or $CuSO_4$, at pH = 5, 500 ppm of biomass dosage and T = (303 ± 1) K.

The sorption capacity of *Sargassum sp.* was consistent regardless of the used counterion. Although some studies evaluate the influence of adding background anions on the aqueous solution,[50,51] to the best of our knowledge, no other studies consider the potential influence of the metal counterion on sorption. The non-influence of the metal counterion on metal sorption is related to the complexation constant of each metal with their respective counterion and the biomass functional groups. The metal interaction with the biomass binding sites is stronger than its interaction with the selected counterions.[52][53] For this reason, Cu^{2+} can bind effectively onto the biomass, regardless of the counterion. Overall, the non-influence of the metal counterion is beneficial for metal recovery from wastewater.

Kinetic studies

Sargassum sp. consistently achieved the best sorption capacity values among the studied biomass. For this reason, this biomass was selected to study the kinetics of the simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} at pH = 5, total initial metal concentration of 70 ppm, biomass dosage of 500 ppm and T = (303 ± 1) K. To better understand the sorption mechanism in quaternary metal systems, the Lagergren's pseudo-first order model and Ho's pseudo-second order model were fitted to the obtained data, as seen in Figure 5.

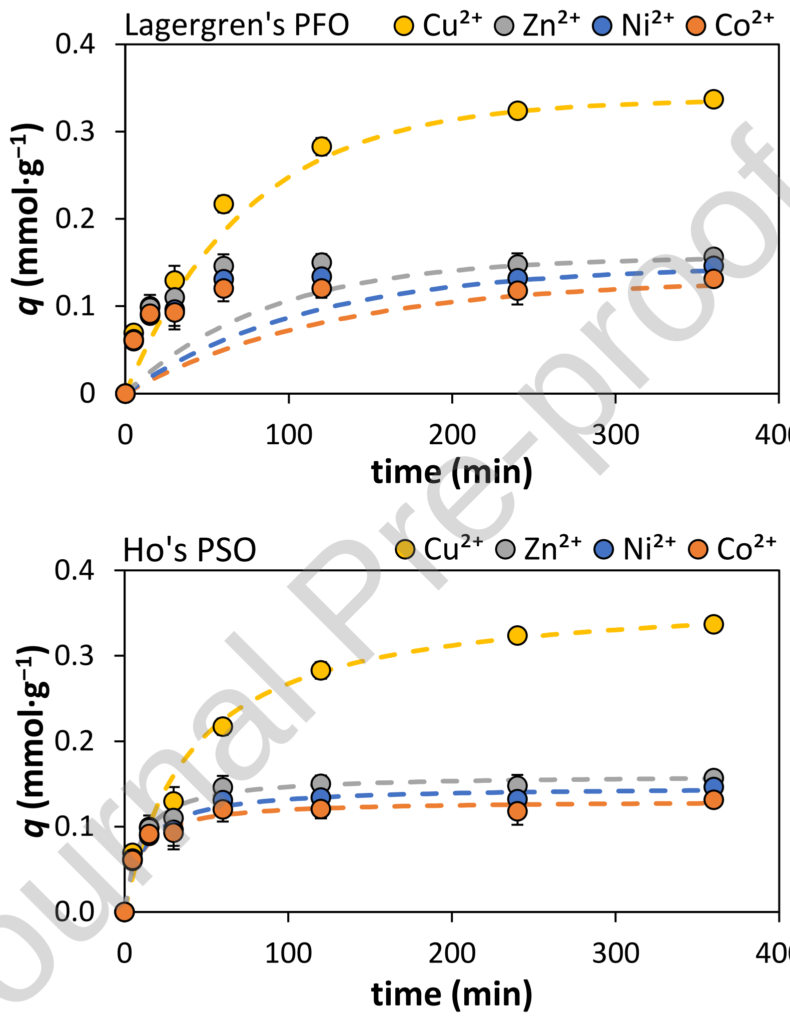


Figure 5. Kinetic study of the simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+} or Zn^{2+} at pH = 5, 500 ppm of biomass and T = (303 ± 1) K and corresponding fit of the Lagergren's and Ho's models. Symbols and lines were used to differentiate the experimental data (○) and the fitting (dashed line), with equal colors corresponding to the same metal.

Overall, metal sorption occurred rapidly. The sorption of Co^{2+}, Ni^{2+} and Zn^{2+} reached equilibrium after 60 min of contact with *Sargassum sp*. Despite the preferential sorption of Cu^{2+}, its sorption only reached equilibrium around 360 min. While Co^{2+}, Ni^{2+} and Zn^{2+} kinetics are in agreement with the results obtained by *Sargassum sp.* in mono-elemental solutions,[55,56] the sorption of Cu^{2+} was slower than in mono-metal solutions.[46,56]

Lagergren's pseudo-first order (PFO) model and Ho's pseudo-second order (PSO) model were fitted to the experimental data. The values of q_e (calculated and experimental), calculated k_2, k_1 and the respective correlation coefficients are presented in Table 1.

Table 1. Comparison of the calculated sorption rate constants with the respective experimental data and correlation coefficients of the PFO and PSO kinetic models to describe the sorption kinetics of the simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by Sargassum sp.

	Lagergren's (PFO)			Ho's (PSO)			Experimental value
Metal	k_1 (h^{-1})	q_e ($mmol \cdot g^{-1}$)	R^2	k_2 ($g \cdot mmol \cdot h^{-1}$)	q_e ($mmol \cdot g^{-1}$)	R^2	q_e ($mmol \cdot g^{-1}$)
Co^{2+}	0.008	0.052	0.508	0.843	0.130	0.996	0.131 ± 0.005
Cu^{2+}	0.013	0.295	0.994	0.067	0.375	0.994	0.337 ± 0.001
Ni^{2+}	0.009	0.067	0.599	0.599	0.147	0.996	0.146 ± 0.003
Zn^{2+}	0.011	0.066	0.618	0.652	0.161	0.999	0.157 ± 0.005

Ho's kinetic model afforded better correlation coefficients than Lagergren's model. The better fitting of Ho's model is also corroborated by the similarity of the calculated q_e values and the experimental data. Ho's model assumes that sorption follows a second-order mechanism, with chemisorption being the rate-limiting step.[42] Hence, in the evaluated system, sorption occurs *via* a chemical reaction between the biomass and the metals, culminating in a covalent bond formation. This mechanism seems to be transversal to most sorption systems in general, with *circa* 87 % of the sorption systems being better fitted by Ho's model.[57] The slower Cu^{2+} sorption rate in *Sargassum sp.* is also reflected by the pseudo-second order constant. Intra-system competition plays a vital role in Cu^{2+} sorption. Initially, Cu^{2+} sorbs to the available binding sites, similarly to the remaining transition metals. Once biomass saturation is reached, Cu^{2+} is sorbed through cation-exchange, causing the displacement of the other transition metals. This is further supported by Figure 2, where Cu^{2+} sorption selectivity improves as the initial metal concentration increases due to the lower sorption of Co^{2+}, Ni^{2+} and Zn^{2+}.

Ion-exchange

To better understand the sorption mechanism, the release of K^{+}, Ca^{2+} and H^{+} from *Sargassum sp.* to the aqueous solution was monitored throughout time, as depicted in Figure 6.

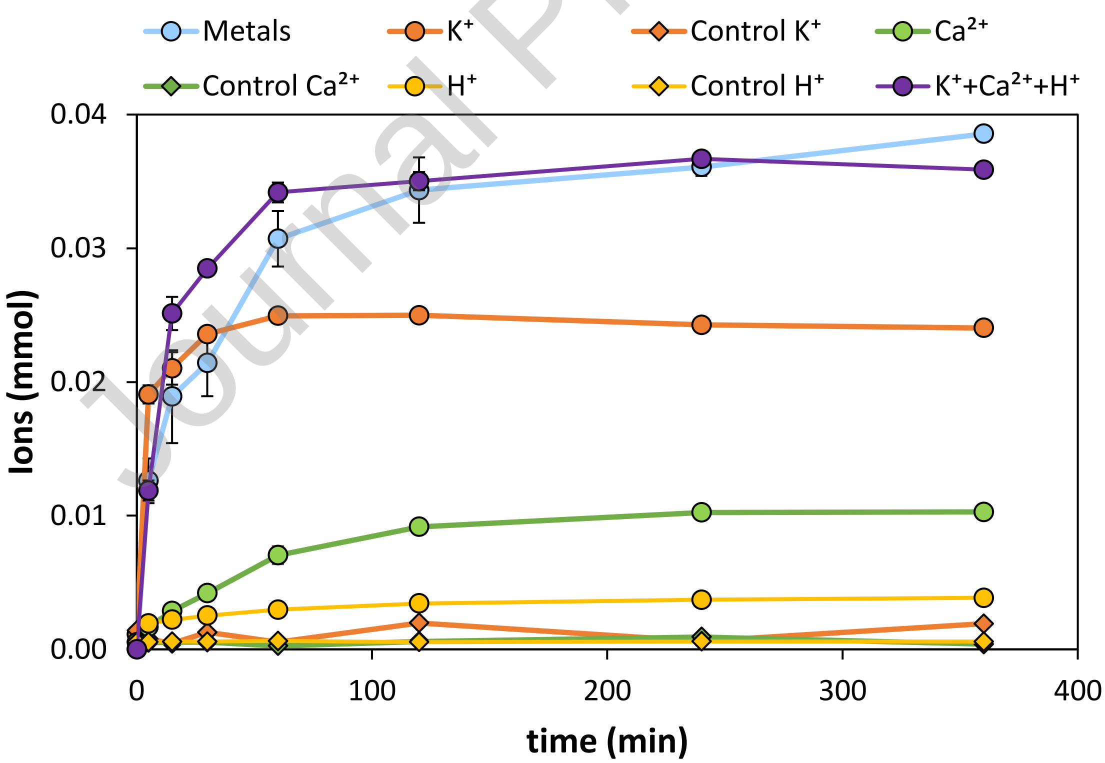


Figure 6. Comparison of the uptake of metals (Co^{2+} + Cu^{2+} + Ni^{2+} + Zn^{2+}) with the release of K^+, Ca^{2+}, H^+ and the sum of all released ions (K^+ + Ca^{2+} + H^+) over time from *Sargassum sp*. to the solution, at pH = 5, 500 ppm of biomass and T = (303 ± 1) K. The ions (mmol) found in the controls were subtracted from the sum of the released ions.

Across time there was a significant release of K^+, Ca^{2+} and H^+ from *Sargassum sp.* to the aqueous solution. Among these ions, K^+ presented the fastest release rate. Most K^+ ions (76 %) were released after 5 min and equilibrium was reached within 60 min. The release of Ca^{2+} and H^+ reached a plateau around 240 min. The release of H^+ inherently lowered the solution pH from 5.1 to 4.4. Besides having different release kinetics, these ions were also released at different extents. The amount of displaced ions increases as follows: $H^+ < Ca^{2+} < K^+$. This is connected to the constant complexation between these ions and relevant functional groups in the biomass surface, such as carboxylic groups.[43] For instance, the complexation constant of the metals and ions with oxalic acid at 298 K and 0 ionic strength is as follows: -0.8 K^+, 3.0 Ca^{2+}, 4.3 H^+, 4.7 Co^{2+}, 6.2 Cu^{2+}, 5.2 Ni^{2+} and 3.4 Zn^{2+}.[43] Ions with lower complexation constants are more readily exchanged with metals. When combined, the released amount of K^+, Ca^{2+} and H^+ (mmol) tends to overlap with the total amount of metal bound to the biomass. Still, to maintain electroneutrality two moles of K^+ or H^+ must be exchanged for one mol of M^{2+}. To consider electroneutrality, the moles of K^+ or H^+ were divided by two. By doing so, the ratio between metals sorbed and ions released is 1.7 at t = 6 h, showing that ion-exchange accounts for at least 59 % of the metals sorbed into the biomass. Other ions may be involved in ion-exchange but their quantification is not possible by TXRF.

The correlation between the sum of the released ions and the sorbed metals across time is presented in Figure 7.

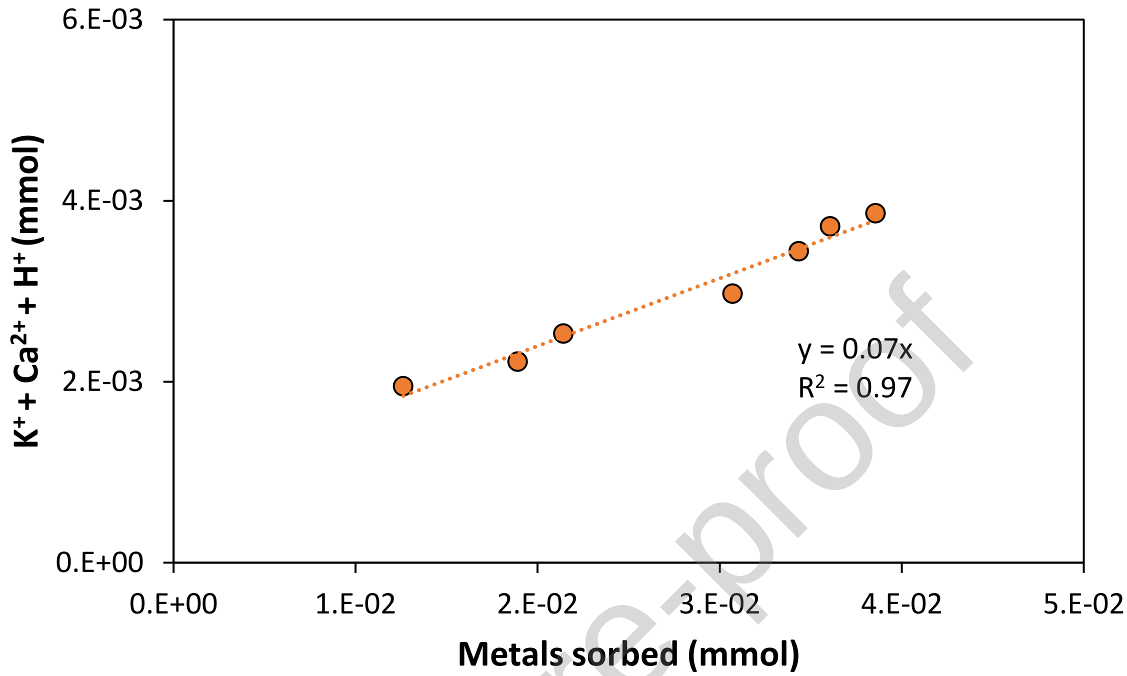


Figure 7. Correlation of the sum of K^{2+}, Ca^{2+} and H^+ release with the total metal sorbed (mmol) upon contact of *Sargassum sp*. with the quaternary system at 5, 15, 30, 60, 120, 240 and 360 min.

Overall, the obtained data indicates the occurrence of a synergistic mechanism of ion-exchange, with a strong correlation between metal sorption and ion release.

Metal recovery

Using sorption as a pre-concentration tool is an innovative perspective. The optimization data and the new mechanism insights described in this work are essential for developing an efficient sorption process targeting metal recovery. Herein, metal recovery was accomplished by incineration of the metal loaded *Sargassum sp.* The algal char content was quantified by TXRF and the concentration of the recovered metals was compared to the metal concentration in the initial aqueous solution (Figure 8).

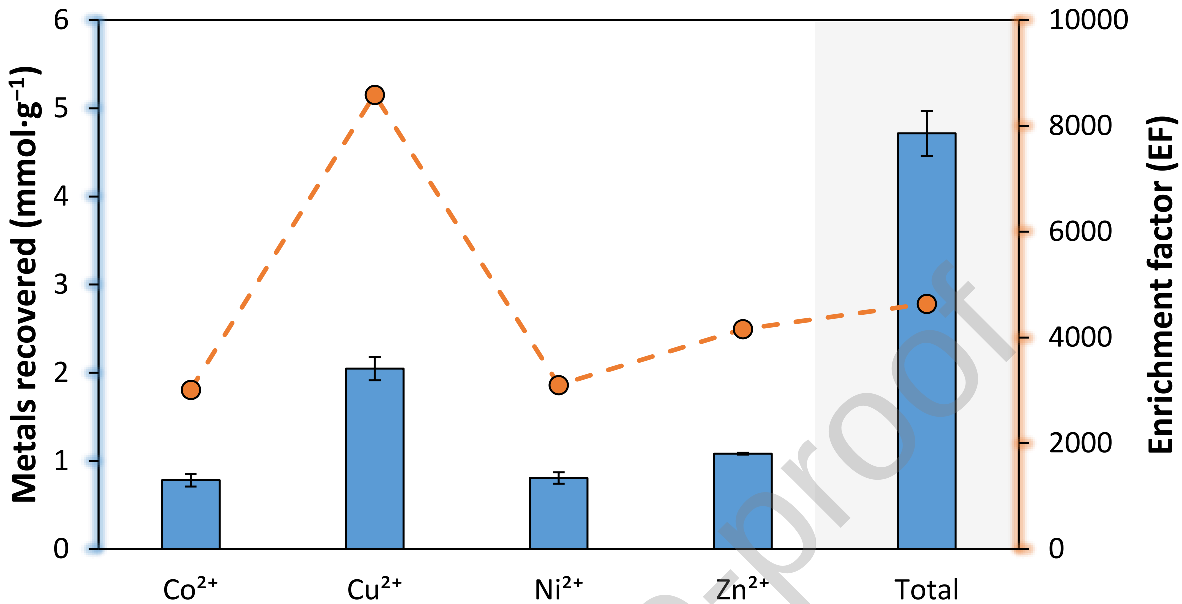


Figure 8. Concentration of the recovered metals per gram of biochar (blue bars) and respective enrichment factor compared to the initial metal solution (orange dashed line).

All metals were successfully pre-concentrated in the *Sargassum sp.* char. The enrichment factor of each metal increases as follows: 3013-folds Co^{2+}, 3102-folds Ni^{2+}, 4157-folds Zn^{2+} and 8590-folds Cu^{2+}. The highest concentration increase of Cu^{2+} is related to its preferential sorption by the biomass. In total, the combination of sorption and incineration enabled a metal pre-concentration of 4639 folds compared to the initial metal solution. Ultimately, around 30 % of the biochar mass corresponds to metal. Metal recovery *via* incineration unlocks the possibility of using metal-loaded biochar as a template for the design of ecological catalysts.[58,59] Using biochar as a catalyst can reduce greenhouse gas emissions by up to 93 % and reduce energy consumption by up to 96 % compared to conventional metal catalyst production.[60] Incineration of metal-loaded biomass can be a viable metal recovery approach while enabling their reuse as functional materials. From the perspective of metal recovery, it is redundant to perform optimization sorption studies if the final product is disregarded. Still, most sorption studies overlook the potential of metal recovery from biomass, resulting in a research gap. The approach explored in this work intends to fill this gap while promoting sorption as a pre-concentration step for metal recovery from multi-metallic solutions, to simulate wastewater.

Conclusions

Metal sorption depends on experimental conditions such as pH, initial metal concentration, metal competition and time of contact. In this work the effect of these parameters was studied and optimized on the metal sorption by macroalgae, microalgae and cyanobacteria from multi-metal solutions of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}. Although metal competition is often disregarded, the obtained results show that metal sorption is hampered in multi-element assays. The brown macroalgal *Sargassum sp*. was the most promising sorbent, with its optimum conditions being pH = 5, 70 ppm of the total initial metal concentration and 360 min of contact time. The evaluated biomass showed a better affinity to Cu^{2+}. Herein, metal counterion effect was evaluated for the first time. The nature of the counterion – sulfate, chloride or acetate – did not exert any influence on the metal sorption efficiency. The experimental data was better fitted by the pseudo-second order model, showing that the metal sorption occurred *via* covalent bonds. The quantification of Ca^{2+}, K^+, and H^+ ion release from the biomass to the aqueous solution over time provided a deeper insight of the sorption mechanism. A good correlation ($R^2 > 0.97$) was found between metal sorption and the release of these ions. The metal-laden biomass was incinerated. The obtained biochar had a metal concentration 4639-folds higher than the initial metal concentration in aqueous solutions. Aiming towards a circular process, the obtained biochar could be reused as a ecocatalyst.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Ana R. F. Carreira acknowledges FCT for the Ph.D. grant SFRH/BD/143612/2019. Nicolas Schaeffer acknowledges the national funds (OE), through FCT–Fundação para a Ciência e a Tecnologia, I. P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29th, changed by Law57/2017, of July 19th. Helena Passos acknowledges FCT – Fundação para a Ciência e a Tecnologia, I.P. for the researcher contract CEECIND/00831/2017 under the Scientific Employment Stimulus - Individual Call 2017. The authors would like to thank ALGAplus, Lda. for providing algal samples.

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Conflicts of interest: The authors declare no conflicts of interest.

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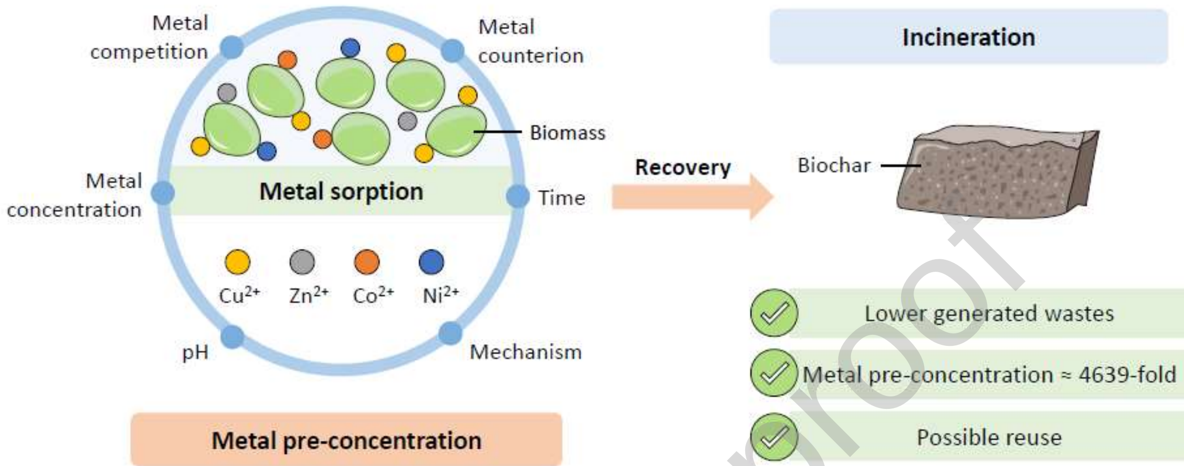
Graphical abstract



Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Metal pre-concentration onto macroalgae, microalgae and cyanobacteria was optimized.
- *Sargassum sp.* had the greatest sorption capacity.
- Chemisorption and ion-exchange played a key role in metal sorption.
- Metal-laden biomass was incinerated into biochar to promote metal recovery.
- The biochar had a metal concentration 4639-folds higher than the initial solution.