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Marine materials as innovative metal sorbents suitable for applications in wastewater treatments

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ABSTRACT

The growing interest for urban mining strategies has pushed the research towards innovative strategies for metal recovery from electronic waste. Nevertheless, the treatment of the resulting metal-rich wastewater is still an issue. In this context, the present paper shows a method to use the capacity of Ulva algae to adsorb metals for the treatment of a synthetic solutions which simulates that resulting from a printed circuit board recycling process. The experiments considered a copper-zinc-iron system, showing a copper adsorption capacity of biomaterial up to 65 mg/g, at pH 5, favoured by iron presence. The process needs a short time (around 15 min) and it is suitable to be performed in a fixed-bed column able to treat more than 30 L of copper-contaminated wastewater, decreasing the energetic costs for mixing (compared to the typical slurry-reactor configuration) with an almost completed metal removal. The sustainability of the process is further improved by the selection of a macroalga which often accumulates on beaches (becoming a waste to remove) complying with the circular economy pillars.

1. Introduction

The intensification of industrial activities is a consequence of the last decades growth of human population. As a result, many compounds have been released into the environment with high-concentrations, causing changes in biological, chemical-physical environmental factors. Among these substances, heavy metal such as copper, zinc, iron, lead, cadmium, and others produce many adverse ecological effects and bioaccumulation in the environment [1,2].

Printed circuit boards (PCBs) represent the essential part of all electrical and electronic devices and they are at the base of the electronics industry. The worldwide production of PCBs is driven by the continuous market demand for ever more advanced and updated devices. All of this leads to the huge availability of waste PCBs that need to be disposed of [3–5]. PCBs contain both strategic metals (essential for their applications and critical for the global reserve shortage) and hazardous substances [4]. Therefore, their incineration or disposal represent a great threat to ecosystems, but also a loss of valuable secondary raw materials [3]. Copper is the most abundant metal in PCBs (20–25 wt %), followed by iron and zinc (2 wt%), but also precious metals such as gold (0.04 wt%), silver (0.15 wt%) and palladium [5,6]. Currently, the most typical approaches used for PCBs recycling include hydrometallurgical and pyrometallurgical treatments. As an alternative to these common approaches, the innovative bio-hydrometallurgical processes generally involve three phases: (1) bio-leaching, to bring the metal or one of its compounds into solution, (2) concentration and purification of the leach liquor solution, (3) recovery of the metal or one of its compounds [3,7,8]. In this regard, Becci et al. (2021, 2020a, 2020b) recovered metals from PCBs through innovative bio-hydrometallurgy techniques, where the protagonists are bacteria (e.g., *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*) and fungi (e.g., *Aspergillus niger*) for copper and zinc extraction [6,9,10]. The introduction of biotechnology aims at the environmental impact reduction, nevertheless it cannot avoid the resulting wastewater, characterized by a low concentration of metals, that is not yet suitable for the discharge in sewers [3]. The available techniques for the treatment of these flows (e.g., activated sludge, activated carbon, anaerobic membrane bioreactors, etc.) have limitations in their application. Indeed, in addition to being expensive, they are ineffective if used to clean up pre-treated wastewater containing low concentrations of metals and of metalloids as proved for arsenic, very toxic even at low concentrations (i.e., range of 1–100 mg/L) [11,12]. Moreover, they require a huge amount of energy and cause pollution for the material synthesis and production of toxic sludge [13,14]. On the other hand, previous studies proved that biosorption

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gives excellent results for the removal of small concentrations of metal in wastewater [12,15]. Biosorption is an alternative and eco-friendly method that uses inactive and dead biomass for the recovery of contaminants from wastewater solutions. It consists of the removal of pollutants, even in small concentrations, like heavy metals, metalloids, and industrial dyes by the passive binding to a dead biological surface [15–17]. The process is based on the development of physicochemical bindings, like van der Waals forces or ionic and covalent bonds, between the active site on the biological material and the metals in wastewater solution. Previous literature hypothesized that ion-exchange is the dominant mechanism involved in the process and it is generally assumed that each active site on the biomaterial is previously occupied [15,18–20]. In this context, the development of new biosorbent materials has been focused particularly on macroalgae and microalgae, for their high accessibility in almost unlimited amounts and their sorption capacity [15,17,21–23]. They allow the development of a low-cost and sustainable technique that employs cheap and renewable resources [16,24,25]. Moreover, it is important to point out that biosorbents have also the ability to concentrate metals on their surface and to release them after an elution process with a desorbing agent. This process can regenerate the biosorbent without damaging its binding capacity and at the same time, it concentrates metal ions in a small volume to reduce waste [15,18,26].

In the sustainability context, the industrial wastewater treatment allows a double benefit for the environment thanks to the possibility of a water reintroduction into the environment and the recovery of valuable metals such as copper, zinc, and iron [16,17]. Many types of biosorbents have been investigated for their ability to sequester metals and other pollutants, i.e., fungi, moss, bacteria, yeast, and algae [15,19]. Among these, the use of algae biomass can be very advantageous because of their wide distribution, large surface area, high sorption capacity, and low cost [15,19,27,28]. The high metal-binding capacity is due to the presence of functional groups (i.e., carboxyl, carbonyl, sulphonate, hydroxyl, and amine groups) on their cell wall, which can be protonated or deprotonated in relation to the pH value of the solution [15,19]. Furthermore, some species are characterized by a very rapid growth that can cause environmental problems, like *Ulva*, the most representative genus inside the Chlorophyta phylum [29,30]. Its high photosynthetic rate and efficient uptake of nutrients, together with its tolerance to a wide range of environmental conditions result in the formation of large blooms called "green tides" in areas affected by a high input of nitrates and global warming [29–34]. *Ulva*-based green tides represent a global marine ecological disaster that directly affects the economic and touristic expansion of coastal towns and their ecological care. Many parts of the world are affected by this problem such as France, Italy, the United States, Japan, China, the Netherlands, Australia, Egypt, New Zealand, South Africa, and others [29,33,35,36]. Its capacity to accumulate nitrogen, carbon, and phosphorus in the tissue makes *Ulva* a potentially live biomaterial for phytoremediation of seawater polluted [29,37], while other studies used non-living thalli for heavy metal biosorption [2,20,38–40].

The present study aimed at the development of an innovative sustainable solution suitable for the treatment of wastewater resulting from the PCB recycling proposed by Amato et al. (2020), characterized by low concentration of metals (Table 1) which makes it not suitable for the discharge [3]. The method, developed by using a synthetic solution able to simulate the process wastewater, allows multiple benefits thanks to the enhancement of high amounts of beached green tides (otherwise disposed of) and the concentration of valuable metals (copper, iron, and zinc), potentially recoverable.

Table 1
Metal concentrations in the final liquor after metal recovery from PCB leaching solution [3].

Metal	Concentration (mg/L)	
	Mean	Dev. st.
Copper	180	±50
Iron	52	±3
Zinc	36	±3

More in detail, the present study evaluated the metal sorption capacity of green waste material to determine the optimum operating conditions by testing different pH values and comparing single- and multi-metal systems to identify the possible competition for the active sites. The further implementation of the process in a laboratory pilot-scale system, equipped by a continuous flow column filled with waste material, represents a strength of this innovative application designed to turn waste into resources.

2. Materials and methods

2.1. Biomaterial collection and preparation

Algae used as sorbent material belong to the Chlorophyta phylum (*Ulva lactuca*, Linnaeus, and *Ulva linza*, Linnaeus) were sampled in Passetto beach (Ancona, Italy). The algal taxa were identified using the light microscope (ZEISS Axioscop) and cryostat (ZEISS HM 505 N) to produce sections of the thallus. Taxonomic scientific literature was consulted for the identification of the taxa [41].

For the performed experiments, it was not necessary to divide the species belonging to the genus *Ulva*, due to their similar structure (Linnaeus). After the collection, the material was washed by deionized water to remove all the impurities. Then, it was left to in an acid solution (hydrochloric acid 0.1 M) for about 20 min to free the biomass ligand sites from metals (Fig. 1a). This step is necessary to make free all adsorbent active sites by other cations ensuring high process performance and high experiment reproducibility, irrespective of the algae collection site [20,42,43]. The choice of utilizing a 0.1 M molarity acid solution was driven by its non-aggressive behaviour towards the sorbent material [17,23].

Subsequently, thalli were dried on the thermostatic oven (MEMMERT)at 60 °C for about 24 h (Fig. 1b). The temperature of the oven was electronically checked by a specific sensor. Thalli were evenly placed above a filter paper to ensure the total water removal to favour the following shredding. Indeed, the sorption tests, the sample of *Ulva* sp. was shredded to increase the surface area involved in the process (size fraction of 0.5–1 cm).

2.2. Batch adsorption

Batch experiments were carried out to obtain the best equilibrium conditions. 2 g of dried material were placed into 200 mL of deionized water, under stirring for about 10 min to rehydrate it. After this step, a quantity of 10 g/L stock solutions of copper, iron (as ferrous iron), and zinc, prepared by the corresponding sulphates (as $CuSO_4{\cdot}5H_2O$, $FeSO_4{\cdot}7H_2O$ and $ZnSO_4{\cdot}7H_2O$, respectively) were added to reach the established metal concentrations. More in detail, iron and zinc concentrations were fixed to 50 mg/L. On the other hand, six tests were carried out using copper concentrations from 10 to 1500 mg/L. The pH was adjusted to 3.5 or 5.0 using 1 M sulphuric acid or 1 M sodium hydroxide and it was monitored during the whole experiment. pH conditions higher than 5.0 were not tested to exclude copper and iron precipitation in hydroxide form. The results of the MEDUSA software (proved by speciation analysis) demonstrate that the three considered metals (copper, ferrous iron and zinc), at the selected pH range, remain soluble and no precipitation phenomena take place (Fig. 2) [44].

Starting from the metal addition, 5 mL of solution was periodically collected to determine the metal concentration trend over time, i.e., the reaction kinetics. Samples were centrifuged (3000*g* for 5 min centrifuge 5810 R) to eliminate any suspended material, preventing the sorption process from going on, and were diluted with 5 mL of acidic water at pH 2 to stabilize metals before the analytical determinations (final dilution

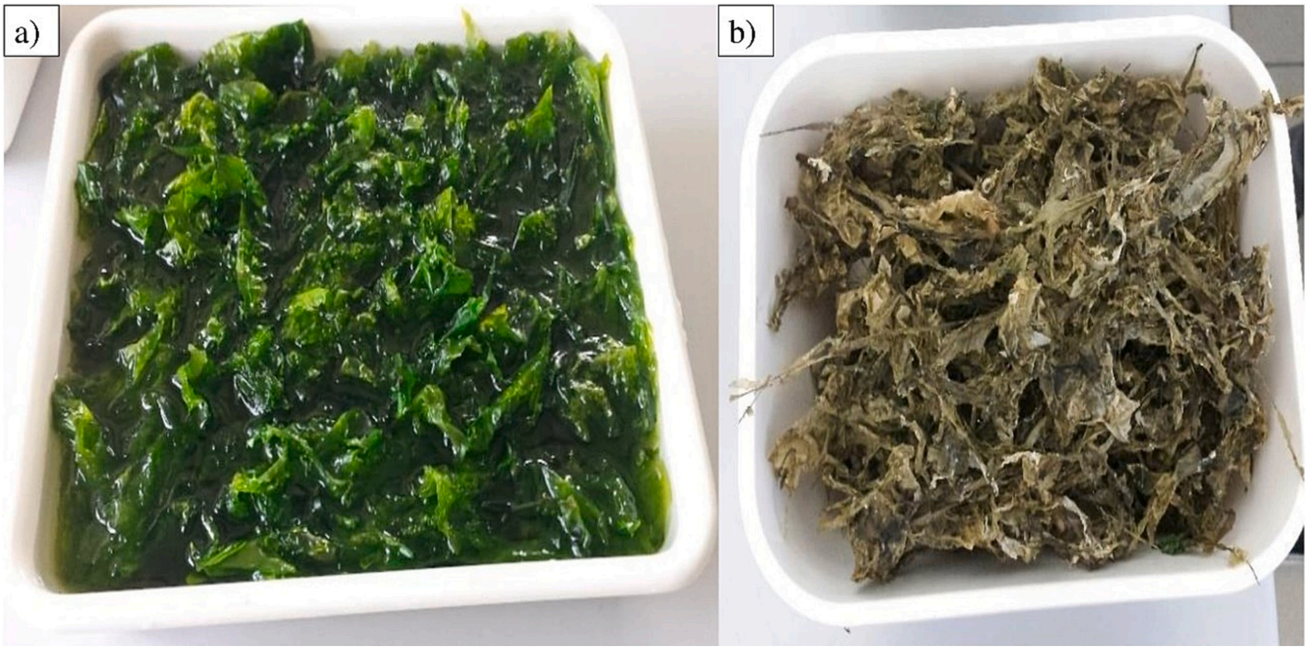

Fig. 1. *Ulva* spp. pre-treatment (a) and dried algae (b).

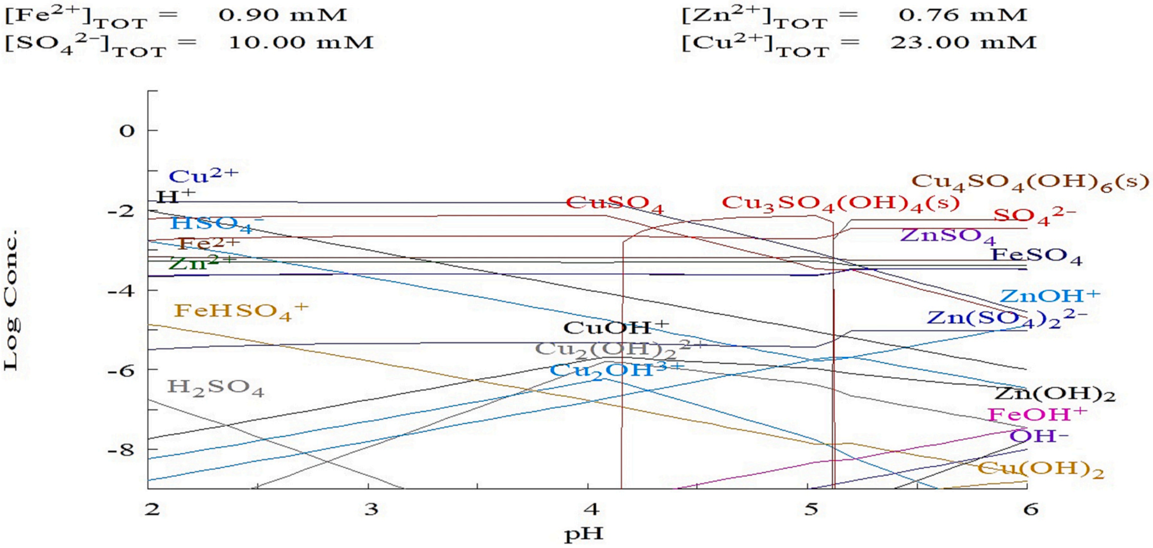

Fig. 2. Results of the MEDUSA software for the solubilization of the three considered metals.

of 2×). Iron concentrations were determined by spectrophotometry using the potassium thiocyanate dye while the concentrations of copper and zinc were obtained using Atomic Absorption Spectroscopy (AAS). Metal uptake, q_e (mg/g) was calculated considering the variation in the metal concentrations before and after sorption using the equation according to Pennesi et al. (2013) (Eq. (a)) [23]:

$$q_e = \frac{V\left(C_i - C_{eq}\right)}{W} \tag{a}$$

where, V corresponds to the volume of the solution (L), C_i and C_{eq} (mg/ L) are the initial and equilibrium metal concentrations, respectively, and W (g/ L) is the biomass concentration. Experimental results were then fitted to Langmuir adsorption isotherm [45] by nonlinear regression analysis to obtain the constants of the equation (Eq. (b)), applied for each metal system studied:

$$q_e = \frac{q_{max} {}^* C_O}{k_S + C_O} \tag{b}$$

where q_e is the sorption capacity (mg/ g), q_{max} is the maximum adsorption capacity (mg/ g), C_O is the initial concentration (mg/ L) and k_S is the equilibrium constant of the sorption reaction (mg/ L). The model utilized stated that all binding sites had an equivalent similarity for the adsorbable with the consequent creation of a monolayer of adsorbed particles [46,47].

2.3. *Experimental design in batch adsorption*

The solutions of single (Cu), double (Cu-Zn; Cu-Fe), and multi (Cu-Zn-Fe) metal- systems, (able to simulate the solution resulting from the PCBs recycling treatment) were used to evaluate the copper biosorption ability of *Ulva* spp. material. Table 2 lists all factors and levels studied.

Table 2
Items and levels examined in the study of copper biosorption by *Ulva* sp. also consider its interaction with iron and zinc.

Experimental system	Factorial projects			
	Items	Levels		
	Metal	Cu	Zn	Fe
Single metal system	Conc. (mg/L)	10, 20, 50, 100, 500, 1500	0	0
	Initial pH	3.5	5.0	
Double metal system	Conc. (mg/L)	10, 20, 50, 100, 500, 1500	50, 0	0, 50
	Initial pH	3.5	5.0	
Multi-metal system	Conc. (mg/L)	10, 20, 50, 100, 500, 1500	50	50
	Initial pH	3.5	5.0	

All the experimental processes were conducted at room temperature (20–25 °C) keeping constant both the total volume (200 mL) and the sorption material concentration (2 g/L). Sorption isotherms were evaluated at different initial pH (i.e., 3.5 and 5.0) both in the single, double, and multi-metal systems.

2.4. Fixed-bed column

The experiment was performed in a fixed-bed adsorbing column (10.5 cm × 1.00 m). It was a glass tubular vessel, where the algae material (200 g of dried algae) was packed, and the fluid wastewater was continuously flowing, at a constant rate, through the adsorbent bed with a downflow setting.

The column was packed with *Ulva* sp. and expanded clay, used as support material, with a algae and support material ratio of 1:3 (w/w), reaching a height of about 50 cm. Algae were plugged wet to facilitate the right packing, since both their weight and their volume are much larger than those of the dry material. Glass wool was placed on the top and on the bottom of the column to obtain the double benefit of ensuring a good distribution of solution and preventing the biomass loss. The wastewater solution (30 L of 100 mg/L of copper as $CuSO_4$, pH 5.0) was fed to the top of the column using a peristaltic pump which ensure a constant flow rate of approximately 15 $cm^3\ min^{-1}$. The concentration of the effluent stream was monitored by periodic sampling, until the saturation of the sorbent to obtain the breakthrough curves (Fig. 3).

The theoretical duration of the adsorbent bed was calculated using the mass balance on the metal given by the following equation that equals the quantity of the adsorbed metal with the one remained inside the column (c):

$$q_e{}^*M = (C_O - C_B)^*V \tag{c}$$

where q_e is the sorption capacity (8.56 mg/ g) (estimated by the previous Langmuir adsorption isotherm considering the copper initial concentration equal to 100 mg/L), M is the mass of the algae put into the column (g), C_O is the inlet metal concentration (mg/ L), C_B is the breakthrough concentration set as 10 % of the inlet metal concentration (mg/ L) and V is the volume of the treated solution (L). From the estimated volume in the Eq. (d), the time required to reach the break-through (t_B, min) is predicted by the following Eq. (d):

$$V = Q^*t_B \tag{d}$$

where Q is the volumetric flow rate ($cm^3\ min^{-1}$).

Nonlinear regression analysis of the experimental results was used to determine the Thomas model parameter [27] (e):

$$\frac{C_{eff}}{C_O} = \frac{1}{1 + e^{\frac{k_{TH} q_e \rho_P A L}{Q} - k_{TH} C_O t}} \tag{e}$$

where C_{eff} and C_O are the effluent and initial metal ion concentration, respectively (mg cm^{-3}), k_{TH} is the Thomas rate constant ($cm^3\ min^{-1}\ mg^{-1}$), q_e is the maximum metal sorption capacity of the algal biomass (mg/ g), ρ_P is the packing density bed height of column (g cm^{-3}), A is the cross sectional area of column (cm^2), L is the bed height of column (cm), Q is the volumetric flow rate ($cm^3\ min^{-1}$) and t is the operating time (min). The column was eventually regenerated using hydrochloric acid 0.1 M recovering the metal ions in a solution ten times more concentrated than the treated wastewater.

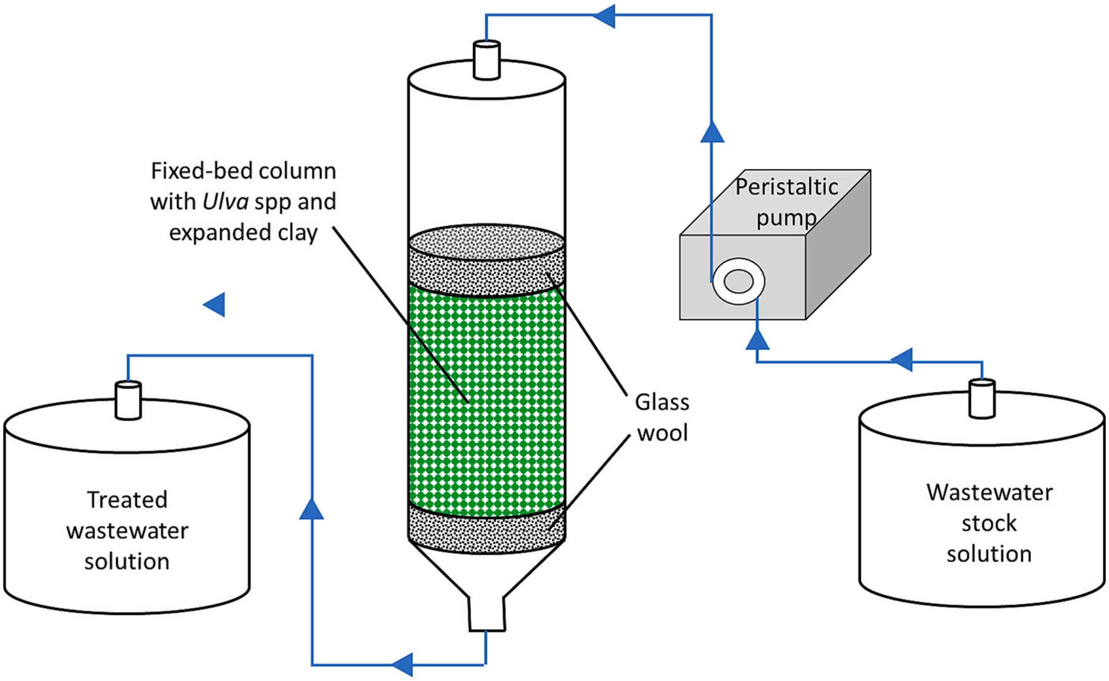

Fig. 3. Fixed-bed column scheme used in the adsorption experiments with *Ulva* sp.

3. Results

Ulva sp. sorbent material used in the experimental phase was composed by *U. lactuca* and *U. linza* which showed similar structural characteristics. Thalli were arranged to form laminar structures composed by two cell layers as showed in Fig. 4.

3.1. Sorption equilibrium isotherms

Fig. 5 shows the adsorption equilibrium isotherms of copper in single- and multi-metal systems at two different initial pH values (i.e., 3.5 and 5.0) concerning the biosorbent materials used (i.e., *Ulva* sp.). The process efficiency improved with pH increase (Fig. 5b). However, at both pH conditions, sorbent material showed a general increase in the adsorption capacity when copper is associated with iron [Cu-Fe] in the treated solution, while the presence of zinc [Cu-Zn] usually reduced the sorption efficiency (Fig. 5). More in details, Cu removal efficiencies of 30 % and 43 % were reached in Cu-Fe system, compared to the single-system, where the percentages were 25 % and 30 %, at pH 3.5 and 5.0, respectively. The multi-metal systems formed by all metals [Cu-Zn-Fe] showed the worst adsorption data in both considered pH values (Fig. 5).

A deeper analysis showed that at an initial pH value of 3.5 *Ulva* sp. had a maximum uptake sorption capacity of about 44 mg/g (Fig. 5a), while at initial pH 5.0 the biomaterial adsorption capacity increased up to of 65 mg/g (Fig. 5b). The correlation coefficients (R^2) were found to be extremely high indicating that the metal ions sorption in this study can be described using the Langmuir model. Several low values of C_{eq} (up to 300 mg/L) were tested to study the sorption trend within the first order kinetic zone. The highest C_{eq} allowed to understand the saturation tendency of sorption equilibrium process.

3.2. Competition among cations in multi-metal systems

Fig. 6 shows the iron and zinc uptakes as a function of the initial copper concentration, considering the two initial pH values analysed (i.e., 3.5 and 5.0). The sorption capacity of these metals decreased with the increase of copper concentration in the solution, regardless of initial pH. Moreover, the maximum iron uptake was much greater than zinc adsorption and this trend can be observed in all the experiments performed.

3.3. Break-through curve

For the characterization of *Ulva* sp. materials as biosorbent, the adsorption isotherm curves were performed using a fixed-bed column (Fig. 7). Moreover, these experiments were important for adsorptive separation technologies [48]. In the dynamic flow test, an initial pH value of 5.0 was selected since it gave the best data for static adsorption. Experimental data followed the typical trend for the column adsorption as reported in the literature [18]. The time at the breakthrough point was about 24 h, very close to the result of the mathematical predictions ($t_B = \frac{q_e \bullet M}{(C_0 - C_B) \bullet Q}$, Eqs. (c) and (d)). Furthermore, the biosorbent saturation was reached immediately after the breakthrough time (Fig. 7). The correlation coefficient obtained in this study ($R^2 = 0.96$) demonstrated that the absorption of metal ions on the biomaterial in the fixed bed column can be described using the Thomas model [49,50].

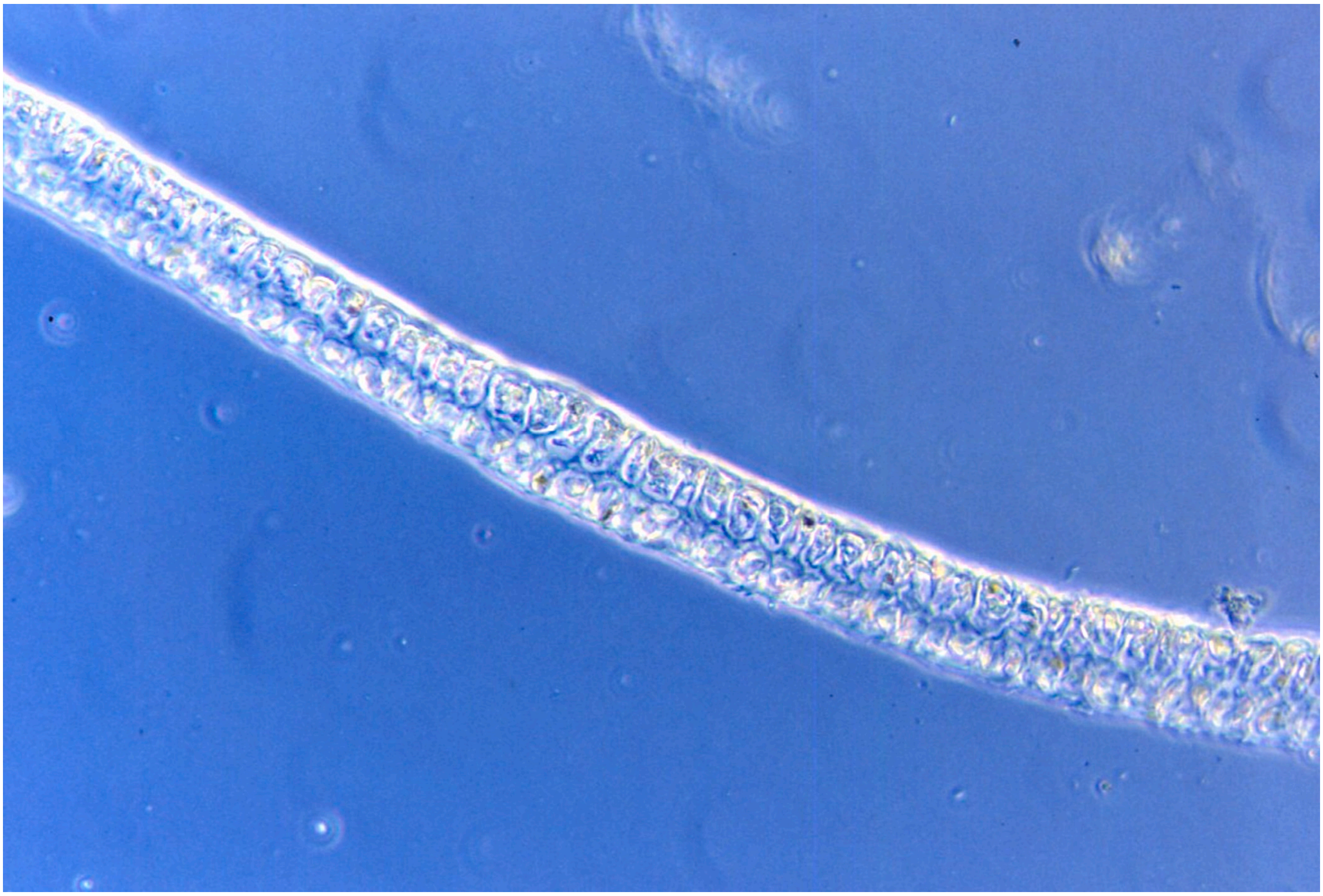

Fig. 4. Transversal section of the laminar thallus of *Ulva lactuca* (Light microscopy, Zeiss 40× Objective) from Passetto beach (Ancona, Italy).

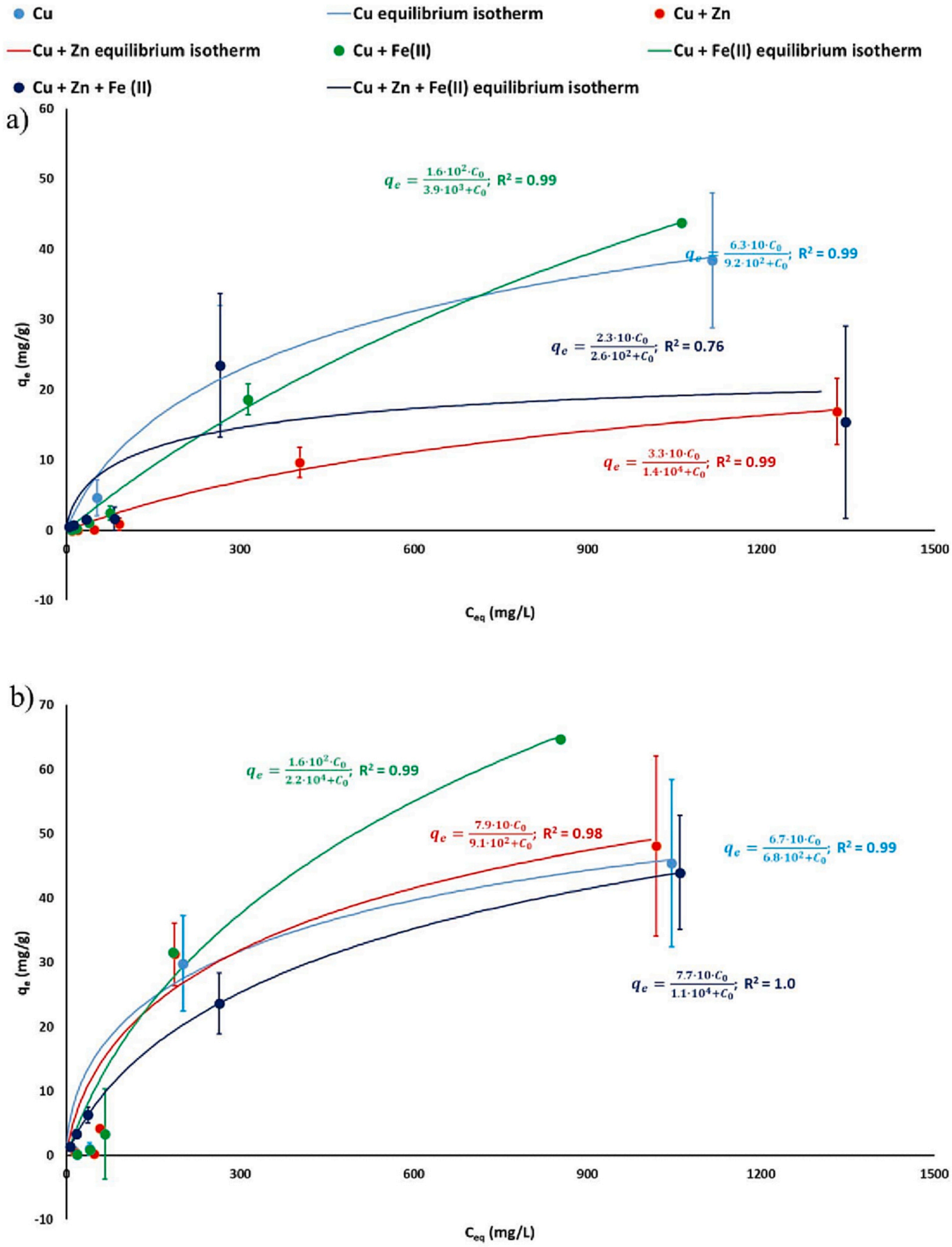

Fig. 5. Adsorption equilibrium isotherm of single and multi-metal systems on *Ulva* sp. at initial pH 3.5 (a) and 5.0 (b).

4. Discussion

The biotechnological approach for the recycling of PCBs produces wastewater flows with low concentrations of metals, but not yet fitting for discharging into the sewer. Metal contamination can be considered one of the most hazardous environmental issues due to the persistence and the tendency of these pollutants to accumulate in living beings. For this reason, the presence of metal ions in a water body prevents its potential uses requiring depuration treatments to reach the concentrations defined by law to avoid negative consequences [51]. However, traditional techniques often result in low efficiency and high costs and, in many cases, there is the additional issue of generating by-products that need to be disposed of [15]. So, more and more scientific studies are focusing on the development of sorption processes using low-cost and renewable materials such as algae [17,38,39,52]. This study has investigated the possibility to use green macroalgae, commonly present on the Adriatic beaches (often removed and considered a waste since they become an issue for tourist activity) as metal biosorbent for the treatment of industrial wastewater. Green macroalgae may have excessive growth, especially in closed and nutrient-rich areas, so their use as biosorbent can be an alternative way to enhance this waste material [12,20]. Biomaterials employed were previously washed with hydrochloric acid to free the ligand sites because it was demonstrated that algae collected in a semi-polluted area close to harbours or refineries have functional groups partially occupied so their sorption capacity decreases [12,20]. Also, biomass fragmenting was performed to improve the sorption process, as reported by other literature data such as in Ajjabi and Chouba (2009) [53]. The authors showed how fragmented algae result to be better sorbents compared to the entire algae. The size fragment analysed were: size 1 (entire algae), size 2 (100–315 μm) and size 3 (500–800 μm) [53]. This was probably due to the largest surface area provided by smaller biosorbent particles which led to reach the

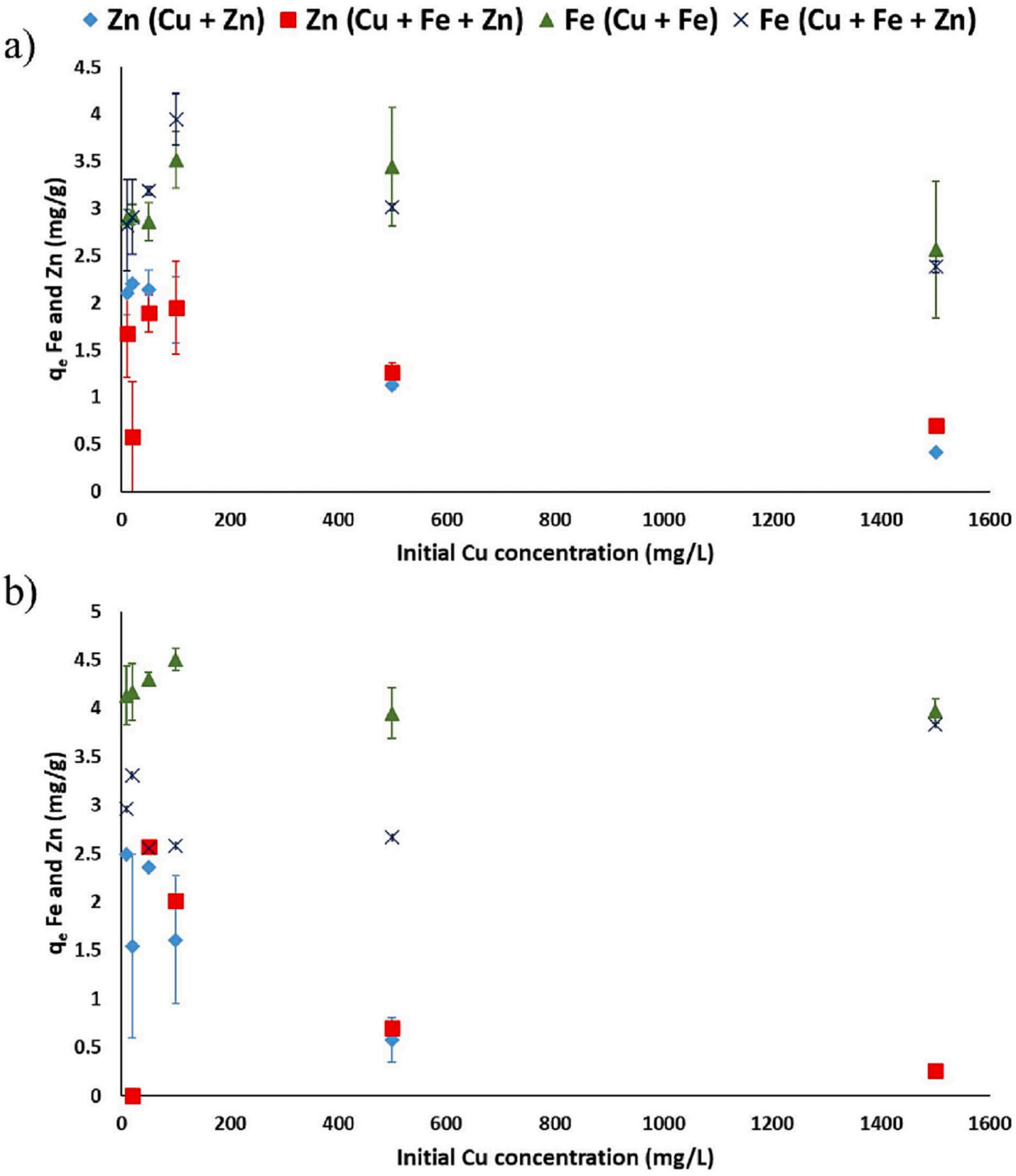

Fig. 6. Zinc and iron adsorption on *Ulva* sp. in multi-metal systems at initial pH 3.5 (a) and 5.0 (b) expressed as a function of initial copper concentration.

equilibrium faster. The results achieved in the present paper showed that the metal uptake resulted be faster in the first 15 min of contact, in which biosorbent reaches almost its maximum sorption capacity because of the large number of free ligand sites available, as also reported by other authors [54]. After that, a slowing down can be observed corresponding to the difficulty in binding to the remaining functional groups due to repulsive forces between the metal ions in the solution and those onto sorbent material. The same trend was observed by Lee and Chang (2011) studying copper and lead removal by *Cladophora* and *Spirogyra,* whose sorption occurred mostly within the first few minutes of the experiments and declined gradually until the optimum contact time, showing no appreciable changes after 30 min [55]. The obtained adsorption isotherms clearly highlighted the pH effect on the sorption process as it was also explained by Areco et al. (2012), using *Ulva lactuca* to remove copper, cadmium, and zinc [40]. The high dependence on pH is probably due to both the speciation and the solubility of metals and to the dissociation degree of functional groups on biomass surface [56]. Assuming the ion exchange as the dominant mechanism that takes place in biosorption, the high proton concentrations compete with metals to bond the active sites when the pH is extremely low, leaving metal ions in the solution [57]. Moreover, Deng and Ting (2005) suggested that, at low pH values, hydronium ions are close to the ligand sites preventing the copper ions approach due to repulsion forces [58]. Ebrahimi et al. (2016) demonstrated that enhancing pH, biosorbent surface charges become more negative so the electrostatic interactions are stronger, and the sorption efficiency increases [59]. Considering copper, iron, and zinc, the best initial pH value resulted to be 5.0 in agreement with those reported in the literature [53]. As shown in other studies, the binding capacity is due to both the metal ions and the biosorbent properties [60,61]. Biosorbent material contains weak acidic and basic groups whose dissociation state control metal cations binding with pH ranging from 2.5 to 5.0 [62]. In particular, green macroalgae (i.e., *Ulva* spp.) cell wall matrix is made of complex heteropolysaccharides with carboxyl, amino, and sulphate groups involved in the sorption process [19]. According to Jafari and Senobari (2012), at low pH values these binding sites are protonated so metal cations are rejected, while negative charged groups are exposed increasing pH thus leading to the attraction of metals in solution [60]. Considering the results of the present study, it can also be noticed a marked rise in the uptake capacity, corresponding to the increase of the initial metal concentration. The possible

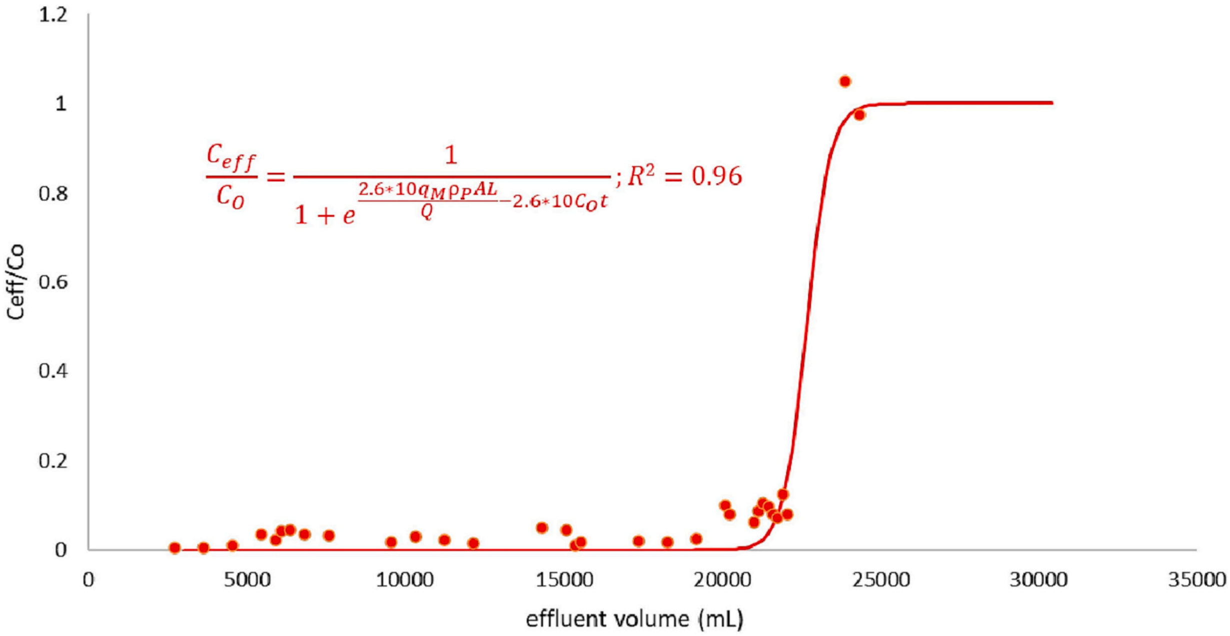

Fig. 7. The break-through curve of copper contaminated solution at pH 5.0.

explanation is the highest availability of metal ions in the solution that provides a huge driving force to overcome mass transfer resistance between solid and liquid phases, enhancing the probability of casual bonds [54]. Our study demonstrated a higher biosorption capacity compared to previous investigations that explored the adsorption properties of *Ulva* sp. for sequestering copper from aqueous solutions [62–64]. However, Karthikeyan et al. (2007) achieved a slightly higher maximum biosorption capacity at a pH of 5.5 ± 0.5, specifically 73.5 mg/g, compared to our results of 65 mg/g [39]. This comparison underscores the strong performance of the adsorbent material derived from *Ulva* spp. in effectively copper recovering, demonstrating its effectiveness in the sequestration process.

Another important aspect that comes out from this study is that in multi-metal systems, the competition for the active sites is established by the cations present in the treated solutions. The different metal ions' affinity for the biomaterial may lead to sorption inhibition or enhancement and this feature seems to be related to the electronegativity, ionic radii, surface state, and steric configuration of each metal. All these parameters are resumed in the k_s constant of the Langmuir adsorption isotherm that can be compared with each other to see which metal ion shows the best affinity for the analysed biosorbents [65]. According to the results of this work, it seems that the presence of iron in wastewater increases copper uptake while zinc often reduces sorption capacity as it probably competes with copper for the binding sites. As it can be expected, both iron and zinc removal decrease with the enhancement of copper concentration in solution for all the metal systems analysed. This result suggests that the high amount of copper ions increases the probability of interaction with the biosorbent at the expense of the other cations contained in wastewater, overcoming their major affinity. Biosorption can be considered a competitive process only if it is implemented in continuous systems to treat huge volumes of wastewater, although few studies have focused on it on an industrial level yet [66–68]. To reach this purpose, fixed-bed columns were designed using experimental data resulting from batch systems, used to determine the optimum operative conditions. Scientific studies demonstrated that break-through time, i.e., the time required to reach a limit concentration in the outlet stream, is influenced by bed height, flow rate, and particle diameter [69]. Using the parameters chosen for the performed experiment, the column worked for about an entire day and was able to treat more than 30 L of copper-contaminated wastewater. The proposed system it is very attractive to decrease the operating costs, to recover metals removed from wastewaters from the resulting concentrated solutions, to regenerate the biosorbent material [44]. So, it can also be avoided the additional problem of disposal of biomass which has become hazardous due to metals bound on its wall [40]. The desorption of metal ions by algae biomass was studied using different concentrations of deletants to evaluate both efficiencies of desorption and preservation capacity of the biomass. Several studies showed that high amounts of metal ions recovery are obtained using hydrochloric acid [70,71]. The performed experiment proved that the use of hydrochloric acid 0.1 M results in a copper recovery of 100 % using a solution volume equal to 10 % of the treated one (3 L) with a final Cu concentration of 1.0 g/L. This step, comparable with the biomass pre-treatment described in materials and methods section, guarantee the biomass re-use for two or three cycle, at least, without the material damage. Thereafter, the metal removal allows the possible biomass incineration (with energy recovery) with lower emission releases. According to Kratochvil and Volesky (1998), after the desorption a neutralizing process with an alkaline solution could be needed to restore the metal sorption potential of biosorbent materials [72]. So, if this additional process isn't necessary, it will make the used macroalgae very attractive for metal removal.

5. Conclusions

The study demonstrated the effectiveness of using green macroalgae as a biosorbent for the treatment of industrial wastewater. The results showed that the sorption process was pH-dependent and the best initial pH value for copper, iron, and zinc was found to be 5.0. The binding capacity was due to the presence of weak acidic and basic groups on the biosorbent material, and the increase in the initial metal concentration resulted in a marked rise in the uptake capacity. The use of macroalgae from green tides as a biosorbent not only provides a low-cost and renewable alternative for the treatment of industrial wastewater, but also offers a solution for the recycling of waste material commonly present on the Adriatic beach and commonly disposed in landfilling sites. Since the synthetic solution used for the experiments simulates that resulting from an innovative biotechnology for PCB recycling, the proposed solution could be integrate within the process (as an alternative to the most common chemical approaches), further increasing its biotech footprint. Overall, the findings of this study carry significant implications since it supplies a solution to solve multiple issue, such as the purification of metal-contaminated wastewaters, the recovery of copper, classified as strategic element by European Commission and the enhancement of a biomass, currently managed as a waste. Considering all these strengths, the developed technology is able to fit the principles of circular economy.

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Declaration of competing interest

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.

Data availability

Data will be made available on request.

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