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Supplementary Material

Metal biosorption onto non-living algae: a critical review on metal recovery from wastewater

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Methodology

The dry brown macroalgae *Sargassum sp*. was supplied by ALGAplus Lda. The algae was frozen with liquid nitrogen and immediately grinded. The obtained product was mechanically sieved (< 200 µm). Acid mine drainage (AMD) was collected in Minas de São Domingos, Portugal. The AMD pH was adjusted from 1.7 to 4.0 or 5.0 by addition of NaOH and subsequent determination in a Mettler Toledo SevenMultiTMdual pH meter (± 0.02). Metal content, Ca^{2+}, K^+ and Cl^- were determined via total reflection X-ray fluorescence spectrometer (TXRF) using a Picofox S2 (Bruker Nano). Quartz carriers were coated with 10 µL of silicon in an isopropanol solution and dried at (353 ± 1) K for at least 20 min. The diluted sample containing a known yttrium concentration was applied to the sample carrier and dried for at least 30 min. The sorption capacity (*q*, mmol·g^{-1}) of the biomass was calculated according to Equation 1:

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

where C_0 (mmol·g^{-1}) is the initial metal concentration, C_t (mmol·g^{-1}) is the metal concentration at that time (*t*), *V* (L) is solution volume, and *m* (g) is the dry biomass mass. All studies were conducted in an orbital shaker (IKA KS4000 ic control, 200 rpm) in Schott Duran® glassware (100 mL) at (303 ± 1) K for 6 h. An algae-to-metal ratio of 0.83 was maintained throughout the experiments, meaning that the added algae was customized to the amount of metal in the AMD. *Sargassum sp.* was added to all solutions except to control solutions which were used to monitor possible metal losses. Sorbent suspensions were collected and centrifuged to remove residual biomass. All assays were performed in triplicate. Synthetic solutions containing a total of 75 ppm of Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} were prepared by adding the proper amount of metal salts to deionized water. The pH of the synthetic solutions was adjusted to 5. $CoSO_4·7H_2O$ (> 99 wt %), $CuSO_4·5H_2O$ (> 99 wt %) and $ZnSO_4·7H_2O$ (> 99 wt %) were acquired from Merck. $NiSO_4·6H_2O$ (> 99 wt %) and calcium chloride anhydrous (>95 %) were purchased from Riedel de Haen and Panreac, respectively. The prepared multi-metallic solution was then spiked with 8 to 204 mg·L^{-1} Ca^{2+} to better understand the effect of this ion on metal sorption. Yttrium standard (1000 mg·L^{-1} of Y(III) in 2 wt % HNO_3), Triton® X-100 (for analysis) and poly(vinyl alcohol) (> 99 wt %) were obtained from Sigma Aldrich. Synthetic solutions were prepared using ultra-pure water from a Millipore filter system MilliQ®.

Table S1. Total metal sorption capacity of non-living algae in real wastewater, including AMD, industrial wastewater (IWW), tannery sludge and treated IWW.[1–5]. The numbers following the wastewater label refer to their respective pH value.

Wastewater	Non-living algae	q_{total} (mmol·g^{-1})	Reference
AMD 1.7	*Sargassum sp.*	0.668	This work.
AMD 4.0		0.114	
AMD 5.0		0.088	
AMD 4.0	*Fucus vesiculosus*	0.044	[5]
AMD 5.0		0.086	
IWW 4.0		1.044	
IWW 5.0		1.035	
IWW 1.9	*Pelvetia canaliculata*	2.100	[2]
IWW 8.6	*Porphyra leucosticta*	0.006	[3]
IWW 6.0	*Laminaria hyperborea*	0.023	[4]
Tannery sludge	*Rhizoclonium hieroglyphicum*	2.776	[1]
Treated IWW		0.010	

Table S2. Comparison of cost (€·kg^{-1}) and sorption capacity (mmol·g^{-1}) of different Cu^{2+} sorbents and respective bibliographic sources.

	Sorbent	Cost (€·kg^{-1})	Sorption capacity (mmol·g^{-1})	Reference
Algae	*Palmaria palmata*	117[a]	0.20	[6]
	Gracilaria gracilis	54[a]	0.59	[7]
	Ulva rigida	84[a]	0.34	[8]
	Fucus vesiculosus	44[a]	1.81	[9]
	Spirulina sp.	90[a]	1.07	[10]
Commercial	Amberlite IR-120	91[b]	1.03	[11]
	C-160 resin	300[c]	1.64	[12]
	Lewatit TP-207	304[b]	1.08	[13]
	Activated carbon	2.9[a]	0.58	[14]
	Bentonite	128[b]	3.92	[15]
	Dowex® 50WX4	880[d]	1.12	[9]
Waste	Eggshells	2.4[a]	6.65	[16]
	Banana peels	14[e]	1.12	[17,18]
	Scrap tire	0.4[a]	0.55	[19]
	Coffee waste	0.9	0.93	[20]
	Walnut shell	0.4[a]	0.46	[21]
	Rice husk	1.1[a]	0.65	[12]
	Pristine steel slag	0.3[e]	1.73	[22,23]
	Crab carapace	2.3[a]	1.25	[9]

[a]Marketplace acquisition price; [b]Sigma-Aldrich acquisition price; [c]Lenntech acquisition price; [d]Fisher Scientific acquisition price; [e]taken from literature;

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