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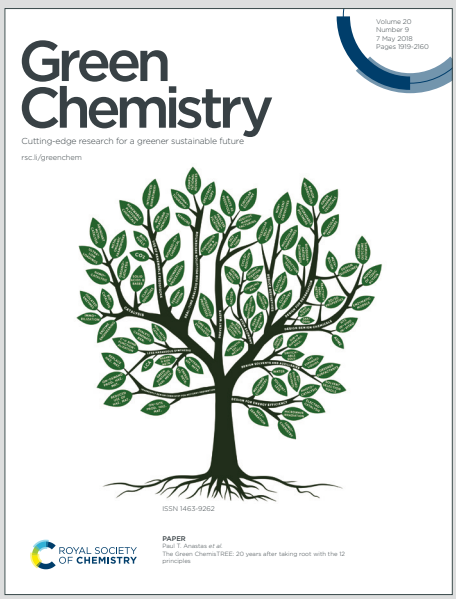

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Microalgae: A sustainable adsorbent with high potential for upconcentration of indium(III) from liquid process and waste streams

Nina Ricci Nicomel[a,*], Lila Otero-Gonzalez[a], Larissa Arashiro[a,b], Marianna Garfí[b], Ivet Ferrer[b], Pascal Van Der Voort[c], Kim Verbeken[d], Tom Hennebel[e], Gijs Du Laing[a]

[a] Laboratory of Analytical Chemistry and Applied Ecochemistry, Department of Green Chemistry and Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

[b] Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya·BarcelonaTech, c/ Jordi Girona 1-3, Building D1, 08034 Barcelona, Spain

[c] Center for Ordered Materials, Organometallics and Catalysis, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium

[d] Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark Zwijnaarde 46, 9052 Zwijnaarde, Belgium

[e] Center for Microbial Ecology and Technology, Department of Biochemical and Microbial Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

* Corresponding author:

E-mail: NinaRicci.Nicomel@UGent.be

Tel.: +3292646131

Fax: +3292646232

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ABSTRACT

Indium (In) is a critical raw material heavily demanded in the optical-electronics industry. With its high supply risk, sustainable technologies are needed to recover In(III) from secondary sources, such as leachates from sludge produced by zinc processing industries (e.g., jarosite) and indium tin oxide etching wastewater. This study presents In(III) biosorption as an eco-friendly alternative to conventional physicochemical recovery technologies. The characteristics of In(III) adsorption by microalgal biomass were investigated in batch experiments. Adsorption isotherm was well-fitted by the Freundlich model. The estimated maximum adsorption capacity of In(III) was 0.14 mmol/g of microalgae, which is higher than that of some chemically modified adsorbents reported in the literature. Selectivity of In(III) was also observed over other metals, such as Cu(II), Zn(II), and Al(III). Furthermore, the microalgae biosorbent was regenerated using a 0.1 M HCl solution, with up to 80% In(III) recovery, for several cycles. From these results, microalgae prove to have potential for In(III) biosorption from aqueous solutions.

Keywords: Indium, microalgae, biosorption, desorption, wastewater

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1. Introduction

Indium (In) is a relatively rare metal present in minor amounts in the Earth's crust at approximately 0.05 ppm and 0.072 ppm for the continental and oceanic crusts, respectively (Schwarz-Schampera and Herzig, 2002). Because of these low concentrations, the mining of In(III) as primary commodity is uneconomic (Schwarz-Schampera, 2014). Nonetheless, traces of In(III) occur in some minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), cassiterite (SnO_2), and galena (PbS) (Felix, 2000), which enables In(III) extraction from the by-products formed during zinc, copper, and tin production (Alfantazi and Moskalyk, 2003).

In(III) is extensively used in electronic and energy-related industries, particularly in the production of indium tin oxide (ITO) thin-film coatings for flat-panel displays and solar cells (Hasegawa et al., 2013; USGS, 2018). Due to this increasing demand and limited supply of primary resources, the European Commission has listed In(III) as one of the 27 raw materials critical for the European Union (EU) (European Commission, 2017). Two particular concerns for In(III) criticality are the geopolitical challenges associated with the concentration of reserves and production in particular countries and the low substitution and recycling rates. For example, In(III) from waste liquid crystal display (LCD) panels is barely recycled (European Commission, 2017; Sun et al., 2017). For these reasons, there has been a growing interest in the recovery of In(III) from secondary sources, such as leachates from polymetallic sludge produced during zinc refining and waste solutions from ITO etching processes (Chou et al., 2016; Orko et al., 2016). For instance, jarosite ($MFe_3(SO_4)_2(OH)_6$, where M is a metal cation (e.g., Na, K, Pb) or ammonium) is a solid industrial byproduct produced from the iron removal in the hydrometallurgical zinc winning process (Wegscheider et al., 2017, Orko et al., 2016). This sludge contains some critical raw materials, including In(III) and Ag(I). In a pre-feasibility study of processing jarosite sludge to value-added products performed by Orko et al. (2016), the In(III) content in jarosite was approximately 0.9 mol/t, which is equivalent to 0.36

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megamoles In/yr for a plant processing 400,000 t/yr of jarosite. Being an abundant source of In(III) and other critical metals, interest in jarosite leaching has been increasing during the last few years, especially taking into account that worldwide jarosite production ranges from 5 to 6 Mt per year (Wilson et al., 2016). Depending on the leaching agent and operational parameters used in leaching the jarosite sludge, the concentration of In(III) in the leachate normally ranges from 0.5 to 2.2 mM (Koleini et al., 2010; Zhang et al., 2016).

Many technologies have been proposed for In(III) recovery from liquid process and waste streams, with solvent extraction and commercial ion exchange resins being two of the most widely used (Yang et al., 2013; Chou et al., 2016; Fortes et al., 2003). However, these conventional methods present disadvantages, such as high reagent and energy requirements, high capital and operational costs, and generation of toxic sludge or other waste products (Ogi et al., 2012). Furthermore, when In(III) concentration of the stream is low, these technologies are unfavorable because of the resulting low recovery (Hasegawa et al., 2013). For instance, applying solvent extraction to dilute streams would require an aqueous/organic solvent ratio of about 1 to provide satisfactory phase separation (Tarkan and Finch, 2005). However, maintaining this ratio would not result to concentration enrichment. In many cases, waste streams have dilute In(III) concentrations, such as those obtained from leaching end-of-life LCD panels (Rocchetti et al., 2015). Thus, it is important to develop more economical, effective, and environment-friendly methods to recover In(III).

Biosorption can be an alternative technology considering that a number of biosorbents can effectively bind and concentrate metals even from very dilute solutions (Ogi et al., 2012). This technique has not been much explored for In(III) recovery, although it presents a great potential and an eco-friendly alternative to conventional physicochemical technologies. Among widely available biosorbents, microalgal biomass possesses relatively high binding capacities for several metals (Wilde and Benemann, 1993; Aksu, 2002). This can be explained by the presence

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of carboxylic, hydroxyl, amino, phosphate, and sulfhydryl groups in the microalgal cell wall that can act as metal binding sites (Suresh Kumar et al., 2015). To date, the potential of using microalgal biomass to remove and/or recover In(III) from aqueous solutions has not been investigated.

In the present work, the use of microalgal biomass was studied for the removal and recovery of In(III) from aqueous solutions. Different process parameters—pH, contact time, initial indium concentration and presence of competing ions—were studied to assess their effects on In(III) biosorption. In addition, the desorption of indium ions adsorbed on the microalgal biomass was investigated with various desorbing agents.

2. Materials and methods

2.1 Chemicals

All chemicals were of analytical grade. Single-metal stock solutions (20 mM) were prepared by dissolving $InCl_3$, $AlCl_3$, $CuCl_2 \cdot 2H_2O$, $SnCl_2 \cdot 2H_2O$, $ZnCl_2$, and $FeCl_3 \cdot 6H_2O$ in ultrapure water (resistivity > 18.2 MΩ·cm). Solutions of 1 M HCl and 0.1 M NaOH were used to adjust the pH. The laboratory glassware was washed with 5% HNO_3 and rinsed with ultrapure water before use.

2.2 Cultivation and preparation of the microalgae biosorbent

Microalgae were cultivated in an outdoor pilot plant at the laboratory of the GEMMA Research Group (Universitat Politècnica de Catalunya, Barcelona, Spain). The system treated real municipal wastewater that received a screening pre-treatment before being pumped into a homogenization tank. The wastewater was pumped from this tank into a primary settler followed by a high rate algal pond (HRAP) (nominal volume of 0.5 m^3) and a secondary clarifier, where the effluent was separated from the microalgal biomass. The biomass used in this study was harvested during June 2017. The culture was dominated by *Chlorella* sp. and diatoms (mostly *Nitzschia* sp. and *Navicula* sp.), with the presence of grazers (ciliate and

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flagellate protozoans). More details regarding the operational parameters and microbiological characteristics can be found in a previous study (Arashiro et al., 2019). Harvested biomass was thickened in laboratory Imhoff cones stored at 4°C for 24 hours. Thickened microalgal biomass was then centrifuged at 4,200 rpm for 10 minutes (Orto Alresa, Spain). The supernatant was discarded and the microalgae paste was frozen at −80°C overnight in an ultra-freezer (Arctiko, Denmark) and finally lyophilized for 24 hours (−110 °C, 0.049 hPa) (Scanvac, Denmark). Because of its high pH, the microalgal biomass was repeatedly washed with ultrapure water and dried in an oven at 50°C for 24 hours. Afterwards, it was ground to a particle size <1 mm. Light microscope images of the microalgal biomass before and after grinding are shown in Figure S1 in the Supplementary Information. These indicate that the preliminary grinding does not affect the cellular structure and cell wall integrity of the microalgae.

2.3 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy spectra were used to identify the functional groups on the microalgal biomass surface and to determine which of these functional groups are possibly responsible for In(III) biosorption. FTIR measurements were performed on raw and In-loaded microalgal biomass using a Thermo Scientific Nicolet 6700 FT-IR Spectrometer. The In-loaded microalgal biomass was obtained by performing In(III) biosorption. Afterwards, the phase separation was done through centrifugation, wherein the supernatant was discarded and the pellet was dried at 50°C for 24 h. For both raw and In-loaded biosorbents, a dried and ground sample (ca. 15 mg), mixed with a few milligrams of potassium bromide (KBr), was placed on a disc of KBr powder pressed in a micro-cup. FTIR spectra were recorded within the wavenumber range of 400 to 4000 cm^{-1} with spectral resolution of 4 cm^{-1} and 256 scans. Background measurements were performed with pure KBr and automatically subtracted from each sample spectrum. All spectra were plotted using the Thermo Scientific™ OMNIC™ Specta software.

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2.4 Scanning electron microscopy

The effects of adsorption and desorption on the surface morphology of the microalgal biomass were investigated using scanning electron microscopy (SEM). The tests were conducted using raw, In(III)-loaded, and In(III)-desorbed microalgal biomass. Before measurement, the samples were fixed in 3% glutaraldehyde with 0.1 M phosphate buffer for 3 hours at room temperature. The samples were then rinsed three times with 0.1 M phosphate buffer for 10 minutes each. Afterwards, the samples were dehydrated for 10 minutes in each of the graded ethanol solutions of increasing concentration (i.e., 30%, 50%, 70%, 80%, 90%, 95%, and 100%). The dehydrated microalgal biomass was dried using the chemical drying agent hexamethyldisilazane (HMDS). The dried samples were mounted on a stub and gold-sputtered prior to measurement. The images of the microalgal biomass were taken with a JEOL JSM-7600F field emission scanning electron microscope.

2.5 Acidic and basic surface properties

The surface groups of the microalgal biomass causing the acidic and basic surface properties were estimated using Boehm titration (Boehm, 2002). Microalgal biomass (0.45 g) was added to a series of 50-mL centrifuge tubes containing 45 mL of the following solutions each: 0.1 M $NaHCO_3$, 0.05 M Na_2CO_3, 0.1 M NaOH, and 0.1 M HCl. The suspensions were shaken in an orbital shaker at 115 rpm. After 48 hours, these were filtered using membrane syringe filters of 0.45-µm pore size. Subsequently, 10 mL of each filtrate was titrated with either 0.1 M HCl or NaOH depending on the starting solution. The concentrations of the surface oxygen groups causing the acidic properties were calculated based on the following assumptions: (1) $NaHCO_3$ deprotonates carboxylic groups only, (2) Na_2CO_3 deprotonates carboxylic groups and reacts with lactones through hydrolytic ring opening, and (3) NaOH deprotonates both carboxylic and phenolic groups, and reacts with lactones through hydrolytic ring opening. Similarly, the amount of basic sites was calculated from the amount of HCl that reacted with the biosorbent.

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2.6 Effect of pH on indium biosorption

The effect of pH on indium biosorption was investigated to determine the optimum pH required for the adsorption kinetic and equilibrium experiments. An indium solution (0.15 mM) was prepared from the In(III) stock solution. Ten milliliters of this solution was transferred into each 12-mL polypropylene centrifuge tube containing 100 mg of microalgal biomass. To avoid precipitation of $In(OH)_3$, which starts at around pH 2.7 as determined from control experiments (Figure S2 in the Supplementary Information), the initial pH was adjusted to values from 1 to 2, considering the increase in the final pH of the solution once this is put in contact with the microalgal biomass. Samples were shaken in an orbital shaker at 115 rpm for 24 hours. Afterwards, the final pH was measured using a Thermo Scientific Orion Star A211 pH meter. The phase separation was done through filtration using membrane filters of 0.45 µm pore size. Indium concentrations in the filtrate were measured using inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer NexION 350). All experiments were conducted in duplicate and data are presented as mean values with standard deviation.

The removal efficiency and adsorption capacity of the microalgal biomass were calculated using equations 1 and 2, respectively.

$$Removal\ efficiency\ (\%) = \frac{C_0 - C_e}{C_0} x\ 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)\ x\ V}{m} \quad (2)$$

Where q is the amount of In(III) adsorbed per unit mass of microalgal biomass (mmol/g), C_0 is the initial In(III) concentration (mM), C_e is the equilibrium In(III) concentration (mM), V is the volume of In(III) solution (L), and m is the mass of the biosorbent (g).

2.7 Biosorption kinetic experiments

Batch experiments were performed to study the kinetics of In(III) adsorption on microalgal biomass. Samples were prepared as described in Section 2.6. The initial pH values of the

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solutions were adjusted to the optimum pH. Immediately after putting the biosorbent in contact with the In(III) solution, the suspensions were shaken for different time intervals ranging from 30 minutes to 24 hours. After the predefined intervals, each sample was filtered using a syringe-type membrane filter of 0.45 µm pore size to separate the biosorbent from the liquid phase. The In(III) concentrations of the filtrate were then determined by ICP-MS.

2.8 Biosorption equilibrium experiments

The adsorption of In(III) on microalgal biomass was assessed at different concentrations in order to study the effect of concentration on the amount of In(III) adsorbed and to determine the maximum adsorption capacity of the microalgal biomass. Batch biosorption experiments were performed using the same procedure described in Section 2.6, except that the optimum pH was used and that the initial In(III) concentration was varied from 0.05 to 10 mM. After reaching equilibrium, the final pH values of the samples were measured, followed by phase separation. The In(III) concentrations of the filtrate were measured using ICP-MS. The obtained results were fitted to Langmuir and Freundlich adsorption models, which are presented by equations 3 and 4, respectively. The adsorption isotherms and the corresponding parameters were determined using SigmaPlot Version 13.0.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (3)$$

$$q_e = K_f {C_e}^{1/n} \quad (4)$$

Where q_e is the amount of In(III) adsorbed per unit mass of microalgal biomass at equilibrium (mmol/g), q_{max} is the maximum adsorption capacity (mmol/g), b is the Langmuir adsorption equilibrium constant (L/mmol), C_e is the equilibrium In(III) concentration (mM), K_f is the Freundlich constant ($mmol^{1-1/n} L^{1/n}/g$) and 1/n is a dimensionless parameter that varies between 0 and 1.

2.9 Effect of competing ions on indium biosorption

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The competing ions studied in this work were Cu(II), Zn(II), Sn(II), Al(III), and Fe(III). Stock solutions were prepared by combing In(III) and the ion of interest. In order to allow competition for adsorption sites, the concentration of the competing ions should be high enough to saturate the microalgal biomass. By determining the maximum adsorption capacity of the microalgal biomass for each of the competing ions at an initial pH of 2 (Table S1 in the Supplementary Information), a concentration of 10 mM was chosen for the competing ions. The initial In(III) concentration was set to 1 mM and the initial pH of the solution was adjusted to around pH 2. Samples were shaken in an orbital shaker for 24 hours at 115 rpm. This was followed by phase separation through filtration, then by the analysis of In(III) concentrations using ICP-MS.

2.10 Desorption experiments

Prior to desorption, an In(III) adsorption experiment was first completed. This was carried out at pH 2 with an initial In(III) concentration of 0.15 mM. Specifically for this adsorption experiment, phase separation was carried out through centrifugation at 10,000 rpm for 10 minutes using an Eppendorf Centrifuge 5804 R. The amount of In(III) adsorbed by the microalgal biomass (m_{ads}) was calculated from the initial and final In(III) concentrations in the solution using equation 5.

$$m_{ads} = (C_0 - C_e)V \quad (5)$$

Where C_0 is the initial In(III) concentration (mM), C_e is the equilibrium In(III) concentration (mM), and V is the volume of In(III) solution (L).

For the desorption experiments, the supernatant was removed from the centrifuge tubes. This was followed by the addition of 10 mL of 0.1 M desorbing agent to the previously In-loaded microalgal biomass. Tested desorbing agents include HCl, HNO_3, NaCl, $CaCl_2$, and ethylenediaminetetraacetic acid (EDTA). The suspensions were shaken at 115 rpm using an orbital shaker at room temperature for 24 hours. The In(III) desorption efficiencies were

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calculated as the ratio of the amount of In(III) desorbed to the amount of In(III) adsorbed. After choosing the most favorable desorbing agent, the optimal desorption conditions (i.e., liquid-to-solid (L/S) ratio and desorption time) were determined.

For the regeneration experiments, five adsorption-desorption cycles were performed in the most effective desorption conditions. After each desorption step, the microalgal biomass was washed three times with Milli-Q water to remove traces of the desorbing agent. The biosorbent was dried afterwards at 50°C for 24 hours, and weighed to obtain the mass lost after the desorption step.

3. Results and Discussion

3.1 FTIR analysis

The FTIR spectra of the microalgal biomass (Figure 1) showed different characteristic peaks implying that a variety of functional groups may be present on the biosorbent's surface. These peaks were observed at around 3275 cm^{-1}, 3000-2840 cm^{-1}, 1600 cm^{-1}, 1525 cm^{-1}, 1200 cm^{-1}, and 1100 cm^{-1}, which are indicative of –OH, $–CH_n–$, C=O, C–N, P=O, and C–O–C groups, respectively. The shifts in band wavenumber or differences in vibration intensity between the spectra of raw and metal-loaded biosorbents may indicate the functional groups primarily involved in metal biosorption (Dmytryk et al., 2014). For the spectrum of the In-loaded microalgal biomass, marginal differences were observed compared to that of the raw microalgal biomass.

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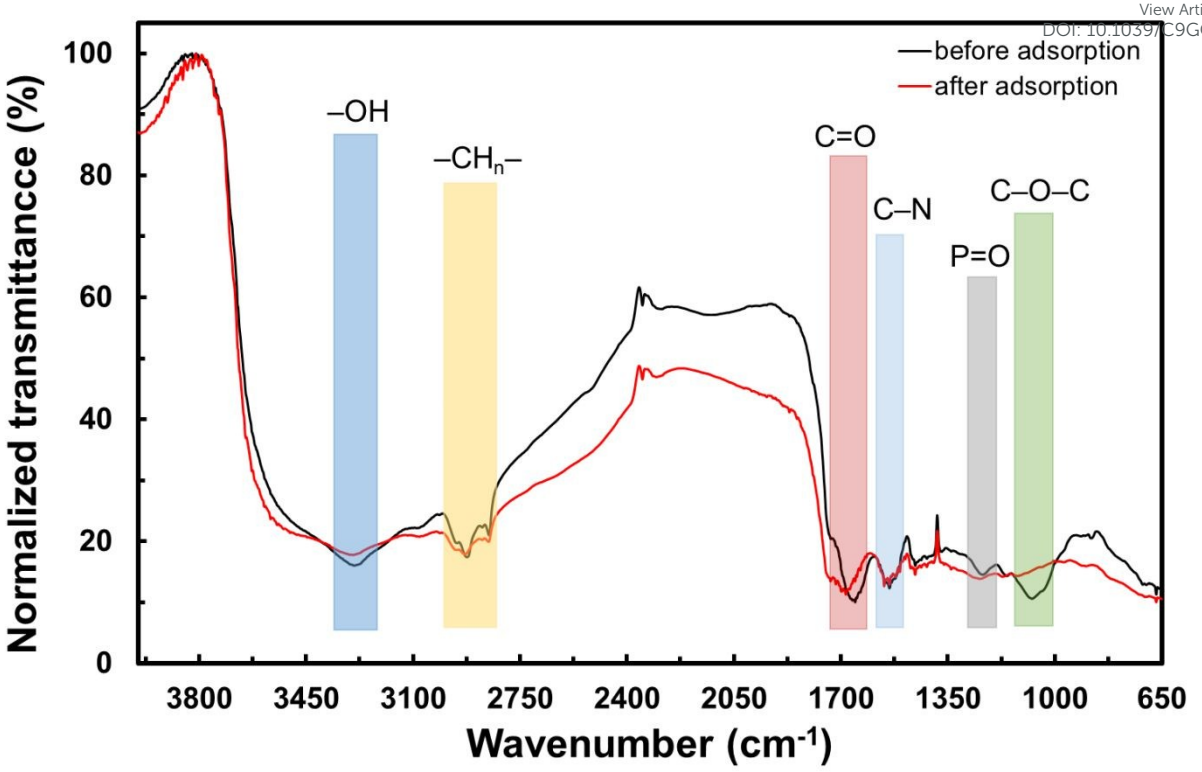

Figure 1. Normalized FTIR spectra of microalgal biomass before (black) and after (red) In(III) biosorption.

3.2 Scanning electron microscopy

The surface morphological characteristics of the microalgal biomass before and after In(III) biosorption were compared through SEM images. The image of the microalgal biomass before biosorption revealed that the microalgal biomass has an irregular surface and very low porosity (Figure S3A in the Supplementary Information). The pores have different shapes and sizes, which are mostly mesoporous. Nitrogen sorption measurements confirmed the low porosity of this biosorbent with a pore volume of 0.000303 cm^3/g. Figure S3B in the Supplementary Information shows a SEM image of the microalgal biomass after biosorption. In general, there is no significant difference between the surfaces of the microalgal biomass before and after In(III) biosorption. It can also be seen in Figure S4 that the structure of the particles did not change before and after the biosorption process.

3.3 Surface groups of the microalgal biomass causing acidic and basic surface properties

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Boehm titration was used to characterize the surface chemistry of the microalgal biomass. This method has the advantages of being simple, fast, and usually reproducible. However, one disadvantage of this method is that all groups are classified as oxygen-containing acids. All other groups, which contain nitrogen, phosphorus, or sulfur for instance, will be considered as carboxylic acids, lactones, or phenols because the selectivity is based on the pK_a values of the surface species (Bandosz et al., 2003). Table 1 shows the amounts of carboxylic, lactonic, phenolic, and basic groups that were estimated on the surface of the microalgal biomass. The results indicate that more basic groups (1.79 mmol/g) are present on the biosorbent's surface compared to the other surface groups giving the acidic properties. It was also observed that the carboxylic group is the predominant group causing the surface acidity at 0.36 mmol/g. Carboxylic groups are widely reported as the main functional group involved in metal binding in microalgae (Dmytryk et al., 2014; Monteiro et al., 2012; Suresh Kumar et al., 2015).

Table 1. Amount of surface groups giving the acidic and basic properties of the microalgal biomass as determined through Boehm titration.

Surface groups	Amount (mmol/g)
Carboxylic	0.36
Lactonic	0.21
Phenolic	0.23
Basic sites	1.79

3.4 Effect of pH on indium biosorption

Solution pH plays an important role in metal biosorption since it influences both the surface charge of the biosorbent and the distribution of metal species in the solution (Suresh Kumar et al., 2015). In(III) removal increased with increasing pH (Figure 2). Particularly, the In(III) adsorption largely increased by 70% as the final pH increased from 1.23 to 2.45. The maximum

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In(III) adsorption (94.7% of initial In) was obtained at the initial pH of 2, so this pH value was chosen for further biosorption experiments.

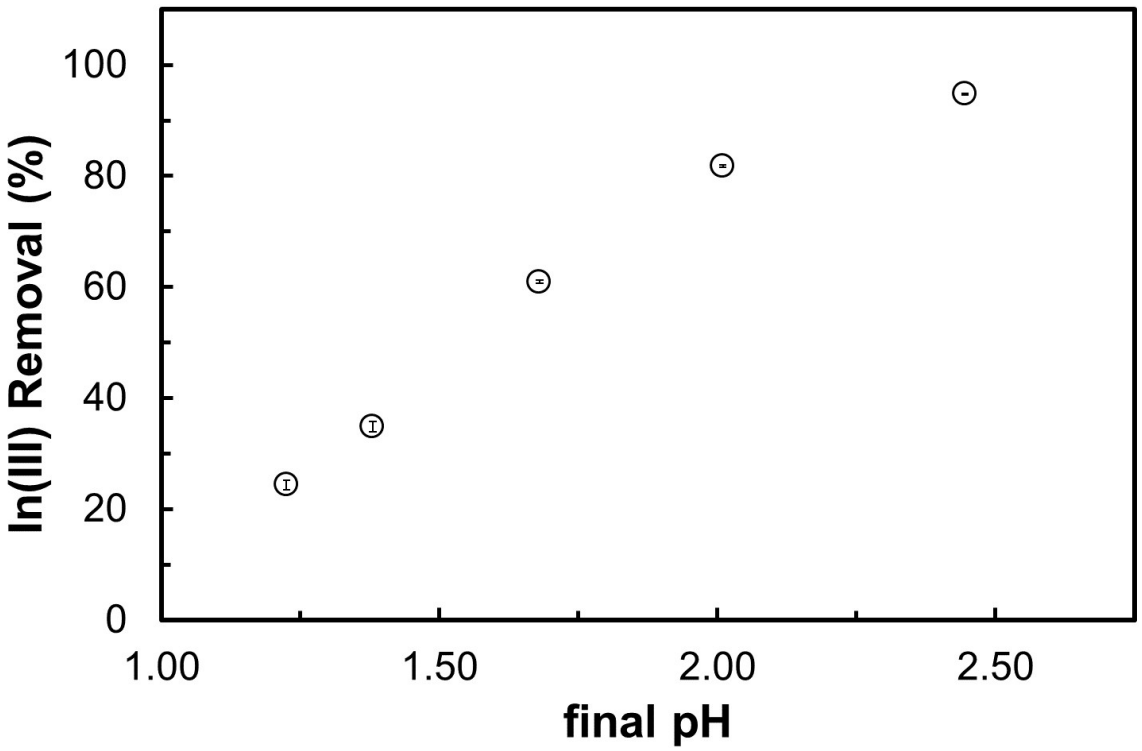

Figure 2. Effect of pH on indium removal efficiency. Experimental conditions: initial In(III) concentration = 0.15 mM; L/S ratio = 100 mL/g; contact time = 24 hours; room temperature.

In the studied system and pH range, the main chemical species of indium in the solution is In^{3+}. This is based on the speciation diagram of 0.15 mM indium in aqueous solution (Figure S5 in the Supplementary Information) modelled using the Hydra-Medusa software, which is based on SOLGASWATER and HALTAFALL algorithms (Puigdomenech, 2013). Under extremely acidic conditions (i.e., pH 1), In(III) removal efficiency was low at around 25%. This could be explained by the high concentration of hydronium ions competing for binding sites on the surface of the microalgal biomass. Once associated with the functional groups of the biosorbent, hydronium ions restrict the adsorption of In^{3+} due to repulsive forces (Monteiro et al, 2012). However, at higher pH values, several functional groups deprotonate and become available for metal binding if the solution pH is greater than the functional group pK_a (Anslyn

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and Dougherty, 2006; Tran et al., 2017). For instance, the results of Boehm titration (Table 1) suggested that carboxylic groups are present on the surface of the microalgal biomass. The pK_a values of carboxylic acid groups range from 1.7 to 4.7 (Tran et al., 2017). At the upper range of the tested pH values, carboxylic acid groups might have dissociated to form negatively charged carboxylate groups, thus facilitating the higher In(III) adsorption at a final pH of 2.4. The adsorbate-adsorbent system presented in this study was complex. Gadd (2009) commented that the mechanisms involved in biosorption are often difficult to characterize, especially if the biosorbent is biological in nature. Unlike chemically synthesized adsorbents, which have more uniform composition and surface functional groups, different structural components are present in most biosorbents. Many functional groups may be able to interact with the metal species to varying degrees and may be influenced by physico-chemical factors. In general, different metal-binding mechanisms are responsible for metal biosorption. In the case of indium biosorption by microalgal biomass, multiple mechanisms may be involved, including electrostatic and coordination interactions.

The results also indicate that microalgal biomass has an advantage when applied to real wastewater or leach solutions since most of these have an acidic pH. This makes it more competitive compared to most synthetic or chemically-modified adsorbents, which are either unstable or inefficient when used in acidic conditions. For instance, multiwalled carbon nanotubes (MWCNT) were reported to adsorb only 5% of the initial In(III) concentration (0.087 mM) at pH 4 (Alguacil et al., 2016). In another study by Calagui et al. (2014), chitosan-coated bentonite beads were used to adsorb In(III). At an initial pH of 2, only 40% of the initial In(III) concentration (0.17 mM) was removed by this adsorbent.

3.5 Kinetics of indium biosorption

Kinetics studies can give insights into the reaction pathways and mechanisms of the adsorption reactions (Gupta et al., 2010). Indium biosorption kinetics were fast. The removal

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rapidly increased during the first minutes of the process, reaching up to ca. 80% of the initial In(III) after 30 min (Figure 3). Fast kinetics are important for process scale-up. With rapid adsorption, smaller reactor volumes are required, ensuring efficiency and economy (Aksu, 2002).

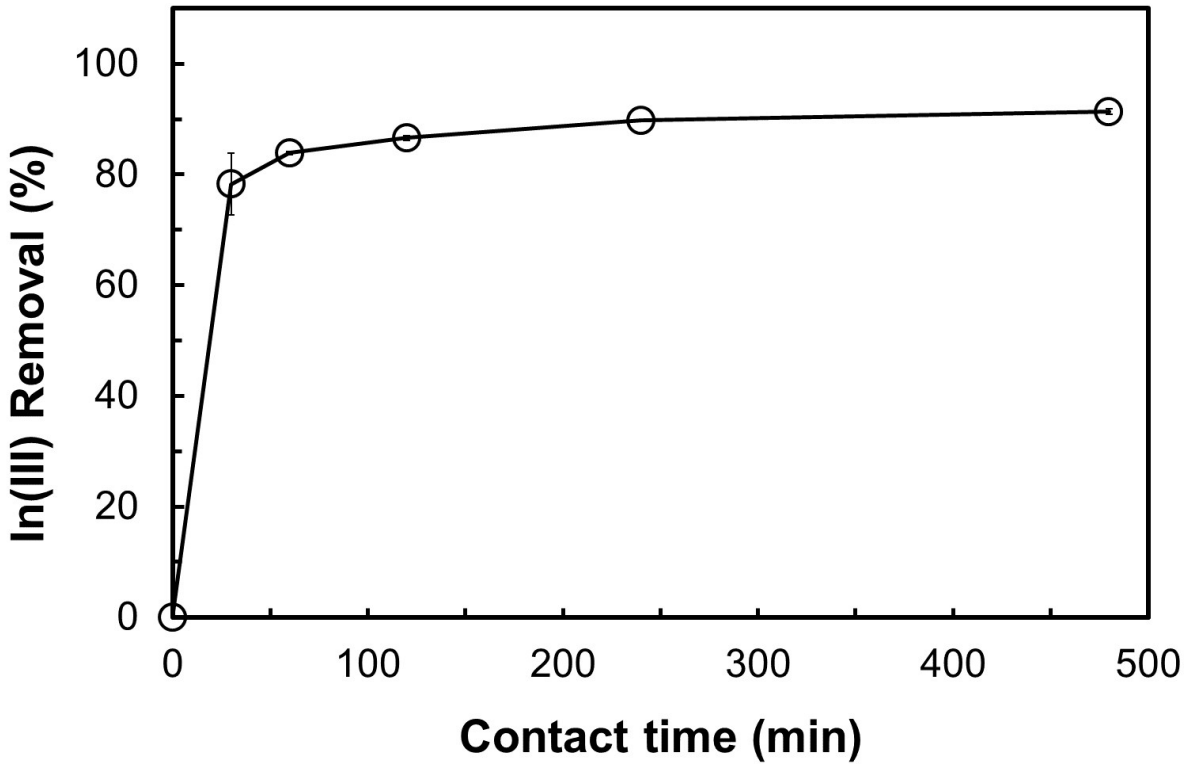

Figure 3. Kinetics of indium biosorption on microalgal biomass. Experimental conditions: initial In(III) concentration = 0.15 mM; L/S ratio = 100 mL/g; initial pH 2; room temperature.

3.6 Biosorption isotherms

Indium biosorption was studied at different initial metal concentrations ranging from 0.05 to 10 mM. Langmuir and Freundlich isotherm models were fitted to the data (Figure 4). The correlation coefficients suggest that the Freundlich model fits the data better than the Langmuir model (Table 2). This can be an indication that In(III) was adsorbed in multilayers onto the active sites of the microalgal biomass surface with lateral interaction between the adsorbed molecules (Hwang et al., 2013).

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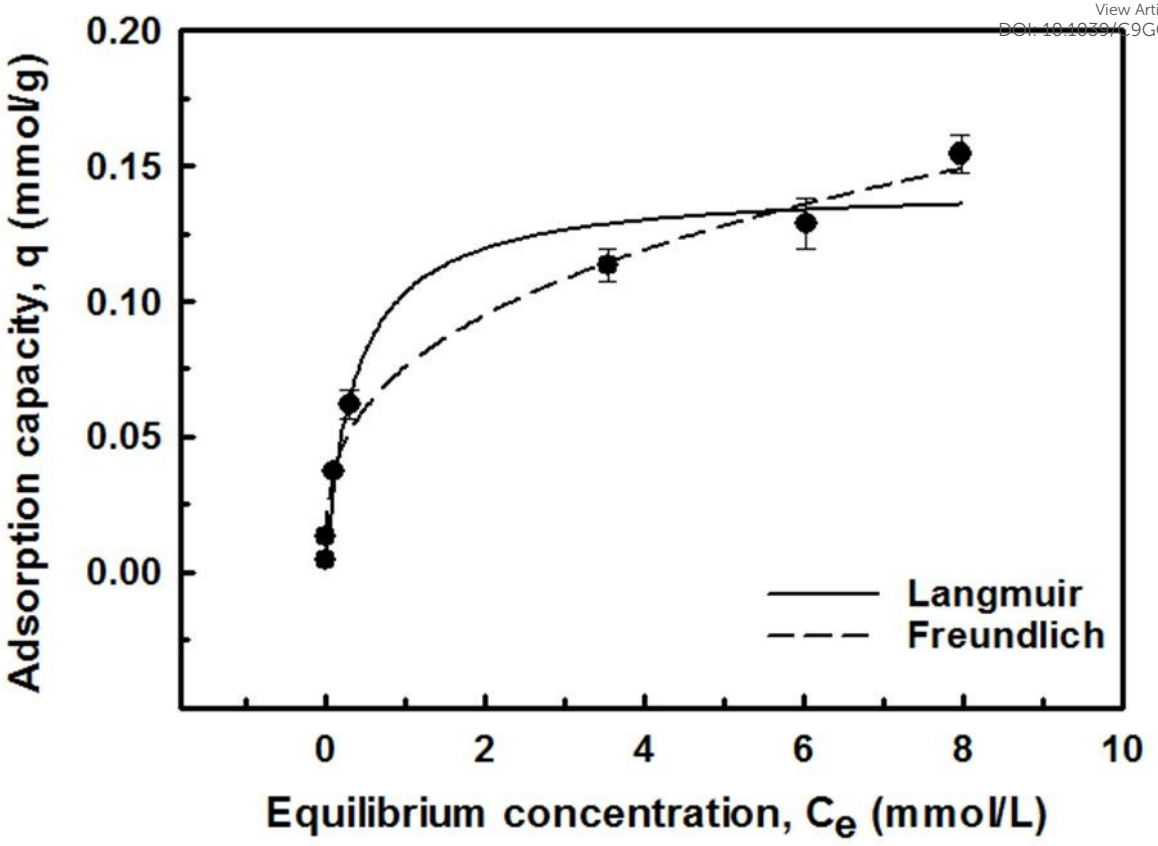

345

346 **Figure 4.** Adsorption isotherms of indium onto microalgal biomass using the Langmuir and
347 Freundlich models. Experimental conditions: L/S ratio = 100 mL/g; initial pH 2; room
348 temperature.

349 **Table 2.** Constants and correlation coefficients of Langmuir and Freundlich models for indium
350 biosorption using microalgal biomass.

Isotherm model	Parameter	Value
Langmuir	q_{max} (mmol/g)	0.14
	b (L/mmol)	2.64
	R^2	0.97
Freundlich	K_f (mmol$^{1-1/n}$ L$^{1/n}$/g)	0.08
	n	3.07
	R^2	0.99

351

352 The maximum adsorption capacity (q_{max}) of the microalgal biomass for In(III) at a final pH
353 of 2.4 was determined from the Langmuir model (Figure 4). The estimated q_{max} value was 0.14

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mmol/g, which is in the same order as those of adsorbents reported in the literature (Table 3). However, because of different experimental conditions, the comparison among studies should only be regarded as directional. Nevertheless, the microalgal biomass achieved a higher q_{max} compared to some chemically modified adsorbents, such as phosphorylated sawdust beads (0.01 mmol/g) (Jeon et al., 2015). Furthermore, some adsorbents with higher q_{max} values, such as MWCNT and magnetite modified with amine polymer, were evaluated at pH values where indium may precipitate as $In(OH)_3$, overestimating the adsorption capacities of these adsorbents (Alguacil et al., 2016; Chiou et al., 2015). Other synthetic adsorbents also showed better adsorption capacity than the microalgal biomass. For instance, microbeads of poly(glycidyl methacrylate-co-poly(ethylene glycol) diacrylate modified with iminodiacetic acid showed a q_{max} four times higher than that of the microalgal biomass (Hwang et al., 2013). However, the production processes of synthetic adsorbents are often costly, complicated, and environmentally unsustainable. These are crucial points to consider in the assessment of new adsorbents, especially if the goal is to use the technology at industrial scale. The microalgal biomass completely meets these conditions considering that no harmful and costly chemicals are needed for its production. Moreover, microalgae can be grown on wastewater while providing an economical and sustainable way of treating the wastewater through reduction of BOD, N or P, and inhibition of coliforms (Abdel-Raouf et al., 2012). The use of the harvested microalgal biomass as an effective In(III) biosorbent can add more value to the whole process of resource recovery. Furthermore, only minimal handling is required before it can be used as a biosorbent. In the current batch process, filtration using membrane syringe filters is a step that accounts to a greater part of the total cost of the process. However, after process parameters optimization through such batch experiments, biosorption could be performed as a continuous flow process in columns with a filtration system that is not disposable and could be more cost-effective in the long run.

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Table 3. Maximum adsorption capacities of different adsorbents for indium ions.

Adsorbent	Adsorbent modification	pH	q_{max} (mmol/g)	Reference
Orange waste	Phosphorylation	2.0[a]	0.71	Ghimire et al., 2008
Poly(vinylphosphonic acid-co-methacrylic acid) microbeads	-	8.0[c]	0.71	Kwak et al., 2012
Poly(glycidyl methacrylate-co-poly(ethylene glycol) diacrylate) microbeads	Iminodiacetic acid	-	0.62	Hwang et al., 2013
Chitosan	Immobilization by bentonite, beads	4.0[a]	0.16	Calagui et al., 2014
Sawdust	Phosphorylation, beads	3.5[b]	0.01	Jeon et al., 2015
Magnetite	Amine polymer	4.5[b]	0.48	Chiou et al., 2015
MWCNT	-	7.0[c]	0.35	Alguacil et al., 2016
Microalgal biomass	-	2.4[b]	0.14	This study

[a] Initial pH value. Authors did not report final equilibrium pH.

[b] Final equilibrium pH

[c] Authors did not report the potential contribution of $In(OH)_3$ precipitation to In(III) removal.

3.7 Effect of competing ions on indium biosorption

The interference of other ions present in the matrix is another key parameter in evaluating the performance of microalgal biomass for indium biosorption. For instance, ITO etching wastewater—a secondary source of In(III)—contains Al(III), Cu(II), and Sn(II) (Swain et al., 2015). The presence of these ions might affect the performance of adsorbents for indium adsorption due to the competition for binding sites. However, most indium adsorption studies reported in the literature only focused on single metal solutions. The possible competition for adsorption sites was not evaluated, presenting a disadvantage considering that the goal of these

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studies is to use the adsorbents in real and complex waste streams. In the present work, the competing effects of Cu(II), Zn(II), Sn(II), Al(III), and Fe(III) on indium biosorption were examined (Figure 5). Despite the concentrations of these competing ions being 10 times higher than that of In(III), selectivity of In(III) was observed over Cu(II), Zn(II), and Al(III). This is remarkable considering that the biosorbent was not treated or modified. For instance, Zn(II) was not adsorbed on the microalgal biomass, favoring In(III) adsorption at ca. 55% of the initial In(III) concentration. In a study by Kwon and Jeon (2012a), selective adsorption of In(III) over Zn(II) was also observed using phosphorylated sawdust. However, the adsorption experiments were conducted at pH 3.5 and the potential contribution of $In(OH)_3$ precipitation to In(III) removal was not reported. Nevertheless, this study by Kwon and Jeon (2012a) explained the possible reason for selective In(III) adsorption through the Hard and Soft Acids and Bases (HSAB) theory. The phosphate groups of the phosphorylated sawdust are classified as hard base. These strongly bind with In(III), which is a hard acid, as opposed to Zn(II), which is an intermediate (borderline) acid. This could be one of the reasons for the selective In(III) removal by the microalgal biomass considering that microalgae cell walls were reported to have phosphate groups (Suresh Kumar et al., 2015), which was also indicated by the FTIR results (Figure 1). However, for future study, nuclear magnetic resonance (NMR) could be performed to further investigate the interaction between the indium ions and the phosphate groups. This could complement the results obtained from FTIR spectroscopy by verifying the active sites of the microalgal biomass.

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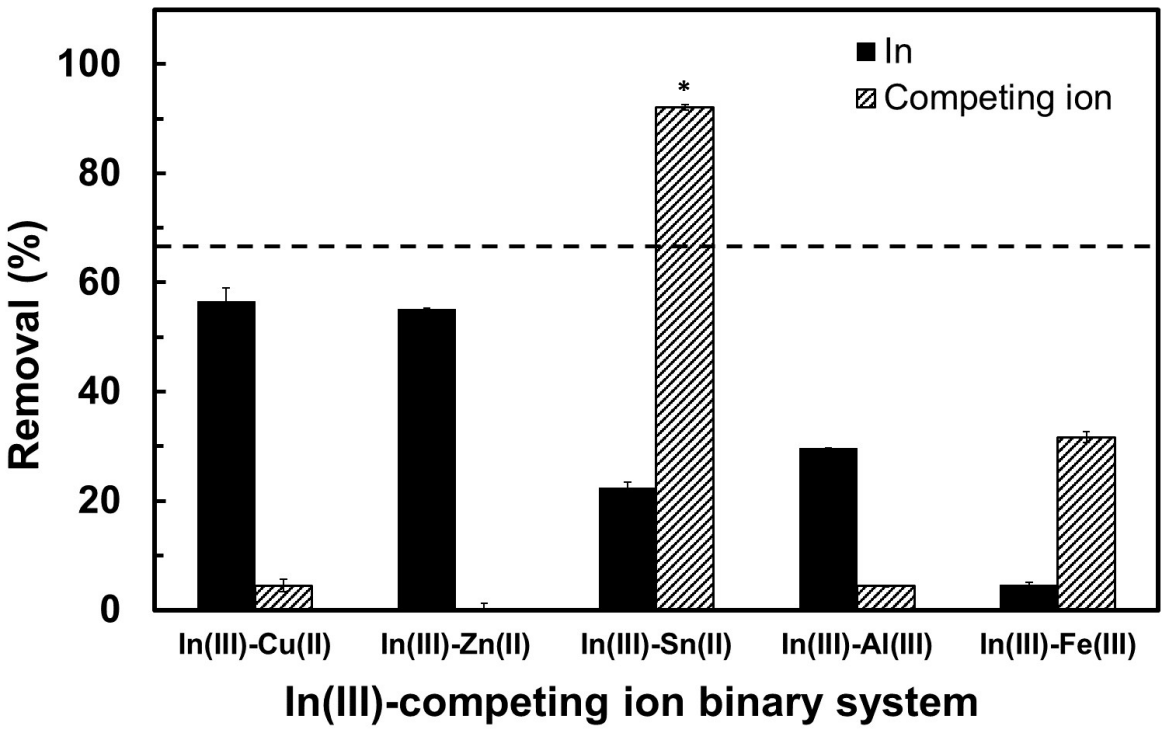

Figure 5. Effect of competing ions on the adsorption of In(III) using microalgal biomass. The dashed line represents the removal efficiency of the microalgal biomass for In(III) without competing ions present in the system. Experimental conditions: initial In(III) concentration = 1 mM; initial concentration of competing ion = 10 mM; L/S ratio = 100 mL/g; initial pH 2; room temperature. * The results of the control experiments showed that Sn(II) removal was mostly because of precipitation.

The results suggest that microalgal biomass can be an effective biosorbent, even in solutions where Cu(II), Zn(II), and Al(III) are present. However, although selectivity was observed, the removal efficiency of microalgal biomass for In(III) decreased to some extent because of the high concentrations of competing ions (Figure 5). The presence of Cu(II) in the solution affected In(III) biosorption the least as the removal efficiency for In(III) decreased only by about 10 %. In order to attain complete removal of In(III) in the presence of Cu(II), the amount of the microalgal biomass can be increased since it is an inexpensive and sustainable material.

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For instance, assuming that the adsorption capacity would remain almost constant, a L/S ratio of 50 mL/g or lower could potentially achieve complete In(III) adsorption in a system with 1 mM In(III) and 10 mM Cu(II). On the other hand, In(III) removal efficiency drastically decreased from 67 % to 5 % when Fe(III) was present in the system. A relatively high Fe(III) removal efficiency was observed for the microalgal biomass (ca. 32 % of the initial Fe(III) concentration), which indicates that Fe(III) and In(III) most likely compete for the same adsorption sites. Co-adsorption of Fe is a problem in Fe-rich solutions. This lack of selectivity between In(III) and Fe(III) was also observed by Van Roosendael et al. (2019) in their study of adsorption of In(III) from aqueous solutions using an Aliquat 336 (chloride) supported ionic liquid phase (SILP). Because of co-adsorption of In(III) and Fe(III), the initial Aliquat 336 (chloride) SILP was replaced with an Aliquat 336 (iodide) SILP on the basis that indium forms complexes with iodide species, while iron does not. An excess of iodide ions was added to the aqueous solution to form indium iodide species, which are adsorbed to the Aliquat 336 (iodide) SILP. Furthermore, Fe powder was added to the solution to reduce Fe(III) to Fe(II), thereby improving In(III) selectivity. This approach emphasizes the need to understand the surface chemistry of the adsorbent and nature of molecular interactions in order to attain In(III) selectivity over Fe(III). However, this also highlights that even costly and synthetic adsorbents encounter problems in Fe-rich solutions. Thus, the balance between the adsorbent performance and its cost-effectiveness should be evaluated.

In the case of the In-Sn system, about 92 % of the initial Sn(II) concentration was removed from the solution, which would correspond to an adsorption capacity of 0.76 mmol/g. However, the Sn(II) removal can be largely attributed to precipitation as it was observed that white insoluble solids were formed during the incubation. Furthermore, light scattering measurements detected the formation of amorphous $Sn(OH)_2$ particles in $SnCl_2$ solutions at pH values between

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2.0 and 2.5 (Cigala et al., 2012). This supports the observation of tin precipitation because the final pH of the solution was around pH 2.

3.8 Microalgal biomass regeneration

Adsorbent regeneration is an essential aspect of the adsorption process as it could contribute to the overall cost-effectiveness of the technology (Lata et al., 2015). For effective regeneration, the desorption process must restore the adsorbent close to its initial properties, especially the preservation of its adsorption capacity, to allow its reuse in multiple adsorption-desorption cycles. However, the desorption of metal-laden adsorbents is a complex process that involves several factors, such as the type of the desorbing agent, desorption time, temperature, solution pH, and the adsorbent surface properties (Lata et al., 2015). In general, metal desorption from biosorbents involves lowering the pH of the solution as this will cause the displacement of metal cations back to the solution (Monteiro et al., 2012). The most commonly used desorbing agents are inorganic acids, followed by inorganic salts, chelating agents, and organic acids (Suresh Kumar et al., 2015).

As an initial step to assess the regenerability of microalgal biomass, the desorption of In(III) was investigated using 0.1 M HCl, HNO_3, NaCl, $CaCl_2$, and EDTA. The highest In(III) desorption efficiency was obtained with EDTA with 87 % In(III) desorbed, followed by HCl with 80 % (Figure 6). Considering both the efficiency and economic feasibility, HCl was chosen as desorbing agent for the succeeding regeneration experiments. Desorption studies of previously adsorbed In(III) on phosphorylated sawdust were also investigated by Kwon and Jeon (2012b). Although the desorption efficiency of HCl was lower than those of nitrilotriacetic acid (NTA) and EDTA, HCl was also chosen as the best desorbing agent for indium ions considering the cost-effectiveness, although a relatively high HCl concentration of 0.5 M was used in this study. The desorption process using HCl as the desorbing agent occurs chemically through the exchange of In(III) for protons. When HCl is added to the In-loaded biomass, the

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biosorbent surface is completely covered with H^+ ions, while the coordination spheres of adsorbed indium ions are disrupted. In this way, the indium ions cannot compete with H^+ ions for adsorption sites, causing the indium ions to be released from the biosorbent surface into the solution (Bansal et al., 2009). The generated effluents from the desorption process are acidic in nature.

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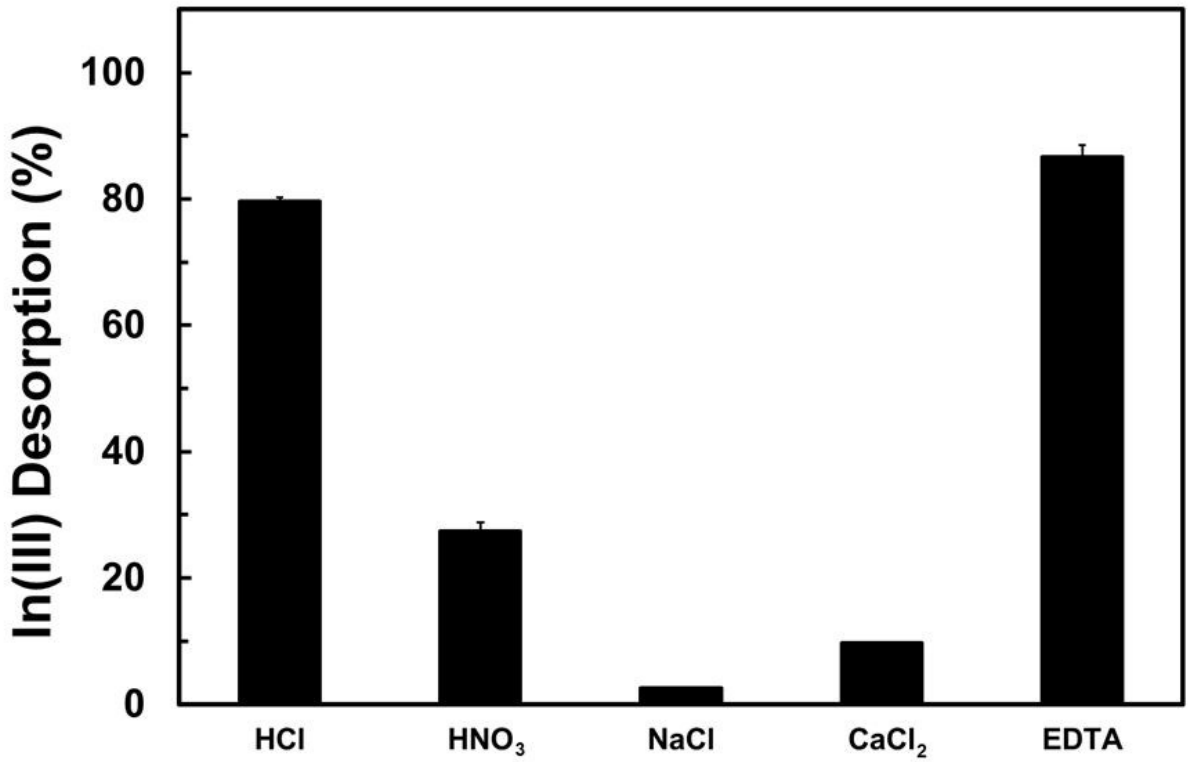

Figure 6. Indium desorption efficiencies of various desorbing agents. Experimental conditions: loaded amount of indium onto microalgal biomass = 1.50 mg/g; concentration of desorbing agent = 0.1 M; L/S ratio = 100 mL/g; contact time = 24 hours; room temperature.

The process of upconcentrating the indium ions was investigated by desorbing the In-loaded microalgal biomass with different volumes of 0.1 M HCl. Several L/S ratios ranging from 20 to 100 mL/g were tested. As the L/S ratio increased, the desorption efficiency increased as well (Figure 7). The highest desorption efficiency (ca. 80 %) was obtained using a L/S ratio of 100

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mL/g. Considering different factors, such as upconcentration, cost-effectiveness, and efficiency, a L/S ratio of 60 mL/g was used for the succeeding desorption experiments. This has a desorption efficiency of 72% after 24 hours. Subsequently, the desorption kinetics using this L/S ratio was investigated. The desorption of the In(III) fraction loosely bonded to the microalgal biomass occurred very fast (Figure 8). After 30 minutes, a desorption efficiency of about 70% was obtained, which is similar to that obtained after 24 hours. Thus, a 30-minute contact time was used for the next adsorption-desorption experiments.

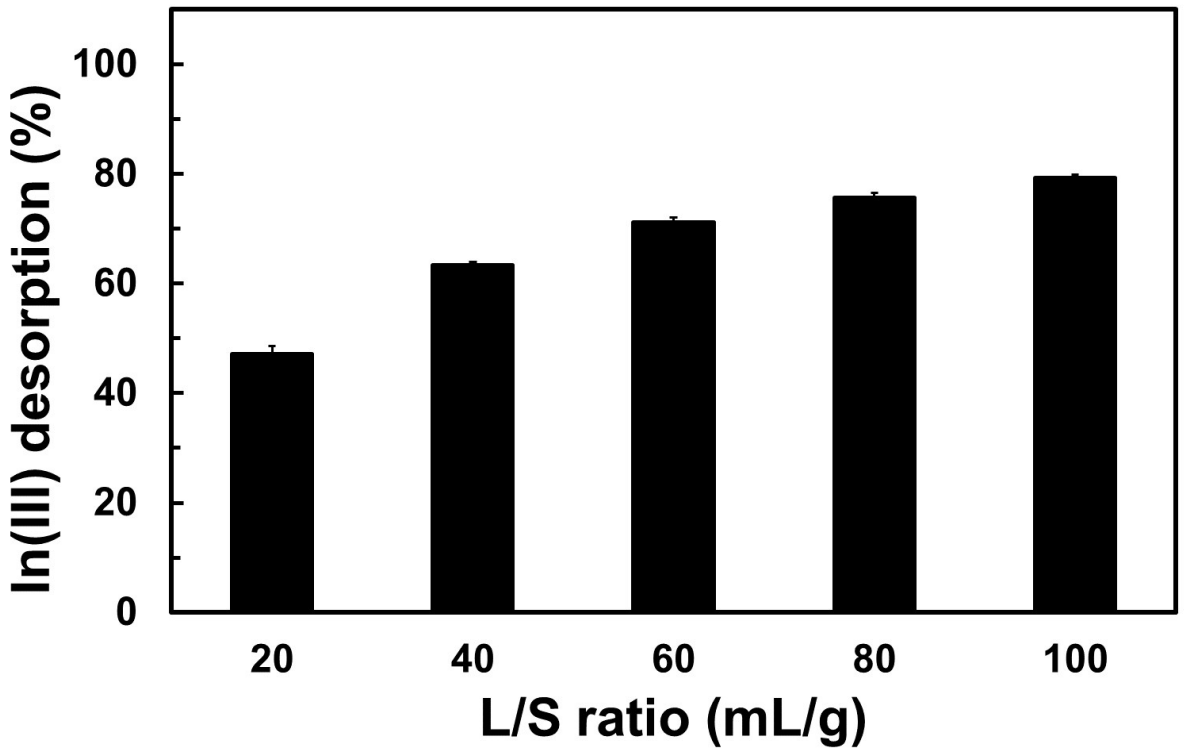

Figure 7. Effect of the liquid/solid (L/S) ratio on the desorption efficiency of indium ions using 0.1 M HCl. Experimental conditions: loaded amount of indium onto microalgal biomass = 1.50 mg/g; contact time = 24 hours; room temperature.

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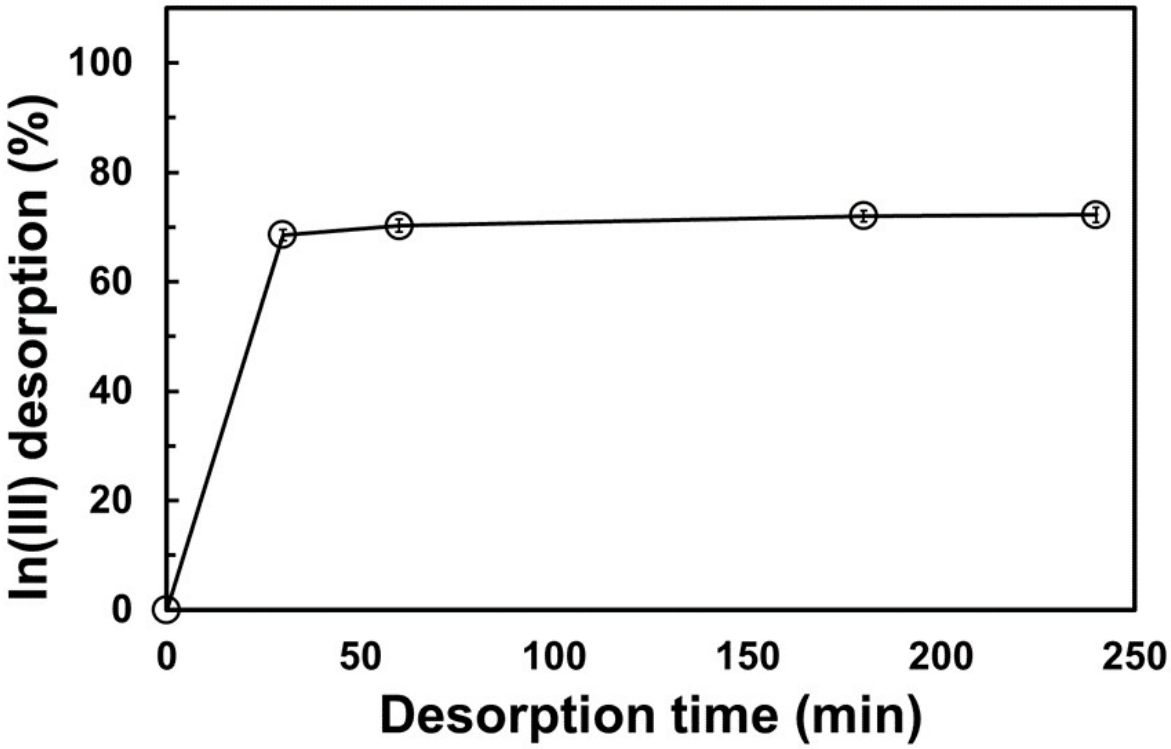

Figure 8. Change of desorption efficiency of indium ions with time using 0.1 M HCl. Experimental conditions: loaded amount of indium onto microalgal biomass = 1.50 mg/g; L/S ratio = 60 mL/g; room temperature.

3.9 Microalgal biomass reusability

Stability of the adsorbent should be investigated if it will be reused in multiple adsorption and desorption cycles. Figure 9 shows five cycles of In(III) adsorption-desorption performed using 0.1 M HCl as desorbing agent. In general, the adsorption capacity of the microalgal biomass for In(III) progressively decreased with increasing number of adsorption-desorption cycles. After five cycles, the In(III) removal decreased from 91.3% to 60.7%. Similarly, cadmium adsorption on the microalga *Spirulina platensis* immobilized in alginate and silica gel decreased by about 30% after five regeneration cycles using 0.1 M HCl as desorbing agent (Rangsayatorn et al., 2004). The decrease in the microalgal biomass adsorption capacity can possibly be due to two reasons. First, the fraction of indium ions remaining on the biosorbent

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surface after every regeneration cycle result in a decrease in the number of available adsorption sites. Second, the active functional groups on the microalgal biomass surface are partially destroyed by the desorbing agent after each desorption step. Figure S6 shows a SEM image of the microalgal biomass after In(III) desorption using 0.1 M HCl. Although the changes in the surface texture of the biosorbent are still not apparent, it can be observed that some parts were damaged. However, even synthetic adsorbents can exhibit decreased adsorption capacities after several adsorption-desorption cycles. For instance, Chiou et al. (2015) determined the reusability of amide group-functionalized magnetite in In(III) adsorption by using 0.01 M HNO_3 as a desorbing agent. During the third adsorption-desorption cycle, the adsorption capacity of the adsorbent exhibited a loss of about 53%, which was reported to be possibly caused by the detachment of the ethylenediamine from the magnetite surface during the recycling processes. This suggests that the stability of the adsorbents should also be part of the assessment of the adsorbent. Furthermore, another factor to consider when assessing adsorption-desorption cycles is the metal upconcentration. In this study, a concentration ratio (i.e., ratio of In(III) concentration in the desorbed solution to In(III) concentration in the initial solution) of about 1.5 was achieved after the adsorption and desorption steps. Since this value is limited, other ways to recover In(III) can be explored, especially that it exhibited a high In(III) selectivity. One option could be burning the indium-loaded microalgae to end up with an indium-rich ash, which could be subsequently processed in a metal-processing plant.

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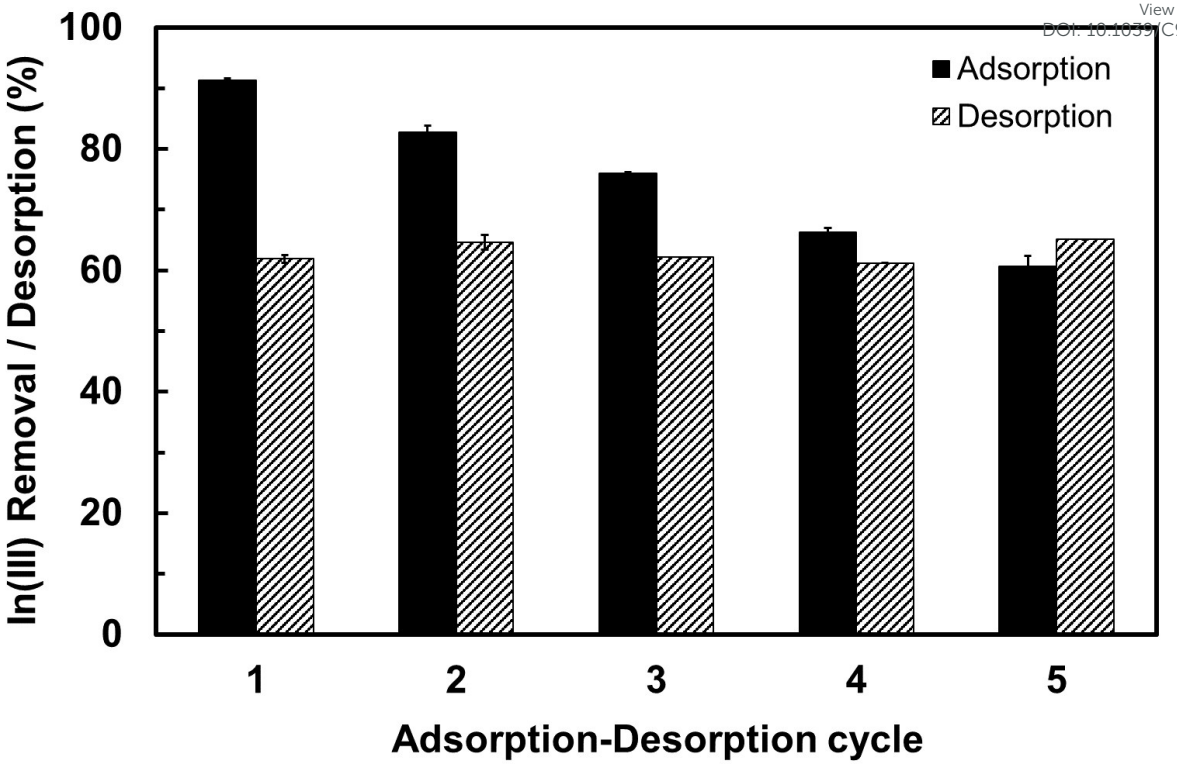

553

554 **Figure 9.** Five cycles of In(III) adsorption – desorption using 0.1 M HCl as desorbing agent.
555 Experimental conditions: Adsorption – C_0 = 0.15 mM; L/S ratio = 100 mL/g; contact time = 24
556 hours; room temperature; Desorption – L/S ratio = 60 mL/g; contact time = 30 minutes; room
557 temperature.

558 **4. Conclusions**

559 This study investigated the effects of various process parameters—specifically pH, contact
560 time, initial metal concentration, presence of competing ions, and desorption—on the
561 biosorption of In(III) onto microalgal biomass. Results showed that this biosorbent has a
562 maximum In(III) adsorption capacity of 0.14 mmol/g at an initial pH value of 2. Further analysis
563 revealed that the adsorption equilibrium data were well-fitted by the Freundlich isotherm
564 model, suggesting that indium ions were adsorbed in multilayers onto the active sites of the
565 microalgal biomass surface. The kinetics data showed that In(III) biosorption by microalgal
566 biomass is a fast process, attaining 80% In(III) removal within a contact time of 30 minutes. In
567 addition, selectivity of In(III) was observed over Cu(II), Zn(II), and Al(III) despite the high

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concentrations of these metals. Moreover, In(III) ions adsorbed on microalgal biomass could be effectively desorbed by 0.1 M HCl, but burning the In-loaded biosorbent to obtain an In-rich ash is also an option to recover In(III). Overall, this study demonstrated the potential of microalgal biomass for In(III) biosorption from aqueous solutions. This potential should now be further explored using real indium-containing wastewaters and leachates. Furthermore, it provided some insight into the adsorption behavior and mechanism of In(III) adsorption on microalgal biomass. This information can now be used as input data for subsequent continuous adsorption experiments in a column setup.

5. Conflict of interest

The authors declare no conflict of interest.

6. Acknowledgements

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