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Heavy metal removal from water using the metallogelation properties of a new glycolipid biosurfactant

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Abstract

Water pollution by heavy metals is a problem of both western and developing countries. Heavy metal pollution can be associated to human activity, such as wastewaters from processing of ore mining, but also to simple contamination from metal rich soils. Whichever the case, chemical and physical methods are generally employed to depollute water. Since most chemicals are themselves polluting agents, there is an increasing interest in finding biobased and biodegradable alternative chemicals, both efficient in removing metals and benign to the environment. Biosurfactants are green chemicals produced by fermentation of yeasts and bacteria and with a good environmental score. Among many applications, this class of compounds has been used to remove heavy metals from contaminated soils. Within this framework, we propose a new mechanism of depolluting water using a glucolipid biosurfactant, G-C18:1, composed of glucose (G) and a C18:1 fatty acid (oleic acid). This compound is able to form a metallogel by complexing cations in water, thus trapping heavy metals (Cu^{2+} , Ni^{2+} , Cr^{2+} and Co^{2+}) in the gel phase. This mechanism allows to remove up to 95% for cobalt and $88 \pm 10\%$, $80 \pm 3\%$ and $59 \pm 6\%$ for Cu^{2+} , Ni^{2+} and Cr^{2+} , respectively. A dedicated structural study shows that this is possible because positively charged species induce gelation of G-C18:1 through a micelle-to-wormlike phase transition, most likely driven by a charge neutralization process. This work shows that wise control of the nanoscale properties of green chemicals can strongly benefit to develop a sustainable future.

Introduction

Wastewater remediation is a crucial challenge worldwide, may it occur in rich or developing countries. Different methods are currently employed together, mainly combining physical processes, like membranes filtration and decantation, associated to a chemical process, involving flocculation. (Lee et al., 2014) In the latter, colloids are coagulated by charge screening and flocculation occurs by inter-colloidal bridging in flocs, which can sediment or filtered out.

In the last decades, metal salts were widely used as flocculants, however of intermediate efficiency, for their low cost compared to more efficient synthetic polymers (Sarika et al., 2005) or bio-flocculants. (Othmani et al., 2020) However, metal salt flocculants have been limited along the years due to the large amounts of toxic metal released in the nature. Aluminium, a well-known flocculant, is known to affect living organisms, (Ward et al., 2006) especially acting as neurotoxic agent for human brain and which could contribute to the Alzheimer disease. (Banks et al., 2006)

Depollution from heavy metals is itself an extensively studied problem (Fu & Wang, 2011) and one can distinguish four methods based on: adsorption by porous materials, membrane filtration, electric separation and chemical flocculation. The latter is well-mastered, but it employs large amounts of non-biodegradable chemicals. (Qasem et al., 2021) Nowadays, other potential chemicals are tested for heavy metal depollution, mostly based on plant mixture or living plants, (Amari et al., 2019; Nedjimi, 2021) hydroxyapatite bones derivatives (Brazdis et al., 2021) or even fly ash, a known by-product of power production. (Gupta et al., 2021) In this context, low molecular weight (LMW) compounds, like surfactants, are well-known flocculants, employed since long time. (Jian-Xiao et al., 2006; Paton & Talens-Alesson, 2001; Somasundaran et al., 1988) However, the environmental concern of surfactants is itself an issue, and other LMW amphiphiles have been looked at as possible substituents for petrochemical compounds. Peptides amphiphiles (Abdellatif et al., 2020; Bhattacharya & Krishnan-Ghosh, 2001; Suzuki et al., 2006) and, more importantly, microbial biosurfactants, like rhamnolipids, sophorolipids or surfactin, (Q. Chen et al., 2021; Hari & Upadhyay, 2021; Malkapuram et al., 2021; Mishra et al., 2021; Catherine N. Mulligan, 2021; Singh & Cameotra, 2013) have been shown to have interesting depollution properties against both organic and heavy metal pollutants. However, in the latter case, the essential work, which has started more than thirty years ago, has been carried out on soil pollution, (Q. Chen et al., 2021; Kim & Vipulanandan, 2006; Malkapuram et al., 2021; Miller,

1995; Mishra et al., 2021; C. N. Mulligan et al., 2001; Catherine N. Mulligan, 2005, 2009, 2021; Catherine N. Mulligan, Yong, & Gibbs, 1999; Catherine N. Mulligan, Yong, Gibbs, et al., 1999; Catherine N. Mulligan & Wang, 2006; Prakash et al., 2021; Sonowal et al., 2022) with relatively less contributions to water depollution. Despite such large engineering efforts, including the development of performing extraction processes like flotation (Dhar, Havskjold, et al., 2021; Dhar, Thornhill, et al., 2021; Malkapuram et al., 2021) or electrokinetic remediation, (Tang et al., 2020) little is still known about the fundamental interaction mechanisms of between heavy metals and biosurfactants, the latter mainly concerning rhamnolipids. (Dahrazma et al., 2008; Ochoa-Loza et al., 2001a)

In this work, we present the heavy metal removal ability of a new glycolipid biosurfactant, G-C18:1 (Figure 1), consisting in a glucose group covalently linked to a C18:1 *cis* fatty acid. This compound, prepared by fermentation of *S. bombicola* Δ ugtB1 in the presence of glucose and vegetable oils, like rapeseed oil, (Saerens et al., 2011) is much less known and studied than other biosurfactants, like sophorolipids or rhamnolipids. Nevertheless, recent results show that G-C18:1 strongly interacts with alkaline earth and transition metal ions, which trigger gelation through micelle-to-wormlike or micelle-to-fiber phase transitions. (Poirier, Bizien, et al., 2022; Poirier, Griel, Hoffmann, et al., 2022; Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022) The structure of the micelles and fibers, as well as the conditions under which they are formed and elastic properties of the gels have been thoroughly studied for selected metal ions by mean of cryogenic transmission electron microscopy, rheology and *in situ* small angle X-ray scattering. (Poirier, Bizien, et al., 2022; Poirier, Griel, Hoffmann, et al., 2022; Poirier, Griel, Perez, & Baccile, 2022) On the other hand, the interactions between G-C18:1 and metal ions have been probed by isothermal titration calorimetry and solid state nuclear magnetic resonance. (Baccile et al., 2022; Poirier, Griel, Perez, & Baccile, 2022) These data are unique in the panorama of biosurfactant science, where their interactions with metal ions have only been rarely studied (Dahrazma et al., 2008; Miller, 1995) and a number of questions are still open.

By controlling the effect of cations on the self-assembled structure and macroscopic properties of G-C18:1, we explore in this work the removal of Cu^{2+} , Ni^{2+} , Cr^{2+} and Co^{2+} , all well-known groundwater pollutants, (<https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#inorganic>, n.d.; Vetrimurugan et al., 2017) through metallogelation. This approach, unprecedented for biosurfactants, is controlled by tuning the [ion]/[G-C18:1] molar ratio and pH. (Poirier, Bizien, et al., 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022) In the process proposed here, complementary to other

existing separation processes, like flotation (Dhar, Havskjold, et al., 2021; Dhar, Thornhill, et al., 2021; Malkapuram et al., 2021) or electrokinetic remediation (Prakash et al., 2021; Tang et al., 2020), the gel is easily concentrated by centrifugation and removed. UV-Vis and atomic absorption spectroscopy are used to evaluate the molar fraction of the cations in the supernatant.

Compared to the use of other biosurfactants for depollution purposes, G-C18:1 is certainly a newcomer. However, its unexpectedly strong interactions with heavy metals make this new molecule an interesting competitor with respect to all other commercial biosurfactants, like sphorolipids, rhamnolipid and surfactin, and in this regard it is certainly interesting to explore its application in the field of environmental remediation.

Material and methods

Chemicals. The monounsaturated glucolipid G-C18:1 ($M_w = 460 \text{ g.mol}^{-1}$) contains a β -D-glucose unit covalently linked to oleic acid. The molecule is obtained by fermentation from the yeast *Starmerella bombicola* *AugtB1* according the protocol given before. (Baccile, Cuvier, et al., 2016; Saerens et al., 2011) The compound is purchased from the Bio Base Europe Pilot Plant, Gent, Belgium, lot N° APS F06/F07, Inv96/98/99 and used as such. According to the specification sheet provided by the producer, the batch (99.4% dry matter) is composed of 99.5% of G-C18:1, according to HPLC-ELSD chromatography data. NMR analysis of the same compound (different batch) was performed elsewhere. (Baccile, Selmane, et al., 2016) Heavy metal chlorides, CuCl_2 , CrCl_2 , and NiCl_2 , were purchased from Sigma Aldrich (Saint-Quentin-Fallavier, France), CoCl_2 came from Fluka (Saint-Quentin-Fallavier, France). For atomic absorption spectroscopy, standard solutions are purchased from Supelco (Saint-Quentin-Fallavier, France) and Sigma Aldrich (Saint-Quentin-Fallavier, France).

Solutions preparation. G-C18:1 is dissolved in milli-Q water at 1 wt% by stirring and sonication, the pH is adjusted to 8 by adding few μL of concentrated NaOH. At pH 8, the G-C18:1 is clear. Cu^{2+} , Co^{2+} and Cr^{2+} solutions are prepared at concentration of 1 M, Ni^{2+} solution is prepared at 0.5 M in milli-Q water. A few μL of each cation solution are added to the G-C18:1 solution so to reach the targeted molar ratio $[\text{ion}]/[\text{G-C18:1}]$ shown in Table 1. The metallogels form at $[\text{ion}]/[\text{G-C18:1}] = 0.5$ for Cu^{+2} , 0.6 for Cr^{+2} , and 1.0 for Co^{+2} and Ni^{+2} , with an approximation on the ratio of ± 0.1 . However, to improve metallogel formation, pH is adjusted for Co^{2+} , Cr^{2+} and Ni^{2+} systems only and according to the values given in Table

1. To remove the metallogel phase entrapping the heavy metals from the supernatant, the solutions (1.5 mL) are centrifuged at 13400 rpm during 5 min using an Eppendorf Minispin bench centrifuge.

Table 1. Molar ratio (± 0.1) and pH conditions employed to prepare G-C18:1 metallogels.

	CuCl ₂			CoCl ₂			CrCl ₂			NiCl ₂		
Replica	1	2	3	1	2	3	1	2	3	1	2	3
[ion]/[G-C18:1]	0.4	0.6	0.5	1.0	1.1	1.0	0.6	0.6	0.6	1	1.2	1.2
adjusted pH	-	-	-	8.5	8.6	8.3	7	6.3	6.3	8	8.5	8.3

UV-Vis spectrometry. The spectra from 300 to 800 nm are collected on a Uvikon XL spectrophotometer (SECOMAM) and its associated software. A 1.5 mL cuvette in plastic (Brand) is used as sample holder. Before each measurement, a few μL of the cation solution are mixed in the surfactant solution, which is then centrifuged. The absorbance is measured on the supernatant. Cation solutions are added in the same supernatant and the same protocol occurs over and over until high molar ratio [ion]/[G-C18:1] ratio are achieved. Since the actual [ion]/[G-C18:1] ratio is not known with precision, due to the content removed by centrifugation, plots report the calculated ratio. For all metal ions except Cu^{2+} , the pH of the supernatant is artificially increase to trigger gel formation.

Atomic absorption spectrometry. The supernatants are analyzed via Atomic Absorption Spectroscopy (AAS) using a PerkinElmer PinAAcle 500 apparatus. The calibration curves are obtained for Cu^{2+} , Co^{2+} , Cr^{2+} and Ni^{2+} by diluting commercial standard solutions at 0.5, 1, 1.5, 2.0 and 2.5 mg/L in a 1.5% HNO_3 solution. The samples are prepared by diluting the supernatants in a HNO_3 solution at 1.5%.

Discussion

In a series of previous works, it was shown how the glycolipid biosurfactant G-C18:1 fibrillates into hydrogels by adding a source of alkaline earth and transition metal ions to its micellar solution at $\text{pH} > 7$ (Figure 1). (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) Specific ions like Ca^{2+} , Ag^+ , Mn^{2+} , Cr^{2+} Fe^{3+} or Zn^{2+} tend to form gels or aggregates with a fibrillar morphology (Poirier, Griel, Hoffmann, et al., 2022; Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022) while Co^{2+} , Cu^{2+} , Fe^{2+} , Al^{3+} and Ni^{2+} drive the assembly towards an intertwined wormlike micellar network. (Poirier, Griel,

Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022) According to the present knowledge, fibers are driven by possible metal-ligand interactions, while wormlike micelles rather form from a charge-screening mechanism, presumably via the interaction between the metal ion and the COO^- of G-C18:1. (Baccile et al., 2022; Poirier, Griel, Hoffmann, et al., 2022) The structure of Ca^{2+} and Ag^+ driven fibrous gels are reported in detail elsewhere, (Poirier, Griel, Hoffmann, et al., 2022) as well as the mechanism of fibrillation and micellization with Ca^{2+} , Ag^+ , Al^{3+} and Fe^{2+} . (Poirier, Griel, Perez, & Baccile, 2022)

Interaction between the carboxylate groups of other glycolipid biosurfactants (e.g., rhamnolipids) is generally used as an argument to explain the good heavy metal removal efficiency of this class of molecules in soil and water treatment. (Q. Chen et al., 2021; Ghaith et al., 2019; Huang & Liu, 2013; Mishra et al., 2021; Catherine N. Mulligan, 2005, 2009, 2021; Catherine N. Mulligan & Wang, 2006) However, studies specifically addressing the nature of the interactions between biosurfactants and metal ions in water solutions are scarce (Baccile et al., 2013; M. Chen et al., 2013; Dahrazma et al., 2008; Shen et al., 2011) and generally show the small impact of cations on the phase behavior of biosurfactants. The effect of metal ions on glycolipid G-C18:1 represents, to date, the only exception to the present state of the art. (Poirier, Griel, Hoffmann, et al., 2022; Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022)

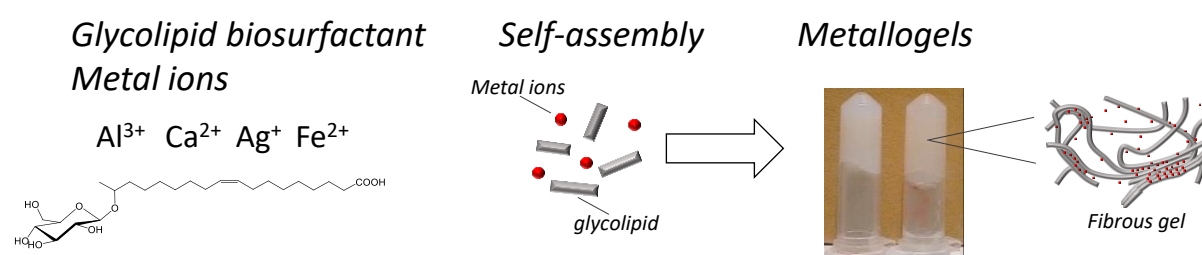


Figure 1 – Process of metallogel formation from glycolipid G-C18:1 biosurfactant in water. (Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022)

Some of the metals tested display renown acute toxicity (<https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#inorganic>, n.d.; Vetrimurugan et al., 2017) and their interaction with G-C18:1 during the fibrillation process could be an effective way to remove the complex through a physical method. In the following, we have opted for centrifugation, which, at a laboratory scale is an easy and effective way to separate the flocculate, here supposed to be a

network of wormlike micelles or fibers, depending on the cation. However, other methods, like flotation (Dhar, Havskjold, et al., 2021; Dhar, Thornhill, et al., 2021; Malkapuram et al., 2021), electrokinetic remediation (Tang et al., 2020) or filtration could easily be employed.

Figure 2 shows the absorbance spectra of Cu^{2+} and Ni^{2+} , added to a micellar solution of G-C18:1 at pH 8. After each addition of the metal ion solution, the mixture containing the cation and G-C18:1 is systematically centrifuged, with no remarkable effect. However, at an appropriate molar ratio of $[\text{Cu}^{2+}]/[\text{G-C18:1}]$ of about 0.5, gelation occurs and syneresis can be easily induced by centrifugation. A colorless supernatant is then collected and further analyzed. Similar observations (appropriate $[\text{ion}]/[\text{G-C18:1}]$) are given in Table 1) are obtained for Co^{2+} , Cr^{2+} and Ni^{2+} , after increasing the pH between pH 7.0 and 8.5. UV-Vis spectrometry is used to follow the above process and to evaluate the cationic content in the supernatant, after each cation addition and centrifugation step.

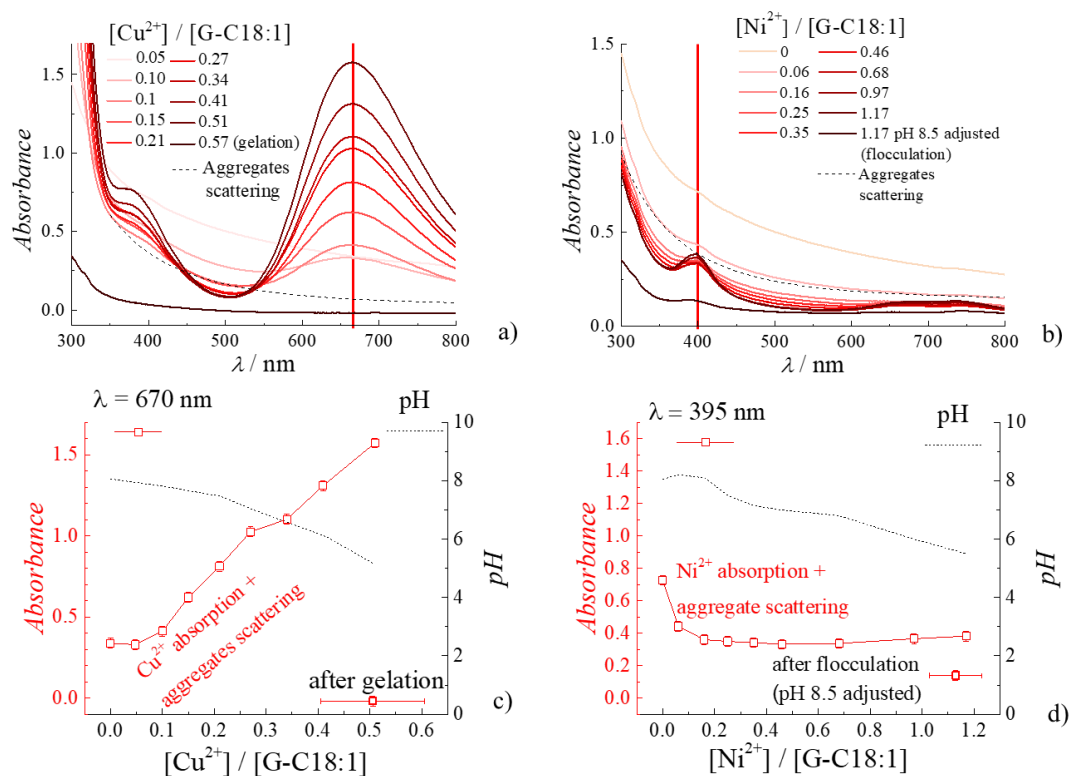


Figure 2 - Absorbance spectra for a) Cu^{2+} and b) Ni^{2+} -containing G-C18:1 solutions ($C_{\text{G-C18:1}} = 1 \text{ wt}\%$) at different molar ratios, indicated in the caption. The vertical red line shows the wavelength targeted to follow the absorbance evolution, c) 670 nm for Cu^{2+} and d) 395 nm for Ni^{2+} addition. The pH is adjusted at 8.5 before the last centrifugation.

Absorbance spectra for Cu^{2+} and Ni^{2+} systems are shown in Figure 2a,b. They represent the typical evolution of the UV-Vis absorption signal as a function of the metal ion content. Two typical trends are observed: increase (with Cu^{2+} or Cr^{2+}) or decrease (for Ni^{2+} or Co^{2+}) in absorbance. Spectra obtained with Cr^{2+} and Co^{2+} are presented in Figure S 1. The

evolution of the absorbance is plotted vs. the cation concentration at a specific wavelength, λ , where the cation displays the maximum of absorption (Figure 2c,d). Centrifugation between each injection of the metal ion solution guarantees the removal of the large aggregates, but neither ions nor any stable self-assembled form of G-C18:1 (e.g., micelles, individual fibers). It is then necessary to discriminate the UV-Vis absorbance peak attributed to the cation absorption and the wavelength-dependency (λ^{-4}) background associated to the Rayleigh scattering produced by the self-assembled structures (wormlike micelles (Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022)), which are reasonably considered here to be at least ten times smaller than the wavelength. To do so, we perform a fit of the Rayleigh scattering contribution to the total absorbance using the simplified expression $A = c\lambda^{-4} + b$, with A being the experimental absorbance in the UV-Vis range. Considering the present qualitative approach, the classical optical and size parameters, which are not exploited here, are integrated in the adjustable constant c , with b being the baseline. This is illustrated by a typical fit curve (black dash line) in Figure 2a,b.

For Cu^{2+} system, the Rayleigh scattering dominates the signal up to a molar ratio of about 0.1, while absorption due to copper ($\lambda = 670$ nm) dominates above about a molar ratio of 0.15. The absorption increases linearly up to a molar ratio close to 0.5, at which gelation occurs (Figure 2a,c and Figure 3a). The gel, constituted by entangled wormlike micelles, (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) is easily removed by centrifugation of the vials. The final supernatant is transparent by the eye, confirmed by UV-Vis spectroscopy, which shows a flat spectrum in the visible range (Figure 2a, solid black line at $[\text{Cu}^{2+}]/[\text{G-C18:1}] = 0.57$). According to UV-Vis, removal of Cu^{2+} is quantitative. However, a precise residual content of copper will be evaluated by mean of atomic absorption, presented below.

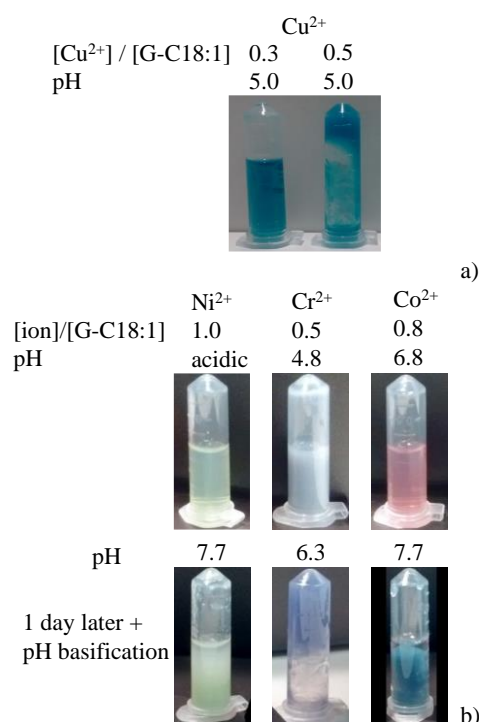


Figure 3 – a) Illustration of the Cu^{2+} solubility in a G-C18:1 solution ($C_{\text{G-C18:1}} = 3 \text{ wt\%}$) at a molar ratio 0.3 and the Cu^{2+} -containing G-C18:1 hydrogel obtained at $[\text{Cu}^{2+}]/[\text{G-C18:1}] = 0.5$. b) Picture of G-C18:1 solution ($C_{\text{G-C18:1}} = 3 \text{ wt\%}$) obtained with Ni^{2+} , Cr^{2+} and Co^{2+} addition before and after basification.

The same balance between the Rayleigh scattering and increase in absorption due to the ion in solution is also observed for the Ni^{2+} system. However, Ni^{2+} has an absorption coefficient lower than Cu^{2+} of about a factor five and adsorption occurs at lower wavelength ($\lambda = 395 \text{ nm}$), two conditions, which favors the contribution of the Rayleigh scattering of aggregates in the measured absorption. The aggregate scattering decreases until $[\text{Cu}^{2+}]/[\text{G-C18:1}] = 0.5$, when the contribution due to the cation absorption compensates the decrease of intensity due to the aggregates scattering (Figure 2c), thus producing a constant intensity (Figure 2d).

To improve the interactions between cations and G-C18:1, selected samples require an adjustment of pH towards neutrality. This is the case for the samples containing Ni^{2+} , Cr^{2+} and Co^{2+} , which form either gels or viscous solutions around pH 7. From a visual point of view, this is shown in Figure 3b, where Ni^{2+} , Cr^{2+} and Co^{2+} induce gelation and aggregation between pH 6.3 and 7.7. The equivalent spectroscopic data are provided in Figure 2b,d for Ni^{2+} and Figure S 1 for Cr^{2+} and Co^{2+} . For all samples, the supernatant is transparent at a specific molar ratio and after pH adjustment and centrifugation, as shown by the black solid lines close to 0 over the entire wavelength range (Figure 2d and Figure S 1c,d). It should be noted that the chrome-containing gel most likely contains a mixture of Cr^{2+} and Cr^{3+} , the

former being unstable and easily oxidizing into Cr^{3+} . (Baes & Mesmer, 1976) The presence of Cr^{3+} is indicated by the poorly defined, grey color of the gel (Figure 3b), as also reported before, (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) but also by the absorption peaks at $\lambda = 420$ nm and $\lambda = 577$ nm in the corresponding UV-Vis spectra in Figure S 1a. These values are intermediate between the expected absorption peaks of carboxylate-complexed aqueous solutions of Cr^{2+} ($\lambda = 410$ nm, $\lambda = 468$ nm) and Cr^{3+} ($\lambda = 432$ nm, $\lambda = 578$ nm). (Vargas-Vasquez et al., 2010)

pH has a strong impact on both the cations' chemistry and G-C18:1 and these are discussed separately below. As a general trend, metallogels of G-C18:1 form in the region of pH neutrality and above. This is most likely explained by the higher abundance of negatively charged carboxylate groups, which are supposed to interact with cations. Metal-induced gelation is well-known for polymers (Cheng et al., 2017; Diener et al., 2020) but also many low-molecular weight (LMW) amphiphiles, (L. Chen et al., 2013; Greenfield et al., 2010; Shi et al., 2011; Westcott et al., 2009; Xie et al., 2016; Zhou et al., 2013) including anionic surfactants. (Qiao et al., 2011; Vasilescu et al., 2004) The difference between hydrogels obtained by LMW amphiphiles and surfactants is generally structural, as the former often assemble into fibers, while the latter into wormlike micelles. Such effects are exploited in chemical depollution methods, which employ surfactants as flocculants to remove heavy metals from wastewater. (Paton & Talens-Alession, 2001; Somasundaran et al., 1988; Talens-Alession, 2007)

Interestingly, G-C18:1 displays both characters according to the type of cation used. (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) However, according to SAXS arguments presented elsewhere, (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) the cations studied in this work drive the formation of wormlike gels. At pH above neutrality, G-C18:1 forms a stable micellar phase in water, where micelles have a spheroidal morphology. (Baccile, Cuvier, et al., 2016; Baccile, Selmane, et al., 2016) Ni^{2+} , Cr^{2+} and Co^{2+} , among others, induce gelation by driving a sphere-to-wormlike transition. Sphere-to-cylinder and sphere-to-wormlike transitions induced by metal salts are well-known in surfactant science, (R. . G. Alargova et al., 2003; R. G. Alargova, Danov, et al., 1998; R. G. Alargova, Ivanova, et al., 1998; Angelescu et al., 2004; Jensen et al., 2014; Vasilescu et al., 2004) and they are generally attributed to the charge-screening effect of ions, which reduce repulsive interactions between negatively-charged headgroups. According to the thermodynamic theory of surfactant self-assembly, (Israelachvili et al., 1976; Tanford, 1973) smaller area-per-headgroup favors transitions from high to low curvature morphologies, like cylinders and

worms. Wormlike gels are also well-known, (Raghavan & Douglas, 2012) although cation-induced viscoelasticity in anionic surfactants is less common, but possible. (Qiao et al., 2011; Vasilescu et al., 2004) Most of the studies reporting cation-induced morphological transitions in surfactants and LMW amphiphiles generally consider the ion in its free M^{Z+} form. Broadly speaking this is imprecise.

The effect of pH on metal ions is well-known in inorganic chemistry and it is responsible for the precipitation of metal oxides. pH determines the form of the ion, whether free (M^{Z+}), although generally hydrated by water, or complexed as hydroxo species ($M(OH)_y^{(z-y)+}$). (Baes & Mesmer, 1976) Speciation is particularly important for transition metal compared to alkaline earth cations. The former generally display a large number of species, depending on the valence of the metal, its polarizability and electronegative character. If speciation of metal in water should be taken into account when discussing the metal-surfactant interactions, this is rarely the case. We have identified a limited number of works, (Jian-Xiao et al., 2006; Paton & Talens-Alession, 2001; Somasundaran et al., 1988) compared to the majority, where speciation is taken into account (refer to Table S 1 in Ref. (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) for a more extended literature survey). Understanding the interactions between G-C18:1 and metal ions is then very challenging on the basis of previous literature. The chemical nature of G-C18:1 also adds another source of complexity.

Most literature studies involve anionic surfactants, generally derivatives of sulfates, which do not chelate metals. On the contrary, G-C18:1 has a carboxylate group, which is known to be a good ligand for metals. (Ringbom, 1963) For this reason, a competition must exist between carboxylates and hydroxyl groups, since pH controls both the amount of carboxylates in solution and the type and relative content of metal hydroxo species. Furthermore, one cannot exclude a charge-screening effect by $M(OH)_y^{(z-y)+}$ complexes themselves, instead of free metal ions, as also hypothesized by others. (Jian-Xiao et al., 2006) It goes without saying that the overall complexity of the system goes far beyond the scope of this work.

We have however attempted to propose a general rationale with some exceptions. (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) Those cations which exist as free ions (M^{Z+}) in the pH region above 7 (e.g., Ag^+ , Ca^{2+} , Mn^{2+}) tend to form strong metal-ligand complexes with G-C18:1 and their mutual interaction drives the formation of fibers. (Poirier, Griel, Hoffmann, et al., 2022) On the other hand, those cations, which have a more complex speciation ($M(OH)_y^{(z-y)+}$) tend to form micellar gels, probably driven by electrostatic

screening between coexisting forms of $M(OH)_y^{(z-y)+}$ and negatively-charged G-C18:1 micelles. This seems to be the case of Ni^{2+} , Cr^{2+} , Co^{2+} and Cu^{2+} . However, exceptions exist, as shown by the gelation of the G-C18:1 at pH 5 containing Cu^{2+} . Complexation phenomena between Cu^{2+} and carboxylic acids, or even glucose, are not excluded.

The atomic absorption spectroscopy (AAS) allows a quantitative analysis of the cations concentration in the supernatants, after centrifugation of the hydrogels. Experiments are performed in triplicate. Preparation of each sample is given in Table 1, while the efficiency of cation removal is given in Figure 4. The higher efficiency is obtained with Co^{2+} where 95 ± 3 % of cation is removed from water and integrated in the gel phase. Cu^{2+} and Ni^{2+} are also removed with a very good efficiency of about 88 ± 10 % and $80\% \pm 3$ % for each cation. Cr^{2+} exhibit the lower efficiency with only 59 ± 6 % removed, probably due to the presence of Cr^{3+} species.

The heavy metal ion removal efficiency found for several ions, like Co^{2+} or Ni^{2+} , is impressively high, especially if one considers that nearly no optimization has been performed, as otherwise found for other systems, (De França et al., 2015; Talbot et al., 2018) and the mixing protocol is relatively simple. The comparison to other biosurfactants is not straightforward, as most work has been carried out on soil depollution, (Q. Chen et al., 2021; Kim & Vipulanandan, 2006; Malkapuram et al., 2021; Miller, 1995; Mishra et al., 2021; C. N. Mulligan et al., 2001; Catherine N. Mulligan, 2005, 2009, 2021; Catherine N. Mulligan, Yong, & Gibbs, 1999; Catherine N. Mulligan, Yong, Gibbs, et al., 1999; Catherine N. Mulligan & Wang, 2006; Ochoa-Loza et al., 2001b; Sonowal et al., 2022) rather than aqueous solutions. (Ghaith et al., 2019; Huang & Liu, 2013; Kim & Vipulanandan, 2006) In the latter case, the biosurfactants (generally rhamnolipids) are not employed alone but in association with biomass, like dry ground grass or bacteria, or the nature of the biosurfactant itself is not clarified. (Kim & Vipulanandan, 2006) The unique metallogelation mechanism of G-C18:1 in the presence of cations (Poirier, Griel, Perez, Hermida-Merino, et al., 2022) displays a high cation removal efficiency compared to other biosurfactants. In the case of water purification, it was reported a removal efficiency of lead in the order of 80%, although the type of biosurfactant used was not clear. (Kim & Vipulanandan, 2006) An interesting study by Ochoa-Loza provides the binding constants between monorhamnolipids and a number of metal ions, showing that the best affinity occurs with Al^{3+} and Cu^{2+} , without however quantifying the removal efficiency from contaminated water solutions. In terms of soil washing, a recent review (Mishra et al., 2021) lists the efficiency of heavy metal removal for a number of biosurfactants, including rhamnolipids, sophorolipids, surfactin and other

unspecified molecules. Although difficult to compare in a direct manner, the water cleaning process using metallogelation from G-C18:1 with Co^{2+} and Cu^{2+} still ranges among the highest standards with respect to all metals reported in Table 3 of Ref. (Mishra et al., 2021). Specifically, the high efficiency values obtained with Co^{2+} ($95 \pm 3\%$) and Cu^{2+} ($88 \pm 10\%$) as well as less impressive values found for Ni^{2+} ($80 \pm 3\%$) and Cr^{2+} ($59 \pm 6\%$), outperform the effect of rhamnolipid, sophorolipid and surfactin on these same cations, which were shown to have efficiencies ranging between 1.68 % (surfactin/chromium) and 74% (rhamnolipid/copper). (Mishra et al., 2021) To the best of our knowledge, the glucolipid presented here seems to be one of the most performing low molecular weight bio-flocculants. Although never tested in depollution of soils, one does not expect sophorolipids, rhamnolipid or surfactin to have such high efficiencies in water treatment. In fact, previous work focusing on the impact of free metal ions on the self-assembly of these molecules did not demonstrate any major impact with noticeable macroscopic behavior in terms of ion trapping. (Baccile et al., 2013; M. Chen et al., 2013; Dahrazma et al., 2008; Shen et al., 2011) The present results are explained by the atypical, bolaform and functional, molecular structure of G-C18:1 but also by the control and fine tuning of its unique phase behavior. (Baccile et al., 2022; Baccile, Cuvier, et al., 2016; Baccile, Selmane, et al., 2016; Poirier, Bizien, et al., 2022; Poirier, Griel, Hoffmann, et al., 2022; Poirier, Griel, Perez, & Baccile, 2022; Poirier, Griel, Perez, Hermida-Merino, et al., 2022)

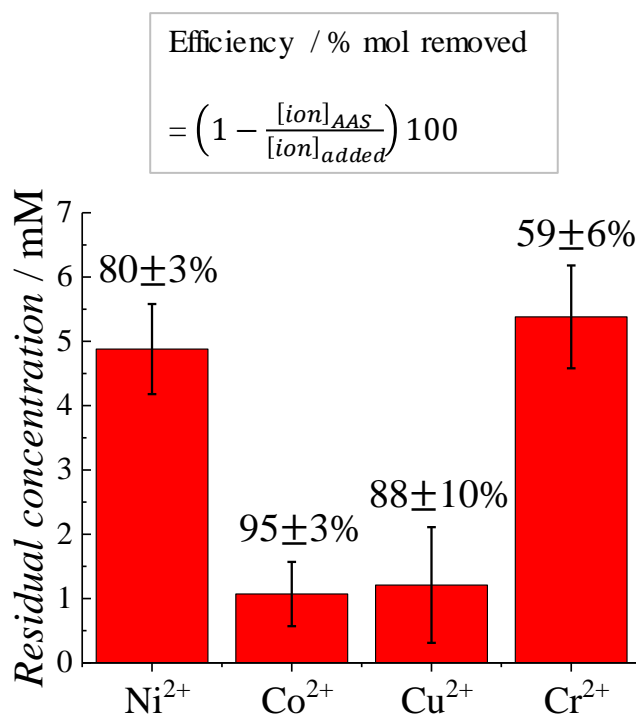


Figure 4 – Residual concentration of heavy metals, measured by atomic absorption spectrometry (AAS), in the supernatant after metallogelation and centrifugation. Composition values are indicated Figure S 1. The molar fraction removed is obtained by ratio of the effective ion concentration measured by AAS experiment $[\text{ion}]_{\text{AAS}}$ in the supernatant over the ion concentration initially added to the glycolipid solution, $[\text{ion}]_{\text{added}}$.

Conclusions

The microbial biosurfactant, glucolipid G-C18:1, forms metallogels with a broad set of heavy metals. The gel phase is employed here as heavy metal adsorbent intended to clean the water phase. G-C18:1 is tested with four well-known heavy metal pollutants of industrial waste and ground waters, Cu^{2+} , Ni^{2+} , Cr^{2+} and Co^{2+} . By increasing the cation-to-biosurfactant ratio up to an optimum value, generally at charge compensation, and adjusting the value of pH between 7 and 8 for some of them, G-C18:1 strongly interacts with all metals in the form of hydroxo species, which are entrapped in the gel phase. The mechanism behind metallogelation, reported elsewhere, involves a micelle-to-wormlike morphological transition driven by the interaction between the carboxylate group of G-C18:1 and the charged metal species.

Centrifugation is eventually used as a practical laboratory-scale process to separate the gel from water. Qualitative observations by the naked eye show nearly complete removal of the heavy metals. This is confirmed by UV-Vis spectrophotometry experiments, which, within the sensitivity of the instrument, show no trace of the heavy metals in the supernatant. Precise quantification has been performed with atomic absorption spectrometry, which reveals the high efficiency in terms of flocculant behavior of G-C18:1 towards selected heavy metals. We find that the efficiency removal is as high as $95 \pm 3\%$ for Co^{2+} , $80 \pm 3\%$ for Ni^{2+} , $88 \pm 10\%$ for Cu^{2+} and $59 \pm 6\%$ for Cr^{2+} . Due to the little work performed on the depollution of water by biosurfactants, these values cannot benefit direct comparison. Nevertheless, in comparison to the extensive work performed on the removal of heavy metals in soil, these values are in the top range and show promising application of G-C18:1 also in soil cleaning.

This study confirms the strong interest of biosurfactants as remediation green chemicals. Moreover, considering the very high efficiency of G-C18:1 for heavy metal removal, it also shows the strong interest in studying this compound further in this field.

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Author contribution statement

A. P., K. O. and J. G. performed the experiments. A. P. and N. B. wrote the manuscript. D. T. performed AAS studies. N. B. conceived and designed the study and finalized the manuscript. All authors contributed to and approved the final draft of the manuscript.

Ethics statement

No human or animal subjects were used in this research.

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Supporting information

Heavy metal removal from water using the metallogelation properties of a new glycolipid biosurfactant

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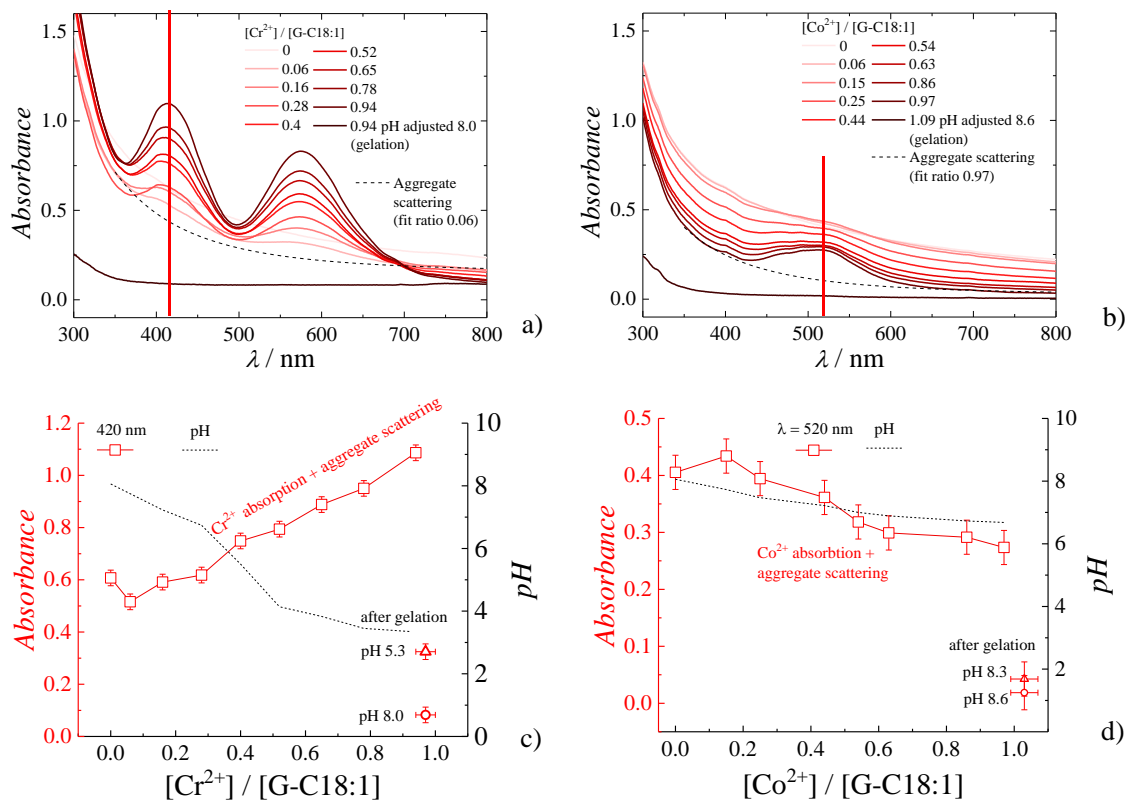


Figure S 1 – Absorbance spectra for a) Cr^{2+} and b) Co^{2+} containing G-C18:1 solutions ($C_{\text{G-C18:1}}=1 \text{ wt}\%$) at different $[\text{ion}]/[\text{G-C18:1}]$ molar ratio, indicated in the caption. The vertical red line show the wavelength targeted to follow the absorbance evolution, c) $\lambda = 420 \text{ nm}$ for Cr^{2+} and d) $\lambda = 520 \text{ nm}$ for Co^{2+} addition.