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Investigation of the Ga Complexation Behaviour of the Siderophore Desferrioxamine B

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Abstract. Gallium (Ga) is a critical element for the electronic industry, however, its long-term supply is not assured. Thus, the recovery of Ga from industrial wastewaters is important. Selective sorption is a recommended technology for the recovery of Ga from industrial wastewaters, however, selective sorbents are elusive. Desferrioxamine B (DFOB), a hydroxomate siderophore that is known to be highly selective towards Fe^{3+}, is tested for its ability to complex Ga. This study demonstrated that DFOB forms 1:1 complex with Ga and the maximum Q_e-Ga is 124.4 mg of Ga complexed per g of DFOB. Further, the complexation mechanism of Ga^{3+} and Fe^{3+} with DFOB is similar, as indicated by NMR, suggesting that the selectivity of DFOB towards Fe^{3+} will be extended to Ga^{3+} as well. Thus, DFOB seems to be a suitable candidate for the sorption of Ga from industrial wastewaters.

Introduction

Gallium (Ga) is the backbone of the electronic industry [1], thus the continuous and uninterrupted supply of Ga is important. However, the European commission report has projected a deficit of 137 tons Ga by year 2020 [2]. As Ga is economically mined as a by-product of bauxite mining, the production of Ga cannot be dramatically increased in near future [2]. Thus, the recovery of Ga from scraps (LED waste) or GaAs fabrication industry wastewater is important to make up for the projected deficit in 2020. Ga recovery from wastewaters such as GaAs fabrication industry wastewaters is usually carried out by solvent extraction, ion-exchange, fractional precipitation or electrochemical deposition [3]. However, such chemical methods are not very successful for the recovery of Ga from wastewaters that usually contain low concentrations of Ga.

Sorption is a cost-effective technology for the recovery of metals from the low concentrated wastewaters [4]. The challenge in the sorption is the low selectivity of the sorbents towards targeted metal [4]. The sorption of Ga from the wastewaters also faces the same challenge as the Ga containing wastewaters normally also contain other metal ions such as As, Mg, Ca, K and Na.

Siderophores are a class of organic ligands released by microorganisms, fungi and plants to capture Fe^{3+} from the environment [5]. They are highly selective towards Fe^{3+} with complexation coefficient as high as 49.0 [5]. Siderophores have also shown selectivity towards other trivalent metal ions such as Ga^{3+} [6]. Thus, the selective properties of siderophores can be exploited for the recovery of Ga from industrial wastewaters. However, there are no studies so far that have exploited the selective properties of siderophores for Ga recovery.

The successful exploitation of the selective properties of the siderophores to recover Ga from industrial wastewaters can only be achieved if the siderophores can be immobilized onto carrier materials. For instance, the immobilization of Desferrioxamine B (DFOB), a hydyoxamate functional group siderophore, for detecting metal ions present in wastewater has been carried out [7]. The present project would utilize a similar strategy to immobilize DFOB for the recovery of Ga from industrial effluents in the further works. Prior to the immobilization, it is important to understand the complexation of Ga with DFOB.

This study studied the complexation of Ga with DFOB. Prior to the complexation experiments, the analytical methods for the detection of DFOB and Ga-DFOB complex in a high performance liquid chromatography (HPLC) were optimized. The ratio of DFOB and Ga in the Ga-DFOB complex was ascertained by isotherms. Finally, the Ga-DFOB complex was analyzed by means of Nuclear Magnetic Resonance (NMR).

Materials and Methods

DFOB and gallium nitrate were bought from Sigma Aldrich. HPLC system was an Agilent 1200, with a ZORBAX Eclipse XDB-C18 4.6 x150 mm, 5µm column and diode array detector (G1315B 1200). The column temperature was maintained at 25 °C. Two solvents, 10 mM KH_2PO_4 (solvent A) and acetonitrile - HPLC grade (solvent B) was used in the following gradient method [9]. The solvent B was increased from 10 % to 20 % in 15 min, 20 % to 50 % in next 15 min, 50 % to 60 % in following 10 min and finally from 60 % to 10 % in next 5 min. 20 min equilibration time at the last concentration was observed. The calibration of HPLC was carried out by preparing different Ga-DFOB complex concentration varying from 0.1 mM to 2.0 mM. Similarly, the DFOB was calibrated for concentration range of 0.1 mM to 2.0 mM. The complexation experiments were carried out by mixing varying concentrations of Ga and DFOB (0.1 mM – 2.0 mM) to 0.8 mM of DFOB and Ga, respectively. NMR spectra were recorded on an Agilent 600 DD2 NMR spectrometer equipped with a one probe head with z-gradients operating at 599.80 MHz for ^1H and 150.84 MHz for ^{13}C, respectively. All samples were measured at 20 °C using standard pulse programs. D_2O, sodium deuteroxide and deuterochloride were purchased at Eurisotop GmbH and used as is.

Results

The HPLC was able to resolve the DFOB and Ga-DFOB complex with the retention times of 9.2 and 3.7 minutes, respectively. The calibration curves for both the DFOB and Ga-DFOB complex has R^2 values greater than 0.999. While varying the concentration of DFOB from 0.1 mM to 2.0 mM and keeping Ga concentration at 0.8 mM, the concentration of Ga-DFOB complex increased from 0.1 mM to 0.8 mM and then remained constant (Fig. 1a). Similarly, when the Ga concentration was varied from 0.1 mM to 2.0 mM and keeping DFOB concentration constant at 0.8 mM, the Ga-DFOB complex increased from 0.1 mM to 0.8 mM and then remained constant (Fig. 1b). Further, the amount of calculated DFOB complexed with Ga, determined by subtracting the remaining DFOB from the total added, was same as the one determined by directly measuring Ga-DFOB complex in HPLC. The Q_e-Ga, amount of Ga complexed per g of DFOB, increased linearly from 16.5 mg g^{-1} to 124.4 mg g^{-1} when the initial Ga concentration increased from 0.1 mM (6.9 mg) to 0.8 mM (55.8 mg) at an equilibrium pH of 5.0. Further increase in the concentration of Ga did not increase Q_e-Ga as the DFOB was saturated.

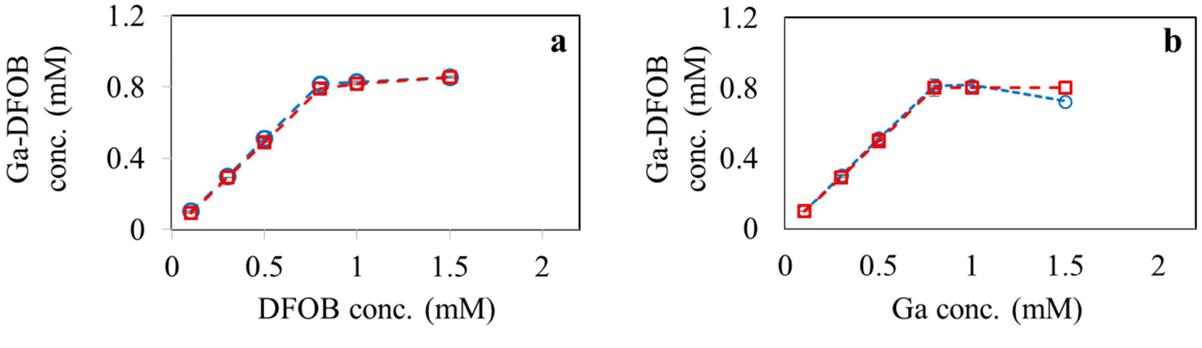

Fig. 1. Ga-DFOB complex identified (o, ----) and calculated (□, ---) while increasing the concentration of DFOB (a) and Ga (b). The concentration of Ga (a) and DFOB (b) was constant at 0.8 mM and equilibrium pH was 5.0.

NMR spectra of DFO-B in the pH range of pH 4 to 5 show drastic changes upon complexation with Ga (Fig. 2). Due to the folding of the complex isotropical rotation of the bonds is hampered and diastereotopic protons become distinguishable. This can be seen by the increasing number of proton resonances associated with a certain carbon resonance in a 2D HMQC-type correlation spectrum (Fig. 2). These results are in agreement with the results of Borgais, et. al (1989) [8].

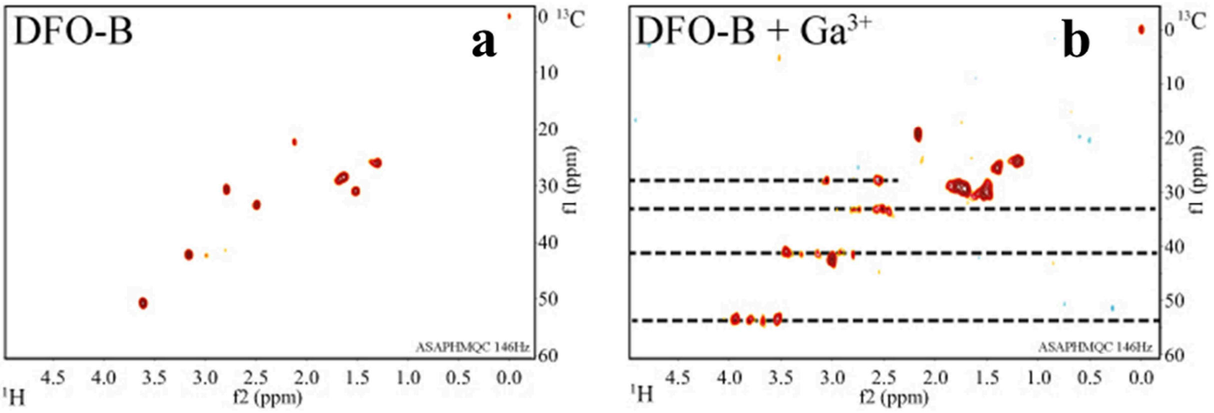

Fig. 2. NMR spectra of DFO-B at pH range 4-5. (a) Free DFO-B in D_2O and (b) DFO-B complex of gallium in D_2O. The shown ASAPHMQ spectra, recorded at 293K with a coupling constant of 146 Hz, show correlations of the resonances of directly bound protons (horizontal) to carbons (vertical; along one chemical bond). The aliphatic region illustrates the increase of the number of resonances of protons while the number of carbon resonances is constant, which is caused by distinguishable diastereotopic protons after complexation (dashed lines indicating carbon resonances showing a number of distinguishable proton resonances upon complexation). It is important to note that the accurate pH determination of Ga-DFOB complex in D_2O is difficult and hence a pH range of 4-5 is assigned. This narrow difference in pH will not affect the NMR spectra as Ga-DFOB species is constant in the pH range of 2-9 [8].

Discussion

This study confirmed that Ga can be complexed by DFOB. The similarity between the identified and calculated Ga-DFOB complex (Fig. 1) suggests that the Ga-DFOB complex is in 1:1 ratio of Ga and DFOB. The maximum Q_e-Ga achieved by DFOB is 124.4 mg of Ga per g of DFOB. This Q_e-Ga value for DFOB is higher than the adsorption of Ga on TiO_2 nanoparticles (70 mg of Ga adsorbed per g of TiO_2 nanoparticles) [10]. The structural similarity in the Ga-DFOB complex with Fe-DFOB complex, as observed with the NMR data in this study and also in a previous study [8], suggests that the DFOB will also demonstrate similar selectivity for Ga^{3+} as has been observed for Fe^{3+} [7]. This is due to similar ionic radius of Ga^{3+} (62 pm) and Fe^{3+} (65pm). Further, more than 90% of Ga species is $Ga[HDFOB]^+$ complex in the pH range of 2-9 suggesting that DFOB will be able to complex Ga from the industry effluent of varying pH [8]. The high Q_e-Ga value, probable selectivity of DFOB towards Ga and stability of Ga-DFOB complex in varying pH makes DFOB a good candidate for the recovery of Ga from the industrial effluents that are generally known for their complex composition. One of the challenge in the recovery of Ga from the industrial effluent is the presence of Fe in the industrial effluent. The log K of Fe and Ga complexes with DFOB is 30.60 and 27.56, respectively. Thus, it is clear that the Fe^{3+} will be preferentially complexed compared to Ga^{3+} when both are present in the industrial effluents. Thus, the Fe has to be removed either by co-precipitation or selective adsorption prior to the adsorption of Ga from the industrial effluents.

Summary

This study demonstrated that the HPLC can easily resolve and quantify the DFOB and Ga-DFOB complex. Further, the isotherm and complexation experiments suggested that the Ga-DFOB complex is in 1:1 ratio. NMR data revealed that binding of Ga^{3+} with DFOB is similar to that of Fe^{3+} with DFOB and thus suggests the high selectivity of DFOB toward Ga. Based on the results of this study, further experiments such as complexation of Ga from real wastewaters, desorption of Ga, regeneration of DFOB for Ga complexation and immobilization of DFOB onto carrier material will be carried out.

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