Chemical immobilization of 8-hydroxyquinoline and 8-hydroxyquinoline on chitosan-silica adsorbent materials for the selective recovery of gallium from Bayer liquor

Joris Roosen,^{ab} Steven Mullens^b and Koen Binnemans^{*a}

^a Department of Chemistry, KU Leuven, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium.

^b VITO, Sustainable Materials Management, Boeretang 200, B-2400 Mol, Belgium.

* Corresponding author. Department of Chemistry, KU Leuven, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@kuleuven.be; Phone: +32 16 3 27356.

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Abstract

Ion exchange is a widely used technique for the recovery of gallium from Bayer liquor of the alumina industry. However, development of cheap, selective, reusable and environmentally friendly resin materials is essential. Novel resins must be resistant to both the highly alkaline environment of Bayer liquor and the acidic media used for stripping. In this study, chitosan was combined with silica. The hybrid chitosan-silica (CS) adsorbent matrix was chemically immobilized with the organic ligands 8-hydroxyquinoline (8-HQO) and 8-hydroxyquinaldine (8-HQA), the latter being the C2-methylated analogue of the former. Adsorption of Ga(III) and Al(III) by CS functionalized with 8-HQO and 8-HQA was studied as a function of kinetics, equilibrium concentration, aqueous pH and temperature, to determine the conditions to get the highest selectivity for Ga(III). With the 8-HQA-functionalized adsorbent, selective stripping of the loaded metal ions by sulfuric acid resulted in a better Ga(III)/Al(III) separation, in comparison with 8-HQO-CS. In contrast to the resins that are currently in use, no significant loss in Ga(III) loading was observed after seven consecutive alkaline adsorption and acidic desorption cycles. It was also possible to separate Ga(III) from a synthetic Bayer solution using an ion-exchange column with 8-HQA-functionalized CS as the stationary phase. The studied adsorbents are considered promising resin materials to make gallium recovery from Bayer liquor of lower environmental impact and less expensive by significantly decreasing the resin cost.

1. Introduction

Gallium is a highly valuable element useful in a range of semiconductor applications, like integrated circuits, optoelectronics (lasers and light-emitting diodes), photovoltaic solar cells, *etc.* (Fowler and Sexton, 2015). Given that gallium is mainly used in green-tech applications, it can be predicted that the demand for gallium will continue to grow in the future. The increasing demand for gallium is associated with an increasing supply risk. No exploitable mines of gallium exist and therefore, it is exclusively produced as a minor element from the primary production of other materials. Major sources for gallium include process streams of the alumina production (*Bayer liquor*), zinc processing, flue dusts and some ores containing up to 200 g/t of gallium (Lahiri et al., 1996; Nishihama et al., 1999; Selvi et al., 2004). In order to ensure a stable supply, it is crucial to develop cheap, efficient and environmentally friendly technologies and materials to produce gallium.

Bayer liquor, the highly alkaline sodium aluminate solution that originates from the production of alumina from bauxite by the Bayer process, constitutes the largest primary source of gallium (Mihaylov and Distin, 1992). However, the process for recovery of gallium from Bayer liquor is very expensive, inefficient, and environmentally unfriendly, due to the high consumption of chemicals and contamination of waste water with organics (Zhao et al., 2012). To recover gallium from spent Bayer liquor, *i.e.* the liquid generated after precipitation of alumina in the Bayer process, small amounts of gallium (100-300 mg L⁻¹) must be separated from a large quantity of chemically similar aluminium (30-60 g L⁻¹) (Filik and Apak, 1994). These elements are present as Ga(OH)₄⁻ and Al(OH)₄⁻ in the roughly 3–6 mol L⁻¹ NaOH Bayer solutions (Zhao et al., 2012). Zhao et al. (2016) reported the composition of a typical Bayer liquor sample, containing a total

Na₂O concentration of 176 g·L⁻¹, 81 g·L⁻¹ of Al₂O₃, 780 mg·L⁻¹ of SiO₂ and 190 mg·L⁻¹ of Ga(III).

There are four main routes to recover gallium from spent Bayer liquor: (1) fractional precipitation, (2) electrochemical reduction, (3) solvent extraction, and (4) ion exchange, with the latter two being the most interesting approaches (Virolainen, 2013). Recovery of gallium by solvent extraction has been investigated extensively (Brunette et al., 1979; Lee et al., 2002; Lupi and Pilone, 2014; Mihaylov and Distin, 1992; Nishihama et al., 1999). It is generally accepted that Kelex[®] 100 and Lix[®] 26, with alkylated derivatives of 8-hydroxyquinoline as the active component, are the only commercially available extractants suited for the recovery of gallium from highly alkaline solutions (Pesic and Zhou, 2012). Although a solvent extraction procedure with Kelex[®] 100 (7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline) was patented in the 1980s, the technique is currently not implemented in industry (Helgorsky and Leveque, 1988; Virolainen, 2013; Zhao et al., 2012). The main reasons for this are: (1) the poor selectivity for gallium over aluminium and sodium, necessitating an extra scrubbing step, (2) reagent loss, due to the solubility of the extractant in the aqueous phase, and (3) the slow kinetics of the overall process (Pesic and Zhou, 2012; Virolainen, 2013; Zhao et al., 2012).

Ion exchange is a more suitable technology for the recovery of low concentrations of (valuable) metals from large volumes of aqueous process streams (Guibal et al., 2007; Hubicki and Koodynsk, 2012). Compared to other separation methods, a higher yield and selectivity can be obtained by ion exchange, explaining why it is the most popular hydrometallurgical separation method for gallium recovery from spent Bayer liquor (Zhao et al., 2012). In contrast with solvent extraction, the need for large volumes of volatile and flammable organic solvents as well as contamination of the aqueous phase with organic molecules can be avoided by using solid-state ion-exchange materials. This, in combination with less energy consumption, leads to a more sustainable process. Energy

savings mainly arise from the fact that ion-exchange processes can be performed in simple, single-stage operations, whereas solvent-extraction processes generally consist of complex, multi-stage cascades of energy-consuming mixer-settlers. Moreover, ion exchange has minimal effects on the main alumina processing and can thus be easily integrated in the flowsheet of the Bayer process.

In general, two types of industrial resins are used for the recovery of gallium from Bayer liquor: resins with an amidoxime functional group, *e.g.* Duolite ES-346/345, and resins that are impregnated with derivatives of 8-hydroxyquinoline (8-HQO), mostly Kelex[®] 100 (Kataoka et al., 1983; Lamerant, 1995; Riveros, 1990; Zhao et al., 2016). The chemical structures of both types are compared in *Scheme 1*. Specific drawbacks are related to both types of resin materials. Amidoxime resins are not stable in acidic environment, due to degradation of the amidoxime groups (Loureiro and Rodrigues, 1998). Two possible degradation reactions are represented in

Scheme 2. As a result of these transformations, the loading capacity of the resin is significantly reduced with each regeneration, even when stripping is performed with dilute acids (Riveros, 1990). Moreover, amidoxime resins are easily poisoned by strongly

coordinating vanadium ions, which are typically present in Bayer liquor (Zhao et al., 2016). Vanadium poisoning is not the case for resins impregnated with Kelex[®] 100, but these resins also suffer from degradation during prolonged use for extraction from Bayer solutions. Here, degradation is due to the solubility of the extractant in the aqueous phase – an issue usually related to solvent extraction (Mihaylov and Distin, 1992). In the resins that are impregnated with 8-hydroxyquinoline, extractant loss occurs because the extractant is merely bound to the resin matrix by physical or chemical interactions, which are much weaker than covalent bonds (Lamerant, 1995). Moreover, Kelex[®] 100 can be prepared only via a multi-step synthesis and is thus very expensive. Hence, regular replacement of the deteriorated resin material has a significant impact on the process cost. Therefore, the challenge to address in the field of gallium production comprises the development of a reusable, low-cost resin that shows a high selectivity for gallium compared to aluminium. The resin must be resistant to highly alkaline environments, not degrade during acidic stripping, and not get contaminated with other compounds present in the liquor.

Scheme 1: Comparison of the chemical structures of a resin with an amidoxime group (left) and derivatives of 8-hydroxyquinoline, like the Kelex[®] 100 extractant (right).

Scheme 2: Two possible degradation reactions of amidoxime groups in acidic environment. Reaction (b) requires more acidic conditions than reaction (a).

Previous work showed that functionalized chitosan-silica (CS) is well suited to recover and separate metal ions from aqueous solutions by ion-exchange adsorption (Roosen et al., 2014; Roosen et al., 2016). Chitosan is a linear biopolymer which is easily derived from seafood waste (Guibal, 2004; Mati-Baouche et al., 2014; Varma et al., 2004). Its low cost, abundant availability, biocompatibility, biodegradability, non-toxicity, and convenient modification possibilities make chitosan an interesting material for various applications, including adsorption of metal ions (Bailey et al., 1999; El Kadib, 2015; Guibal, 2004; Guibal et al., 1998; Mati-Baouche et al., 2014; Varma et al., 2004). Hybridization with silica improves the mechanical strength, porosity and chemical resistance of the resulting material (Repo et al., 2011; Roosen et al., 2014; Zhao et al., 2013). By covalent attachment of selective extractants on the CS matrix, a stable, reusable and sustainable material can be obtained, in contrast with impregnated resins, in which the active components are bonded by secondary interactions. In addition to the longer lifetime of the resin, which significantly reduces the process cost, another advantage of

chemical immobilization arises from the fact that the aqueous phase is no longer contaminated by organic molecules. Hence, the main alumina production process is less interfered when circulating the spent liquor back in the Bayer process. In the selection of an appropriate extractant, attention must be paid to degradation. In contrast to amidoxime, derivatives of 8-HQO are composed of aromatic structures, which are not sensitive to hydrolysis in acidic, nor alkaline environment. Vanadium co-extraction is avoided as well by using derivatives of 8-hydroxyquinoline. In terms of cost reduction, one may decide not to immobilize the specific and sophisticated extractant Kelex[®] 100, but the much cheaper base material 8-HQO, being the precursor and active (complexing) component of Kelex[®] 100. It has been reported that the branched alkyl group on the oxine function in Kelex[®] 100 is in principle to enhance the solubility of the extractant and the extracted complexes in non-polar, organic media (Hughes, 2007), but this is not required for an ion-exchange resin. As well to impregnate polystyrene resins with chelating extractants, the hydrophobic substituent is useful, albeit no longer relevant when the extractant is immobilized by covalent bonds. On the other hand, some studies claim that the branched alkyl substituent in Kelex[®] 100 might additionally cause steric hindrance during metal ion complexation (Merritt and Walker, 1944). As a result, interactions between alkylated derivatives of 8-HQO and the smaller Al(III) ion are said to be less stable in comparison with the larger Ga(III) ion (Ohashi et al., 1996; Stary, 1964). However, Scherer and Fernando (1968) pointed out that this may be due to how well the ligand itself abstracts coordinated water molecules from the hydrated metal ion before ligand coordination, *i.e.* better for the larger Ga³⁺ ion, less so for the smaller Al³⁺ ion. They based this premise on the fact that they were able to precipitate complexes of Al(III)-8-HQA in non-aqueous solvents and that the reason that Al(III) does not complex in aqueous solution may not just be about steric hindrance. In conclusion, the allegedly more selective effect of an alkyl substituent on 8-HQO that is immobilized on an ion-exchange adsorbent matrix is

not clear from the literature and needs further investigation. Therefore, both the native and the C2-methylated derivative of 8-HQO, 8-hydroxyquinaldine (8-HQA), were covalently attached on a CS hybrid polymer matrix. Both adsorbents were compared in terms of their (ion-exchange) adsorption performance towards Ga(III) from alkaline environment.

In this work, we discuss the recovery of gallium from Bayer liquor by adsorption on functionalized CS materials. These are obtained by chemical immobilization of the organic ligands 8-HQO and 8-HQA on the CS matrix. A comparative study between both adsorbent materials is performed in batch mode as a function of different parameters: contact time, pH, capacity and temperature. Adsorption performance and selectivity for Ga(III) are investigated from alkaline, single-element solutions and synthetic mixtures of Ga(III) and Al(III) in NaOH, respectively. The reusability of the functionalized CS particles is studied as well. Finally, the actual separation of Ga(III) from synthetic Bayer liquor is examined by ion exchange using 8-HQA-CS as the stationary phase in a column.

2. Experimental

2.1 Chemicals

Chitosan ($\geq 99.0\%$ pure) was purchased from Sigma-Aldrich (Diegem, Belgium), tetraethyl orthosilicate (TEOS, $\geq 99.0\%$ pure) from Merck KGaA (Darmstadt, Germany), 8-hydroxyquinoline (analytical reagent, AnalAR NORMAPUR[®]), sodium carbonate anhydrous and sodium sulfate from VWR Prolabo BDH (Leuven, Belgium), acetic acid (100%) and sodium hydroxide ($> 97.0\%$) from VWR International (Leuven, Belgium), 2-methyl-8-quinolinol (8-hydroxyquinoline, 98%) from J&K Scientific GmbH (Pforzheim, Germany), sodium aluminate (general purpose grade) from Fisher Scientific UK (Leicestershire, UK), gallium(III) oxide, (99.99+ %), aluminium powder (200 mesh, 99%), gallium metal (99.99% trace metal basis), sodium acetate, (anhydrous, reagent ACS) and hydrochloric acid (fuming, 37% solution in water) from Acros Organics (Geel, Belgium), aluminium hydroxide hydrate, α form (99.99%, 1.5 micron) and gallium(III) sulfate hydrate (Puratronic[®], 99.999%) from Alfa Aesar, Johnson Matthey GmbH (Karlsruhe, Germany), ethanol (Disinfectol[®], denaturated with up to 5% ether), ammonia (25 wt%), *n*-heptane (99+%), nitric acid (65+%) and copper, gallium, aluminium and silicon standard solutions for ICP (1000 $\mu\text{g/mL}$, Plasma HIQU) from Chem-Lab (Zedelgem, Belgium), formaldehyde solution (min. 36.5% purity, p.a., reagent ACS, stabilized) from Riedel-de Haën (Diegem, Belgium) and a Serva silicone solution in isopropanol from SERVA Electrophoresis GmbH (Heidelberg, Germany). All chemicals were used as received without further purification. Water was always of ultrapure quality, deionized to a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ with a Sartorius Arium Pro ultrapure water system.

2.2 Equipment and analysis

Centrifugation was done by an Eppendorf 5804 centrifuge. pH measurements were performed using a Mettler-Toledo SevenCompact pH meter combined with a Hamilton Slimtrode pH-electrode. The FTIR spectra were recorded on a Bruker Vertex 70 spectrometer (Bruker Optics), equipped with a Platinum ATR single reflection diamond attenuated total reflection (ATR) accessory. The CHN (carbon, hydrogen, nitrogen) elemental analyses were obtained with the aid of a Thermo Scientific Interscience Flash 2000 Elemental analyser. Metal ion concentrations on single-element Ga(III) solutions were determined by total-reflection X-ray fluorescence (TXRF) on a Bruker S2 Picofox TXRF spectrometer. The sample preparation consisted of mixing the sample (500 μL) in an Eppendorf tube with a copper standard solution (1000 mg L^{-1} , 100 μL) in a solution of ammonia (25 % (w/w), 400 μL) and stirring. A sample (5 μL) of the prepared solution was put on a small quartz plate, pre-coated with a hydrophobic silicone solution (about 10 μL), and dried in an oven at 60 $^{\circ}\text{C}$. Solutions containing aluminium were analyzed by ICP-OES, with a Perkin Elmer Optima 8300 spectrometer, equipped with an axial/radial dual plasma view, a GemTip Cross-Flow II nebulizer, a Scott double pass with inert Rytan[®] spray chamber and a demountable one-piece quartz torch with an alumina injector tube. Aluminium was measured radially at wavelength 396.164 nm, gallium axially at wavelength 417.206 nm. Samples, calibration solutions and quality controls were diluted in HNO_3 (2 % (v/v)): strip solutions 10-fold, synthetic adsorption solutions 20-fold, Bayer solutions 1000-fold. Each ICP sample was measured in triplicate. The MPLC chromatography separation set-up was composed of a Büchi chromatography pump B-688, to control the pressure and the eluent flow, and a glass Büchi BOROSILIKAT 3.3 column tube, N° 17988 with dimensions 9.6 mm $\times$ 115 mm (bed volume = 8.3 mL).

Separated compounds were collected with the aid of a Büchi Automatic Fraction Collector B-684. The fractions were monitored by *ex-situ* ICP analysis.

2.3 Synthesis

Chitosan-silica hybrid materials were made according to the *in-situ* Stöber based method, as described previously (Roosen et al., 2014). Basically, TEOS (60 mL) was mixed with chitosan (4.00 g) dissolved in an acetic acid solution (2 % (v/v), 200 mL), and stirred for ½ h. Then, this suspension was poured into an aqueous solution of NH₃ (3 % (v/v), 400 mL) and stirred for 24 h. Hybrid particles were filtered, washed and dried. A white powder was obtained (yield: 27.14 g). Compared to the reported procedure, double amounts were used here, which resulted in a relatively higher yield. The chitosan-silica polymer networks were then functionalized with 8-HQO and 8-HQA, respectively, both according to the same procedure, based on a published method to prepare silica-immobilized 8-quinolinol and involving a one-step Mannich reaction (Lan and Yang, 1994). Chitosan-silica particles (7.50 g) were added to a mixture of ethanol (400 mL), 8-HQO/8-HQA (10.00 g) and formaldehyde solution (10 mL, 36.5%). The immobilization reaction in the mixture occurred by reflux at 50 °C in a flask for 3 days. The quinolinol derivatives were filtered and washed with ethanol (three times) and dry diethyl ether (three times) to remove traces of non-reacted quinoline. The solid material was ready for use after washing with HCl (1.0 M, 500 mL), water (500 mL) to remove HCl, and ethanol. During the first (acidic) washing step, the colour changed from off-white/beige to light green in the case of 8-HQO-CS and light yellow in the case of 8-HQA-CS (*Figure 1*).

Figure 1: Pictures of non-functionalized CS (left) and CS functionalized with 8-HQA (middle) and 8-HQO (right).

After drying the powder by exposing to the air overnight, drying was completed in a vacuum oven at 40 °C for 2 h. The yields were 6.80 g (8-HQO-CS) and 5.74 g (8-HQA-CS). The chemical structures of 8-HQO-CS and 8-HQA-CS are shown in *Scheme 3*, where the substituent X is H (8-HQO) or CH₃ (8-HQA).

Scheme 3: Chemical structure of chitosan-silica functionalized with 8-HQO (X = H) and 8-HQA (X = CH₃).

2.4 Metal ion solutions

A single-element Ga(III) stock solution, with a concentration of 25.0 mM (1750 mg·L⁻¹), was made from the corresponding sulfate salt, Ga₂(SO₄)₃·x H₂O. With NaOH (1.0 M), the pH was brought to a value of 12.50 (± 0.01). A synthetic mixture of Al(III)

and Ga(III) was made by dissolving $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ and Ga_2O_3 in NaOH (2.5 M) at 100 °C for 24 h. After preparation, the blurred solution was centrifuged to remove traces of non-dissolved particles. The solution had an Al(III) concentration of 20.0 mM ($540 \text{ mg} \cdot \text{L}^{-1}$) and a Ga(III) concentration of 6.0 mM ($418 \text{ mg} \cdot \text{L}^{-1}$). An industrial recipe was followed for the synthesis of a representative Bayer liquor sample. Ga and Al metal were added to a mixture of free NaOH, NaAlO_2 , $\text{C}_2\text{H}_3\text{NaO}_2$, Na_2CO_3 and Na_2SO_4 , together stirred at 85 °C for 48 h and centrifuged to separate any residue from the liquor. The total metal ion content was 1.3 M (35.0 g L^{-1}) for Al(III) and 2.0 mM ($140 \text{ mg} \cdot \text{L}^{-1}$) for Ga(III). Given the scope of this work to investigate the selectivity of the functionalized adsorbent materials for Ga(III) over Al(III), concentrations of the other impurities were not further considered.

2.5 Adsorption study

CS functionalized with 8-HQO and 8-HQA was investigated for the recovery of gallium from alkaline Bayer liquor. The following parameters were studied by adsorption in batch mode from alkaline, single-element Ga(III) solutions: kinetics, capacity, pH and temperature. For each experiment, aliquots of the stock solution were properly diluted to a final volume of 10.0 mL. The solution pH was adjusted using HCl (1.0 M) or NaOH (0.1 M). Solutions were stirred at room temperature with a magnetic stirring bar at 300 rpm for 6 h, unless stated otherwise. Next, the particles were separated from the aqueous solution by filtration, making use of a regenerated cellulose syringe filter with a pore size of $0.45 \mu\text{m}$. The remaining metal ion concentration of the aqueous solution was measured by TXRF or ICP. The amount of metal ions adsorbed on the chitosan-silica particles was determined using the following formula:

$$q_e = \frac{(c_i - c_e) V}{m_{ads}} \quad (1)$$

Here, q_e is the amount of adsorbed metal ions at equilibrium (mmol g^{-1} adsorbent), c_i is the initial metal ion concentration in aqueous solution (mmol L^{-1}), c_e is the equilibrium metal ion concentration in aqueous solution (mmol L^{-1}), V is the volume of the solution (L) and m_{ads} is the mass of the adsorbent (g).

2.6 Selective recovery

The adsorption selectivity for Ga(III) over Al(III) was investigated for both 8-HQO- and 8-HQA-CS. A certain amount of adsorbent (50.0 mg) was contacted sequentially with a fresh mixture feed of Al(III) and Ga(III) (1000 μL) and shaken for 2 h at room temperature. After each adsorption step, the adsorbent was separated by centrifugation and the cumulative adsorption amount was calculated from the aqueous phase.

In another experiment, selective stripping was investigated. The loaded adsorbent was scrubbed with water for 5 min and contacted with a fresh strip solution (10.0 mL) of increasing H_2SO_4 concentrations for 30 min. After desorption, the cumulative stripping percentage was

as calculated. The stripping percentage is defined as:

$$\% \text{ stripping} = \frac{n_{M, \text{strip solution}}}{n_{M, \text{adsorbed}}} \times 100\% \quad (2)$$

with $n_{M, \text{strip solution}}$ the molar amount of metal in the H_2SO_4 solution and $n_{M, \text{adsorbed}}$ the molar amount of metal that was adsorbed on the adsorbent.

2.7 Reusability

The efficiency of gallium recovery from Bayer liquor was investigated for 8-HQA-CS as a function of the number of adsorption-desorption cycles. Over one cycle, an amount of adsorbent (50.0 mg) was first contacted with Bayer liquor (1000 μL) for 2 h, then scrubbed with water (10.0 mL) for 5 min, then stripped with H_2SO_4 (2.5 M, 10.0 mL) for 30 min and finally washed with water (10.0 mL) for 5 min, all at room temperature. After each stripping step, the aqueous phase was separated from the adsorbent by centrifugation and its composition was analyzed. Then the adsorbent was used again in the following adsorption-desorption cycle. The recovery efficiency was calculated by the following equation:

$$\text{Recovery efficiency} = \frac{q_{e,1}}{q_{e,x}} \times 100\% \quad (3)$$

with $q_{e,1}$ the adsorption amount in the first cycle and $q_{e,x}$ the adsorption amount in cycle x .

2.8 Separation of gallium

Gallium was separated from synthetic Bayer liquor using an ion-exchange column packed with 8-HQA-CS (2.0 g) as the stationary phase. The experimental course of the column separation experiment is tabulated in Table 1. Distinct fractions (10.0 mL) were collected and their composition analyzed *ex situ* by ICP. In between experiments, the column was always stored at neutral pH by extensively washing with water.

Table 1: Course of the column separation experiment

Step	Description	Eluent	Flow rate [mL min ⁻¹]	Volume [mL]
1	Thorough column washing	Water	1.0	100
2	Sample loading	Bayer liquor	0.5	10

3	Column washing	Water	1.0	60
4	pH inversion	H ₂ SO ₄ (0.025 M)	1.0	40
5	Aluminium scrubbing	H ₂ SO ₄ (0.005 M)	2.0	500
6	Breakthrough termination	H ₂ SO ₄ (0.025 M)	1.0	50
7	Gallium stripping	H ₂ SO ₄ (0.250 M)	1.0	50
8	Complete column stripping	H ₂ SO ₄ (2.500 M)	1.0	50
9	Thorough column washing	Water	1.0	250

3. Results and Discussion

3.1 Characterization

Characterization of the quinoline-functionalized CS adsorbent materials by FTIR and Raman spectroscopy is shown in Table 2 (Coates, 2000). Chemical immobilization of the quinoline ligands was demonstrated by particular band shifts, indicating the conversion of primary amine functions (NH_2) in non-functionalized CS to secondary amine functions (NH) in quinoline-functionalized CS.

Table 2: Characteristic FTIR/Raman peaks and corresponding assignments for non-functionalized and quinoline-functionalized CS

	FTIR/Raman	Characteristic peak [cm^{-1}]	Assignment
Non-functionalized CS	FTIR	3600-3200	O-H vibration
	FTIR	1065	Si-O-Si vibration
	Raman	~ 1600	N-H bend primary amine
	Raman	~ 1090	C-N stretch primary amine
Quinoline-functionalized CS	FTIR	3600-3200	O-H vibration
	FTIR	1065	Si-O-Si vibration
	Raman	3059	Aromatic C-H stretch
	Raman	1611	Aromatic ring stretch
	Raman	1576	N-H bend secondary amine
	Raman	1434	Aromatic ring stretch
	Raman	1326	C=N stretch aromatic amine
	Raman	~ 1190	C-N stretch secondary amine

From CHN analysis, the organic adsorbent fraction and the degree of functionalization could be calculated by consideration of the carbon mass percentage (Table 3). The share of silica in the non-functionalized hybrid particles was 84%. Regarding the organic fraction and the degree of functionalization, the values are comparable for 8-HQO-CS and 8-HQA-CS. Both functionalized adsorbents consist of one part of chitosan to four

parts of silica. A functionalization degree of 26-28% means that approximately 1 of 4 chitosan moieties in the functionalized adsorbents contained a quinoline ring.

Table 3: Element composition (C and N mass percentage), organic fraction and degree of functionalization of non-functionalized chitosan-silica, 8-HQO-CS and 8-HQA-CS

	C [%]	N [%]	Organic fraction [%]	Degree of functionalization [%]
Chitosan	40.11	7.45	100.0	-
Chitosan-silica	6.52	0.96	16.3	-
8-HQO-CS	8.32	1.02	20.7	27.5
8-HQA-CS	8.26	0.98	20.6	26.6

3.2 Adsorption kinetics

The kinetics of the adsorption process are presented in *Figure 2*. For the sake of comparison, the performance of the non-functionalized chitosan-silica material is shown as well. The kinetic profiles were quite slow in the sense that about 8 h of adsorption were required to reach a plateau value for the Ga(III) adsorption. In earlier work with CS hybrid materials functionalized with EDTA/DTPA and EGTA, contact times less than 8 h were sufficient to reach equilibrium (Roosen et al., 2014; Roosen et al., 2016). The slow adsorption kinetics observed with these quinoline-functionalized CS hybrid materials may be attributed to different factors, including the ligand strength and the complexation mechanism. Also the highly alkaline environment might hamper certain chemical reactions. Studies on a more fundamental level are required to examine the kinetics into detail. Given the intended application of these adsorbent materials as column resins in industrial separation processes in which many contaminants are encountered, the theoretical equilibration time in synthetic, single-element solutions is of minor

importance. In the case of Bayer liquor, resin saturation with Al(III) that is excessively present in the liquor, will be the more important parameter that determines when to end the loading stage. Saturation of the resin will be much faster than the time needed to reach equilibrium for Ga(III) adsorption.

Figure 2: Kinetics of gallium adsorption for non-functionalized CS, 8-HQA-CS and 8-HQO-CS; $m_{ads} = 50.0$ mg, $[Ga(III)] = 2.5$ mM, $pH_i = 12.25$, solution volume = 10 mL.

It was also observed from Figure 2 that, in the conditions of this experiment, the highest equilibrium adsorption of Ga(III) was obtained with 8-HQO-CS, followed by 8-HQA-CS. As expected, non-functionalized CS yielded the lowest adsorption amount, although adsorption was still significant. This may indicate that adsorption is partially due to secondary interactions, in addition to metal chelation. In order to elaborate on the differences observed between 8-HQO-CS and 8-HQA-CS, the adsorption capacity of both adsorbent materials was studied in detail.

3.3 Equilibrium adsorption performance

The maximal adsorption capacity of the adsorbents was investigated by plotting the Ga(III) adsorption amount at equilibrium as a function of the equilibrium concentration (*Figure 3*). Data confirmed that the immobilized extractant had an influence on the adsorption capacity of the corresponding adsorbent materials. The capacity of 8-HQO-CS was higher ($0.88 \text{ mmol} \cdot \text{g}^{-1}$) than that of 8-HQA-CS ($0.55 \text{ mmol} \cdot \text{g}^{-1}$). This might be surprising, since the degree of functionalization was comparable for both (Table 3). The lower amount of adsorbed Ga(III) could be explained by considering the adsorption mechanism. Gallium and aluminium ions form negatively charged tetrahydroxy complexes in alkaline solutions ($\text{pH} > 9$). As a consequence, coordinated OH^- ligands in the negatively charged $\text{M}(\text{OH})_4^-$ complex are substituted with quinoline ligands during the chelation reaction (Eq. 4).

with $\text{M} = \text{Al(III)}$ or Ga(III) , and R = the quinoline ligand

According to the reaction equation, three quinoline ligands are required for complexation of one metal ion (Ga(III)/Al(III)) (Mihaylov and Distin, 1992). Hence, the presence of a methyl group on the C2-position of the oxine group in 8-HQA (*Scheme 1*) may impede the formation of the chelate complex. The steric effect of alkyl-substituted 8-HQO was discussed in Section 1 for Al(III), but here, it was observed that adsorption of Ga(III) was hampered as well with 8-HQA-functionalized CS, albeit presumably in a lesser extent compared to Al(III). This statement is based on the smaller ionic radius of Al^{3+} (48 pm) compared to Ga^{3+} (55 pm) (Shannon, 1976), so that complexation with three substituted

quinoline ligands is believed to be more sterically hindered for Al(III). However, this should be experimentally confirmed (*vide infra*).

Figure 3: Equilibrium Ga(III) adsorption capacity of 8-HQO-CS and 8-HQA-CS, as a function of Ga(III) equilibrium concentration; $m_{ads} = 25.0$ mg, $pH_i = 12.25$, solution volume = 10 mL.

The influence of the pH on Ga(III) adsorption is shown in Figure 4. In consideration of the highly alkaline nature of Bayer liquor, only pH values higher than 8 were considered. Moreover, equilibrium constants for the formation of monomeric Ga(III) hydroxide complexes (such as $Ga(OH)^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3$ and $Ga(OH)_4^-$) are difficult to measure and therefore comparatively poorly known, but based on a study by Wood and Samson (2006) on the speciation of gallium, it may be expected that the process of gallium precipitation (by formation of $Ga(OH)_3$) may compete with the process of gallium adsorption at $pH < 8$.

The decrease in adsorption with increasing pH was expected from the fact that high pH favours the reverse reaction of Eq. 3. When $pH \geq 13$, Ga(III) loading becomes very low

($30.8 \mu\text{mol}\cdot\text{g}^{-1}$ at pH 13.20). This is due to the high excess of OH^- ions, which compete for the adsorption sites. The NaOH concentration in Bayer liquor is much higher than 0.1 M (pH 13). The adsorption performance will thus be worse in these conditions. There is no option to pretreat the Bayer liquor, for instance by lowering the pH, because the spent liquor has to be recirculated in the Bayer process. Nevertheless, one must realize that such low loading values are common for these systems and comparable values are obtained with the currently used resins. For example, immobilization of 5-palmitoyl-8-hydroxyquinoline on a styrene-divinylbenzene matrix by (Filik and Apak, 1998), resulted in a Ga(III) capacity of $3.9 \mu\text{mol}\cdot\text{g}^{-1}$ at pH 13.50. In fact, the low Ga(III) loading at high pH partially explains why the current process is considered inefficient. Large amounts of resin material are required for the recovery of small amounts of Ga(III). Therefore, it is really important to reduce the resin cost, for instance by avoiding expensive extractants or resin degradation.

Figure 4: Influence of the equilibrium pH on gallium adsorption with 8-HQO-CS and 8-HQA-CS; $m_{ads} = 50.0 \text{ mg}$, $[\text{Ga(III)}] = 2.5 \text{ mM}$, solution volume = 10 mL. The dashed lines indicate the relevant pH region for Ga(III) adsorption; on the left, removal might be partially due to hydrolysis precipitation; on the right, adsorption is very low.

The influence of the temperature on the equilibrium adsorption of Ga(III) was studied in a range varying from 20 °C to 90 °C. No significant differences were observed when the reaction temperature was varied. Although the temperature may influence the kinetics of the adsorption process, its effect on the thermodynamics appeared to be negligible. This indicates that the entropy loss upon adsorption is largely compensated by the release of hydrating water molecules. The temperature stability of the adsorption process allows high flexibility when integrating gallium recovery from a circulating Bayer liquor feed, typically at a higher temperature, in the flowsheet of alumina production.

3.4 Selective recovery of Ga(III)

The efficiency of a metal recovery process is largely dependent on the selectivity for the targeted metal ion. Therefore, the adsorbent materials 8-HQO-CS and 8-HQA-CS were compared in terms of their selectivity for Ga(III) compared to Al(III). Since the feed liquor should be recirculated in the Bayer process after gallium recovery, its composition cannot be adjusted, for instance by changing the pH. Therefore, selectivity was investigated by monitoring the cumulative adsorption amount of Ga(III) and Al(III) over a number of adsorption steps (*Figure 5*). These results showed for both adsorbents a higher adsorption of Al(III) compared to Ga(III). Unfortunately, no selectivity for Ga(III) was observed. Moreover, the enrichment of Al(III) on the functionalized particles increased, at the expense of Ga(III), over the number of adsorption cycles. After 10 adsorption cycles, the amount of adsorbed Al(III) was significantly lower for CS functionalized with 8-HQA (0.66 mmol g^{-1}), compared to CS functionalized with 8-HQO (0.95 mmol g^{-1}), whereas the amount of adsorbed Ga(III) was comparable for both

adsorbent materials. As a consequence, the “selectivity” for Ga(III) adsorption was better with 8-HQA-CS (separation factor = 0.27) in comparison with 8-HQO-CS (separation factor = 0.20). This might be attributed to the presence of the methyl group on the C2-position of the quinoline ring, which might cause steric hindrance during metal complexation. It is not clear whether Al(III) is only partially or fully prevented from complexing with the immobilized 8-HQA-extractant. Possibly, adsorption of Al(III) and Ga(III) could be attributed as well to the presence of other functional groups in the adsorbent matrix, like –OH groups on both chitosan and silica chains. According to the Hard-Soft Acid-Base (HSAB) concept, hydroxyl groups have a high affinity for ‘hard’ acids (Pearson, 1963), thus favoring Al(III), which has a harder character than Ga(III) due to its smaller ionic radius. Moreover, Ga(III) and Al(III) are mainly present as $\text{Ga}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_4^-$ at high pH, so adsorption might partially occur by attractive interactions with these negatively charged tetrahydroxy complexes as well. Nevertheless, it was hypothesized that the respective strength of all involved interactions would be the decisive factor to be exploited in order to obtain the desired selectivity for Ga(III). The stability constants for the formation of a chelate complex between Al(III) and Ga(III) with three 8-HQO ligands are $\log \beta_3 = 31.9$ and 40.5, respectively (Stary, 1979). This indicates that Al(III) can be preferentially stripped as shown in the next section.

Figure 5: Adsorption of Al(III) and Ga(III) from a synthetic mixture on 8-HQO-CS and 8-HQA-CS, as a function of the number of adsorption steps; $m_{ads} = 50.0$ mg, solution volume = 1000 μ L.

Sulfuric acid was chosen as stripping agent from an economic and environmental point of view. Sulfuric acid is a simple, inorganic acid that is not corrosive and fuming like hydrochloric acid and that can be obtained at a much lower cost than nitric acid. Selective stripping percentages as a function of the H_2SO_4 concentration are presented in Figure 6. The stripping results revealed that the largest part of Al(III) was stripped at low concentrations of H_2SO_4 . By comparison of both adsorbents, it appeared that the stripping efficiency of Al(III) from the adsorbent functionalized with 8-HQA was higher than that from the adsorbent functionalized with 8-HQO. At the point at which Ga(III) gets stripped from the adsorbent, about 60% of Al(III) had been stripped from 8-HQO-CS (indicated by a dotted arrow in Figure 6 (a)), whereas about 90% of Al(III) had been removed from 8-HQA-CS at this point (indicated by a dotted arrow in Figure 6 (b)). So on one hand, it may be assumed that Ga(III) is mainly adsorbed by stronger interactions compared to Al(III). On the other hand, since higher acid concentrations were required to strip Al(III) and

Ga(III) from 8-HQO-CS in comparison with 8-HQA-CS, it might be that stronger interactions occur in the former, whether or not by the lack of a sterically hindering methyl group on the oxine ring of 8-HQO.

Figure 6: Selective stripping of Al(III) and Ga(III) from chitosan-silica (CS) materials functionalized with 8-HQO (a), and 8-HQA (b), as a function of $[H_2SO_4]$; $m_{ads} = 50.0$ mg. Initial loadings q_e on 8-HQO: Al(III) = $0.89 \text{ mmol} \cdot \text{g}^{-1}$, Ga(III) = $0.05 \text{ mmol} \cdot \text{g}^{-1}$; on 8-HQA: Al(III) = $0.63 \text{ mmol} \cdot \text{g}^{-1}$, Ga(III) = $0.04 \text{ mmol} \cdot \text{g}^{-1}$.

3.5 Reusability study with synthetic Bayer liquor

Next to the recovery efficiency, one of the most important parameters for the Ga(III) recovery process is the resin cost. With this work, we aimed to develop resin materials that are less prone to degradation compared to the ones that are commonly used for the recovery of gallium from Bayer liquor. We aimed to avoid (1) hydrolysis to non-active (extractant) agents, as observed for amidoximes, by making use of aromatic quinoline molecules, and (2) physical loss of the active component from the solid to the aqueous phase, by chemically immobilizing the quinoline ligands on the chitosan-silica matrix, instead of impregnating them. The reusability of CS adsorbent functionalized with 8-HQA was investigated, since the latter showed the best selectivity for Ga(III) over Al(III). Because of the high number of physical handlings per cycle, the variability of the experimental data was quite high. Therefore, the experiment was performed twice and the analysis measurements done in duplicate. The averaged data for the recovery efficiency are presented in *Figure 7*. The efficiency of Ga(III) recovery remained quite stable. After seven adsorption/ desorption cycles, the adsorption efficiency was still higher than 97%. Moreover, during the several centrifugation steps, small amounts of adsorbent got physically lost each time. These losses only occur when doing these experiments on lab (batch) scale, not when using these materials as a stationary phase in industrial column adsorption set-ups. Therefore, the Ga(III) recovery efficiency is considered constant and it is assumed that the immobilized quinoline ring, the active resin component, is not affected during the alkaline adsorption and acidic desorption steps. On the other hand, it was quite peculiar to observe an increase in the recovery efficiency of Al(III) (> 100%) during these experiments. Since the same particles were (re-)used in consecutive adsorption/desorption cycles, it is hard to explain the increasing capacity for Al(III).

Possibly, these observations can be attributed to a changing pH. Since adsorption improves with lower pH, it is important to wash sufficiently intense after acidic stripping.

Figure 7: Reusability experiment; recovery efficiency of aluminium and gallium (left Y-axis) and silica leaching (right Y-axis) as a function of the adsorption cycle; $m_{ads} = 50.0$ mg (first time)/100.0 mg (second time).

Besides adsorption efficiency, also the leaching of silica during adsorption was investigated, since silica dissolves in NaOH (Iler, 1979). The data for silica leaching during the reusability experiment with 100.0 mg of adsorbent are also presented in *Figure 7*. Partial leaching was observed for the silica matrix of the adsorbent. On average, it was calculated that less than 2% of the silica matrix dissolved during each adsorption step from highly alkaline environment. On the short term, this will have no effect on the resin adsorption performance, but over the long term, damage to the silica networks will result in a deterioration of the superior characteristics of the hybrid chitosan-silica structure, such as mechanical strength, chemical resistance and porosity.

Both regarding the silica dissolution and the co-adsorption of Al(III) by chitosan and silica functional groups, one could debate about the raw material that was used in this

study. It could be argued that an inert polystyrene matrix is probably more useful in industrial applications, in the sense that only the immobilized ligand could exert its coordinating properties on the metal ions in aqueous solution and because a rigid, aromatic matrix does not dissolve in alkaline environment, in contrast with silica. However, the fossil origin of polystyrene is less sustainable than the origin of biopolymers, the latter getting more and more research attention because of their interesting properties. The valorization of chitosan, derived from seafood waste, as the main component in performant adsorbent materials, helps to mitigate the solid waste disposal problem of the seafood industry. Moreover, we showed that degradation of the functional part of the resin was avoided by chemical immobilization of the quinoline molecules on the hybrid adsorbent matrix. The recovery efficiency of Ga(III) remained stable over seven consecutive adsorption/desorption cycles. These results thus comprise a considerable improvement regarding the resin reusability, sustainability, and thus process cost, in comparison with the resin materials that are currently used for the recovery of gallium from Bayer liquor.

3.6 Separation of Ga(III) from synthetic Bayer liquor by column chromatography

The actual separation of Ga(III) from synthetic Bayer liquor was investigated by ion-exchange chromatography with 8-HQA-CS as the stationary phase. After loading the Bayer liquor, the column was washed with water, to remove all non-adsorbed metal ions. Then, the high alkalinity of the column was neutralized. Based on the results from the selective stripping experiments, it was decided to first scrub Al(III) (and other matrix components) carefully from the column by a diluted H₂SO₄ solution. Subsequently, pure Ga(III) could be eluted from the column by stripping with a more concentrated solution of H₂SO₄. The resulting breakthrough curves are presented in *Figure 8*. The loading and washing stages are not shown. The breakthrough of

Al(III) due to neutralization of the resin from alkaline to acidic environment occurred at an elution volume of 150 mL, after which the reaction in Eq. 5 is responsible for elution.

Consequently, a good separation between the high excess of Al(III) and the small amount of Ga(III) was established. *Figure 8* revealed that the main fraction of Al(III) was adsorbed to the solid phase by weak interactions. This fraction (about 90% of loaded Al(III)) was easily scrubbed at pH values higher than 2.00 (elution volume 150-400 mL). A small part of Al(III) (about 10%) was bonded by stronger interactions and only broke through the column at a slower rate and at pH values lower than 2.00 (elution volume 400-700 mL). Nevertheless, it was possible to scrub all Al(III) prior to the breakthrough of Ga(III). Coordinated Ga(III) was eluted from the column at a pH of 1.75 and lower. The separation experiment was thus considered to give a good proof-of-principle for the recovery of pure Ga(III) from Bayer liquor with these kinds of materials.

Figure 8: Breakthrough curves of Al(III) and Ga(III) after loading a synthetic Bayer liquor onto 8-HQA-CS. Elution (neutralization, scrubbing, stripping) was done with

solutions of H₂SO₄ with different concentrations. The cumulative metal percentages are presented as a function of the elution volume (left Y-axis). The dotted line represents the pH of the distinct fractions (right Y-axis).

Some critical remarks must be made about the separation experiment. In order to avoid simultaneous breakthrough of Al(III) and Ga(III), it was important to elute with a diluted solution of H₂SO₄. To limit the elution volume, a neutralization step, to switch from alkaline to acidic environment, was included before the scrub step, by initiating a flow of less diluted H₂SO₄ through the column. Still, the total elution volume required for the full separation experiment was large (800 mL). This was mainly due to the low selectivity of the adsorbent material that was functionalized with the simple 8-HQA ligand. Possibly, with a more selective (but more complex) extractant, and without additionally coordinating functional groups (like -OH) present in the resin matrix, it would be easier to isolate larger amounts of valuable Ga(III) from smaller amounts of Al(III) adsorbed on the resin material. Another disadvantage is the need to reprecipitate Al(III) from the acidic sulfate solution to recover Al₂O₃ for smelting. Nevertheless, the successful separation of Al(III) and Ga(III) with the current adsorbents showed the high application potential of the synthesized adsorbents. Moreover, one should be aware that the reported breakthrough curves resulted from the fifth separation experiment that was performed on the same column, each time reusing the same packing. The observation that the stationary phase performed as well over several adsorption/desorption cycles may be another convincing argument for the high reusability of these quinoline-functionalized CS adsorbents.

4. Conclusions

Chitosan-silica adsorbents were functionalized with 8-HQO and 8-HQA. The adsorption performance for Ga(III) was studied with both materials from alkaline, single-element solutions. Equilibrium adsorption was reached after 8 h. The adsorption capacity increased in the order: non-functionalized CS < 8-HQA-CS < 8-HQO-CS. A higher stability of the chelate complex with Ga(III) compared to Al(III) was exploited during preferential stripping of loaded Al(III) with H₂SO₄ solutions, to obtain a higher selectivity for Ga(III) with 8-HQA-CS compared to 8-HQO-CS. A reusability efficiency higher than 97% was obtained after seven adsorption/desorption cycles. By ion-exchange chromatography with 8-HQA-functionalized CS as the stationary phase, Ga(III) was fully separated from Al(III) out of the highly alkaline aluminosilicate matrix in a spent Bayer liquor sample.

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