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Citation for published version (APA):

DOI:
10.1016/j.elstat.2015.11.007

Document status and date:
Published: 01/01/2016

Document Version:
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:
- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Download date: 21. Feb. 2021
Applying electrohydrodynamic atomization to enhance mass transfer of metal salts from an aqueous phase towards ionic liquids

Dries Parmentier\textsuperscript{a,b}, Anna Rybałtowska\textsuperscript{a}, Jasper van Smeden\textsuperscript{a}, Maaike C. Kroon\textsuperscript{b}, Jan C. M. Marijnissen\textsuperscript{a}, Luewton Lemos\textsuperscript{a*}

\textsuperscript{a} Wetsus, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands

\textsuperscript{b} Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

* Corresponding author. E-mail: Luewton.Lemos@wetsus.nl; Phone: +3158 210 09 19

Abstract

In this work a two coaxial nozzles configuration is used to investigate whether electro hydrodynamic atomization of an ionic liquid in combination with an aqueous metal salt solution could enhance the removal of metal salts. The technique was evaluated for the removal of manganese (II), cobalt (II) calcium and sodium chloride. Good metal salt extraction was observed for the water-presaturated ionic liquid, tetraoctylammonium oleate, at an applied electrical potential of 5 kV, which was slightly lower compared to mechanical mixing, but a higher separation factor was obtained between the transition metals and the alkali and earth alkali metals.
Introduction

Heavy metals are a common source of pollution in water. Their origin is rather diverse. While arsenic (As) normally originates from the oxidation of sulfide minerals like arsenopyrite, lead (Pb) has its origin normally from old metallic distribution and drainage systems and mine machinery maintenance yards. Cadmium (Cd), zinc (Zn), manganese (Mn) and iron (Fe) have their source from industrial processes and mercury (Hg) is normally dispersed from small scale (artisanal) mining. Among them Cd is especially known by its high toxicity and as an environmental hazard. Nowadays, it is mainly As that has been mentioned as a potential health risk for drinking water in many countries.

Several techniques can be used to remove these metals from liquid effluents, e.g. precipitation, solvent extraction, ion exchange, adsorption, membrane filtration (micro, ultra, and nano), coagulation–flocculation, flotation and electrochemical methods. Even though the list of suitable methods is large, the removal of such contaminants from wastewater streams below the standard limits is still a challenge. The main limitations of the current methods are the high capital and/or operational expenditure and the high standards for influent quality.

Among all current techniques, solvent extraction is commonly used for the separation and purification of metals. It comprises basically a chemical extraction process, where an extractant agent is dispersed in a solution containing the contaminant using some form of energy, e.g. mixing or stirring. The removal process can be either an ion-exchange process, or liquid-liquid extraction with metal extractants. Examples of such extractants are di(2-ethylhexyl) phosphoric acid, tris(2-ethylhexyl)amine and liquid phosphine oxides dissolved in organic solvents such as kerosene or toluene. This method is known by its high extraction efficiency, i.e. extraction efficiencies above 99% can be reached. However, it presents high operational costs due to the handling and disposal of the used solvents, which are normally highly toxic, flammable and/or volatile.

If assumed that the volatility of the organic solvents and the toxicity of the extractant and solvent are the main disadvantages of current chemical extraction processes, then finding “green” extractants, i.e. bio-degradable/non-toxic extractants, would represent a big improvement for this industry. Recently, the use of Ionic Liquids (IL) has been considered as a potential solution.

ILs are known as substances entirely formed by anions and cations that melt at or below 100 °C. The composition of an IL is a bulky organic cation combined with an inorganic or organic anion.
The strong electrostatic interactions between the ions result in their characteristic properties, i.e. their negligibly low vapor pressure at room temperature and the high chemical and electrochemical stability. Moreover, other properties like solubility and viscosity can be modified by substituting different anions and cations. As well as their application, i.e. selecting ions with functionalities that interact with metals results in ILs suitable for metal salt extraction.

Currently, metal salt extraction with ILs is carried out using a mixer-settler configuration. This means that mechanical mixing of the IL with the aqueous metal solution is performed to enhance the contact between the extract and the solution containing the contaminant. In practice, any other technique which could create an enhanced interface with less energy would improve the system’s efficiency. A good possibility is to modify this interface using electrical forces, i.e. exposing the liquids to a strong electric field.

A technique that uses such principle is electrohydrodynamic atomization (EHDA). EHDA, or shortly electrospraying, is an atomization process, which implements electric stresses into the liquid leaving the nozzle. These stresses are caused by creating a strong electric field in the breakup region by applying an electric potential between the nozzle and a counter electrode. For a certain nozzle-counter electrode configuration (defining the electrical field strength) and a specified liquid, different spraying modes can be obtained depending on the applied potential difference, and the liquid flow rate. This paper only considers low flow rates. For low flow rates (μL/h – mL/h) the mode changes by increasing the potential from dripping via intermittent to cone-jet mode (Figure 3). By further increasing the potential a multi-jet mode appears. If the electric field strength becomes too high, sparks can take place. In the cone-jet mode the shape of the liquid surface is transformed into a cone and from the apex of the cone a liquid jet emerges, which is much thinner than the nozzle diameter. The jet then breaks up in small, highly charged droplets (nm-μm), which can be monodisperse. Among many other applications, electrospraying is used for drug delivery, in greenhouses, and for controlled deposition.

In EHDA the electric field is created by establishing an electric potential difference (φ) between the nozzle and a counter electrode placed at a certain distance from the nozzle’s tip. Various nozzle/counter electrode configurations can be used. The most known one is the nozzle/plate configuration, in which the counter electrode is a metal plate placed below the nozzle tip. Alternatively, configurations like coaxial cylindrical nozzles and nozzle/ring have also been successfully applied.
For a liquid with a high surface tension, such as water, the electric field necessary to overcome the surface tension stress and to transform the liquid surface into a stable one, is so high that sparking happens before the cone formation can be reached. A possible way to overcome this problem is to use two coaxial nozzles in where the outer liquid is a well electrospayable liquid and the inner one is the non-electrospayable liquid. This process is also known as "electrocoextrusion". Literature also shows that certain ILs can be electrospayed in a stable cone-jet mode. If this is done with a two coaxial nozzle configuration, then also an extended contact surface between the two liquids can be realized.

In this work, a system with two coaxial nozzles was developed so that IL and salt solution can be simultaneously electrospayed in the cone-jet mode, as shown in Figure 1. The combination of EHDA with ILs was investigated for the first time to see whether it can be used to improve the selectivity and extraction efficiency of metals into the IL solution.

**Fig 1.** Ideal cone-jet mode with the formation of encapsulated droplets

**Experiment and materials**

**Materials**

The atomized liquids were an aqueous salt solution and the IL, i.e. tetraoctylammonium oleate ([N₈₈₈][C₁₈:1]). The IL was selected because it is already known as an efficient selective metal extractant for transition metals from light metals. As reported in the literature such mechanism is based on ion-pair extraction. Before using the IL, it was pre-saturated with water to decrease the viscosity and to facilitate electrospaying. The aqueous metal salt solution was prepared by dissolving 0.5 g of each salt (MnCl₂·6H₂O, CoCl₂·6H₂O, NaCl, CaCl₂·2H₂O) in demineralized water. All chemicals were purchased from Sigma-Aldrich. MilliQ water (≥18.2 MΩ·cm) used throughout the synthesis was obtained by a Millipore Milli-Q® biocel, which used a Q-grade® column. The IL used in the experiments was synthesized using the same method as previously described and had a purity of ≥95% measured by ¹H NMR.

The physical properties of both the IL and the aqueous metal salt solution were determined. (see Table 1) Density and viscosity were determined by an Anton Paar SVM 3000/G2 type stabinger, with an uncertainty of ±0.0005 g·cm⁻³ for the density and ±0.005 mPa·s for the viscosity at a fixed temperature which had an uncertainty of ±0.01 K. The water content was measured by a Karl-Fisher titrator (Mettler Toledo, model DL39) with a standard deviation of ± 100 ppm. Surface tension was determined at room temperature with a Krüss K11 MK4 tensiometer using the plate method with a
standard deviation of ± 0.03 mN m⁻¹. Electrical conductivity was measured by a conductivity meter (WTW, TetraCon 325) with an uncertainty of 0.0001 S m⁻¹.

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<th>η (N s m⁻²)</th>
<th>σ (N m⁻¹)</th>
<th>K (μS cm⁻¹)</th>
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<td>2.49E+01</td>
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<td>9.1 at 23.7°C</td>
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<td>Metal salt solution</td>
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<td>1.08E-03</td>
<td>0.070 (±7.0E⁻⁵)</td>
<td>2.3E3 at 22.3°C</td>
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<tr>
<td>Dist. Water</td>
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<td>1.00E-03</td>
<td>0.073 at 25°C</td>
<td>1.4 at 22.0°C</td>
</tr>
</tbody>
</table>

**Experimental setup**

In order to enhance the contact between the two liquids, i.e. create an enlarged interface, two coaxial nozzles were used. Such configuration is largely used in EHDA experiments to provide a liquid-liquid interface and to form encapsulated droplets. For this research, a system with two coaxial nozzles as presented in Figure 2 was fabricated. The system structure was built with PP connectors from Emtechnik®. The concentricity of the nozzles was assured by attaching them to two connected DN 04/06 G /8 “PP female connectors. Two different nozzles (EFD® precision) were used with the following dimensions: The external nozzle had 1.84 mm outer diameter (OD) and 1.54 mm inner diameter (ID), it was placed concentrically with the inner nozzle which had 0.72mm OD and 0.41 ID. First tests were done to stipulate which liquid configuration, i.e. internal nozzle and external nozzle liquid, would be the most appropriated for the experiments. As mentioned before, the best configuration to spray in the cone-jet mode was when the IL is the outer liquid and the aqueous metal salt solution is the inner liquid. To guarantee the controllability of the flow rate in each nozzle, the two liquids were pumped separately using two Aitecs® sp125 syringe pumps (see Figure 2). Due to the different densities (Table 1) a flow rate investigation had to be performed to identify which specific flows had to be used to avoid buoyancy inside the meniscus. Experiments have proven that a flow rate of 1 mL/h for the aqueous metal salt solution (inner nozzle) and 1.2 mL/h for the IL (outer nozzles) avoided buoyancy inside the meniscus and eventually allowed achieving a stable cone-jet mode. Therefore, all the experiments were done using the previously mentioned flows.

The electrical connections were as follows: high voltage was applied to the counter electrode, i.e. a 14 mm copper ring placed 1 cm (distance h1 represented in figure 2) below the nozzles tips, while the nozzles were kept grounded. Preliminary experiments were done varying the electric potential between 0 and 6kV to check which modes would be obtained with which potentials.
as well as to observe whether a stable cone-jet mode could be achieved. After electrospraying, the solution was collected in a 15 mL centrifuge tube placed right under the nozzles (distance $h_2$ presented on figure 2, $h_2 = 0$ cm) and subsequently the aqueous phase was sent to be analyzed.

**Fig 2.** Schematic overview of the setup (left) and a picture of the detailed two coaxial nozzles configuration (right). The IL is injected through the inlet of the outer nozzle (II) and metal salt solution through the inlet of the inner nozzle (I). The potential is applied between the outer nozzle (III) and the counter electrode ring (IV).

To allow the visualization of the spray, the identification of the spraying mode and the characterization of the produced droplets, i.e. droplet size and droplet size distribution, a high speed imaging system was utilized. It consisted of a high speed camera (Photron AS1) with a microscopic lens (Navitar J25 mm) and a back illumination (Dedo light cold source) as represented in figure 2. After acquiring the images a software (Image J®) was used to measure the droplets size. After that Matlab® was used to treat the data.

In all experiments, the solutions were sprayed for one hour inside the plastic collector and then send to analysis (approximately 2.2 mL per tube). To be able to compare the effect of the electrospray system with conventional solvent extraction, solvent extraction experiments were also done using physical shaking (Heidolph multi reax multi-tube vortex mixer) with the same solutions. In these experiments the liquids (1 mL metal salt solution, 1.2 mL IL) were brought into a 15 mL centrifuge cylinder and mixed on a vortex. Lastly, the extraction efficiency in a static extraction was also investigated. For that the two liquids (1 mL metal salt solution, 1.2 mL IL) were placed in a 15 mL centrifuge cylinder without applying any mechanical mixing. In both cases (mechanical mixing and static), the water phase was separated from the IL after one hour, and analyzed regarding its metal content.

**Analytical methods**

Collected samples from electrospraying were, in a next step, placed in an Allegra TM X-12R centrifuge from Beckman coulter for 5 min at 1500 rpm. Afterwards, the aqueous phases were analyzed for cations with a precisely inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) from Perkin Elmer, which used an optical emission spectrometer Optima 5300DV. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 25-250 μg L⁻¹, with an uncertainty of 1.4-2%.
Extraction efficiencies ($E$) were calculated by

$$E(\%) = \frac{c_0 - c_1}{c_0} \cdot 100 \quad \text{Eq. 1}$$

where $c_0$ and $c_1$ are the total metal concentrations in the aqueous phase before and after the experiment. Measurements were performed in triplet. We present both the average values and the standard deviations.
Results and discussion

Electrospray mode identification.

Figure 3 presented below is a representation of a preliminary investigation done to identify which modes would be established at different electric potentials. Electrospraying at different flow rates were also performed, but are not presented. The best flow rates of the 2 liquids (and so their ratio) were visually defined and optimized so that the inner liquid flows nicely inside the outer liquid in the cone-jet mode. Another point observed was the total duration of the experiments. As the chemical analysis required a minimum volume of 1 mL of the aqueous phase, an initial inner nozzle flow of 1.0 mL/h was defined to guarantee that the spraying time, per run, would be no longer than 1 hour. After optimization of the flow rates, 1.2 mL/h for the IL, an electrospray mode analysis was performed by keeping flow rate configuration and nozzle to plate distance constant and applying different potentials to the counter electrode.

![Fig 3](image-url)

**Fig 3.** Different modes observed with different applied potentials. From left to right: A) 0 kV; dripping, with the transparent droplet being the aqueous phase and the dark droplet being the IL, B) 4 kV; intermittent cone-jet mode, C) 5 kV; cone-jet mode and D) 6 kV; multi-jet mode.

It shows that, even for the optimized flows, the water is not encapsulated by the IL when no potential is applied (Figure 3A). It was observed that during this experiment at 0 kV, at a certain point the liquids in the droplet switch position, i.e. the aqueous phase moves to the bottom of the growing droplet, a short time before the droplet falls from the nozzle. For potentials around 4 kV (Figure 3B), an intermittent cone-jet mode could be observed and as can be seen, the shape of inner meniscus is slightly elongated following the shape of the outer meniscus. At 5kV, a stable cone-jet could be achieved (Figure 3C). In this mode, an inner meniscus seems to occur, which is an initial indication of the formation of encapsulated droplets. Some disruptions of the Taylor cone were observed during this mode, most probably caused by the presence of space charges.\(^{46}\) For potentials around and above 6kV a multi-jet mode could be observed (Figure 3D).

Even though these first experiments have indicated the necessary configuration for the cone-jet mode, the extraction experiments were still performed with a range of different potentials to exam the relation between extraction efficiency and applied potential, i.e. electrospray mode.
Extraction results

Figure 4 presents the obtained metal extraction efficiency for each tested metal at different applied potentials and compares it with the metal extraction due to mechanical mixing and no mixing. A high extraction efficiency of cobalt (Co) and manganese (Mn) was noticed for 5 kV, which corresponds to the cone-jet mode. Negative extraction efficiency values were found for calcium (Ca) and sodium (Na) during the experiment. Negative extraction values for Na can be explained that Na could be an impurity in the IL due to the use of NaOH during its synthesis, but to explain the negative extraction values for sodium more research is necessary. It is observed that Co and Mn have similar extraction efficiencies. However, Ca and Na have presented lower extraction efficiencies in some specific voltages, i.e. 3kV for Ca and 3 and 5kV for Na. This is in agreement with previous research, in which it was already observed that the IL, [N\textsubscript{6888}][C18:1], showed good extraction for Co and Mn, but low extraction for Ca and no extraction for Na when physical mixing is applied.\textsuperscript{25,41} Applying EHDA resulted in an improvement of the selectivity towards the valuable transition metals. The separation factor of Co over Ca and Mn over Ca was respectively, 3.68 and 3.69 when applying physical mixing while during electrospraying at 5 kV a separation factor of respectively 5.00 and 4.84 was observed.

**Fig 4.** Extraction efficiencies of Ca (A), Na (B), Co (C) and Mn (D) with the IL when a potential was applied (●) in comparison to mechanical mixing (○) and no mixing (▼).

It seems that there is a lower extraction efficiencies obtained at 3 kV potentials compared to 0 kV. However, these values were within the range of the standard deviation and it was difficult to confirm this trend. It was observed in the cone-jet mode (Figure 3C) that the droplets size was 50-70 μm (in comparison with 2960 μm at 0 kV). Resulting in more contact area per volume between the two liquids in the jet and when they form encapsulated droplets, as suggested in Figure 1.

Unfortunately, it was not possible to visually verify the formation of encapsulated droplets. However, from the literature it is known that the encapsulation process of two liquids depends on: (1) whether the two liquids are immiscible, (2) whether the two liquids are mutually wettable, (3) whether the core liquid has a higher surface tension than the outer one.\textsuperscript{47} All this requirements are met for the liquids used in the experiments, i.e. the IL is very hydrophobic and therefore not miscible with the water phase, the IL is for 10.8 wt% water saturated and from table 1 it can be observed that
the aqueous phase has a higher absolute surface tension then the IL. Therefore, it can be assumed that the process will most probably form encapsulated droplets.

**Fig 5.** Subdivision of the different metal salt extraction processes occurring during EHDA with a hydrophobic IL and an aqueous metal salt solution (not on scale). A) corresponds to the cone-jet, B) are the formed fine (whether or not encapsulated) droplets and C) represents the static extraction after collecting.

To get an overall idea of enhancement of the extraction efficiency with EHDA, a systematic subdivision of the metal salt processes that occur should be taken into consideration, see Figure 5. The process can be divided in the formation of a cone-jet with a big contact time between the 2 liquids (A), followed by the formation of fine droplets and in the ideal case encapsulated droplets (B) and after collecting, separation takes place and static extraction occurs on the interphase between the IL and water phase (C). To see the effect of electrospraying, the results from dripping the liquids out of the two coaxial nozzles at 0 kV has to be compared with the results of electrospraying the liquids at 5 kV, see Figure 4. Dripping the two liquids at 0 kV is a process that can be subdivided in two processes. Droplet formation, in which the droplet is divided into an upper semi-sphere of IL and a lower water phase semi-sphere and static extraction, in which the two liquids separate out in two distinct phases inside a centrifuge tube due to gravity.

In the static extraction, extraction of the metals is regulated only by the metal diffusion through the interphase in both liquids. Dripping the liquids at 0 kV compared to the static extraction, results already in a slight increase of metal extraction, except for Ca. This increase could be explained by the fact that in the dripping mode the liquids are already forced to be in close contact with each other what speeds up the metal extraction. Applying 5 kV resulted in a doubling of the metal extraction for Co and Mn. At this potential an increase of metal extraction efficiency was also observed for Ca, but a negative extraction was observed for Na. Compared to dripping (0 kV), the cone-jet mode (5 kV) mode results into a fine jet and a spray of fine droplets, which increase the contact surface between the two liquids and result in a higher extraction.

It has to be reported that water was being evaporated during electrospraying when an electrical field was applied. A possible explanation for this observation is that not all the water is fully
encapsulated by the IL or that water is evaporating from the IL. This also means that the actual extraction values for Co and Mn by electrospraying are probably higher than what is reported now.

Electrospraying ILs in combination of aqueous samples could result into an interesting technique to purify samples just before analysis. The IL could then extract elements that disturb the analysis of the elements of interest in the aqueous sample or if the IL can be analyzed the enhanced separation factor toward the transition metals could result in a better qualitative analysis of traces of these metals. As electrospray is a low flow technique this process will probably not be applicable in big industrial processes.

**Conclusions**

In this research, a two coaxial nozzles configuration was applied to spray a hydrophobic IL together with an aqueous phase. It was found that the cone-jet mode could be obtained at 5 kV when the IL is the outer liquid with a flow of 1.2 mL/h and the aqueous phase is the inner liquid with a flow of 1 mL/h. It could not be verified if the IL and water form encapsulated droplets, but it was proven that EHDA can enhance the metal extraction towards the IL ($E_{Co}$ 83% and $E_{Mn}$ 80%) close to the values of mechanical mixing ($E_{Co}$ 98% and $E_{Mn}$ 98%). Yet, higher separation factors were observed for the valuable transition metals compared to the light metals due to electrospraying. For example, the separation factor of Co over Ca was 5.00 when electrospraying was applied at 5 kV compared to 3.68 with mechanical mixing.

**Acknowledges**

Financial support from Wetsus is gratefully acknowledged. Wetsus, European centre of excellence for sustainable water technology is a facilitating intermediary for trend-setting know-how development. Wetsus creates a unique environment and strategic cooperation for development of profitable and sustainable state of the art water treatment technology. The inspiring and multidisciplinary collaboration between companies and research institutes from all over Europe in Wetsus results in innovations that contribute significantly to the solution of the global water problems. Wetsus acts as Technological Top Institute for Water technology and is located in Leeuwarden, The Netherlands. Wetsus’ scientific research program is defined by the private and public water sector and conducted by leading universities.
References


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<th>$\sigma$ (N.m(^{-1}))</th>
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