Layer-by-Layer encapsulated nano-emulsion of ionic liquid loaded with functional material for extraction of Cd^{2+} ions from aqueous solutions

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Abstract

Ionic liquids can serve as an environmentally-friendly replacement for solvents in emulsions, therefore they are considered suitable to be used as an emulsified medium for various active materials one of which are extractors of metal ions. Increasing the extraction efficiency is considered to be one of the key objectives when working with such extraction systems. One way to improve the extraction efficiency is to increase the contact area between the extractant and the working ionic solution. This can be accomplished by creating a nano-emulsion of ionic liquid containing such an extractant. Since emulsification of ionic liquid is not always possible in the sample itself, there is a necessity of creating a stable emulsion that can be added externally and on demand to samples from which metal ions need to be extracted. We propose a method of fabrication of a highly-stable extractant-loaded ionic liquid-in-water nano-emulsion via a low-energy phase reversal emulsification followed by continuous layer-by-layer polyelectrolyte deposition process to encapsulate the nano-emulsion and enhance the emulsion stability. Such a multilayered stabilized nano-emulsion was tested for extraction of Cd^{2+} and Ca^{2+} ions in order to determine its extraction efficiency and selectivity. It was found to be effective in extraction of Cd^{2+} ions with near 100% cadmium removal, as well as being selective since no Ca^{2+} ions were extracted. The encapsulated emulsion was removed from samples post-extraction using two methods – filtration and magnetic separation, both of which were shown to be viable under different circumstances – larger and mechanically stronger capsules could be removed by filtration, however magnetic separation worked better for both smaller and bigger capsules. The long-term stability of nano-emulsion was also tested being a very important characteristic for its proposed use: it was found to be highly stable after four months of storage time.

1. Introduction

Ionic liquids, which are salts that are liquid below 100˚C[1], show great potential[1–3] as environmentally-friendly extraction solvents due to their unique properties, such as negligible vapour pressure, high thermal stability, non-flammability[4]. More specifically, hydrophobic ionic liquids may be used for the separation of metal ions from aqueous solutions and wastewaters, where they can be specifically designed to act as extractors themselves[5] or, more commonly, serve as an extraction medium for active materials, such as crown ethers[6,7] or any other ion-specific extractants[8]. However, with all their positive characteristics, most ionic liquids are expensive, therefore the necessity of their efficient usage appeals to a design of extraction systems that would be able to provide maximum extraction efficiency at minimum cost. One of the ways to increase the extraction efficiency is to increase the contact area between the ionic liquid and a solution containing ions that need to be extracted. This can be accomplished by creating a nano-emulsion of the ionic liquid, which greatly increases its surface area, minimising the amount of material required for extraction[9–11]. Moreover, nano-emulsions are kinetically stable, and their small size makes them resistant to sedimentation or creaming[12], providing greater control over the extraction process, and allowing for greater storage times. Several different methods for emulsification of ionic liquids have been reported including dispersing under high temperature[13],

ultrasound[14] and vortex-assisted emulsification[15], all of which are used as a part of dispersive liquid-liquid micro-extraction procedure where emulsions are created within a working sample containing extractable ions[16–19]. Other techniques that can also be used to create emulsions of ionic liquids are high-energy methods such as high-pressure homogenization[20], and low-energy methods such as spontaneous emulsification[21] and the phase inversion temperature method[22].

Since some environments that require ion extraction might not be suitable for in-situ emulsification of the extracting agent within them (large volumes of liquids that would require considerable energy to perform emulsification, or, in the case of low-energy methods, large quantities of chemicals), there is be a necessity for the creation of an extracting emulsion separately that can be further mixed in working solutions. These emulsions therefore must be stable enough for prolonged storage to be available to use on demand. Several methods of stabilisation of ionic liquid nano- and microemulsions have been reported including micro-gel[10], ionic[23] and non-ionic surfactant stabilization methods[24–26]. Emulsions fabricated using the aforementioned methods have been reported to be stable, but it is unclear how stable they will be if used for extraction purposes. There is also a question of resistance of emulsions towards mechanical stress which usually accompanies filtration procedures associated with extraction and dilution.

In the current study we have used a layer-by-layer encapsulated nano-emulsion system based on an ionic liquid as a medium for an active extractant material tested for the extraction of two ionic species, Cd^{2+} and Ca^{2+}. The layer-by-layer technique involves consecutive deposition of oppositely charged materials onto core surfaces of various shapes. It was originally developed by Iler[27], who deposited alternating layers of silica and boehmite onto flat surfaces. The next study concerning this concept was published by Decher[28,29] 25 years later who re-invented the idea using polyelectrolytes to layer oppositely charged surfaces. This method has then been successfully used for layering on flat surfaces, particles and emulsions using a variety of techniques[30–38]. In this study, a flow-based continuous layer-by-layer method for preparation of gram quantities of capsules introduced in our previous paper[39] was used for fabrication of multi-layered polyelectrolyte shells formed around nano-emulsion droplets. The layer-by-layer method has been extensively used for encapsulation of emulsions[40–45] and recently nano-emulsions[46], however, no studies, at least to our knowledge, have been reported regarding layer-by-layer on emulsified ionic liquids acting as a core material. In this paper, we show that it was possible to use an ionic liquid nano-emulsion as a core material for the layer-by-layer process. Two potential problems were anticipated in this work, first being the possibility of reduction of extraction efficiency by the growing thickness of the polyelectrolyte shell impeding the diffusion of ions into capsules, second – post-extraction capsule removal from ionic solutions due to their small size. Another aspect we address is extraction selectivity – the encapsulated nano-emulsion as it was specifically designed to extract Cd^{2+} ions, so the extraction of Ca^{2+} was also investigated. Finally, the long-term stability of the multi-layered nano-emulsion was assessed.

2. Experimental section

2.1. Materials

Trihexyl(tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide ([P$_{14666}$][Tf$_2$N], further referred to as ionic liquid, ≥95.0%) loaded with 1-(2-Pyridylazo)-2-naphthol (transitional metal ion extractant) was emulsified in water using benzyldimethylhexadecylammonium chloride (cationic surfactant). Two polyelectrolytes chosen for fabrication of multilayers on the nano-emulsion were poly(diallyldimethylammonium chloride) (PDADMAC, average Mw 100,000–200,000 (low molecular weight), 20 wt% in H2O) and poly(sodium-4-styrenesulfonate) (PSS, average Mw ~70,000). All chemicals mentioned above were purchased from Sigma-Aldrich. Solutions containing ionic species were made using cadmium chloride (Sigma-Aldrich), cadmium nitrate tetrahydrate (Sigma-Aldrich) and calcium nitrate tetrahydrate (BDH AnalaR).

2.2. Emulsification of ionic liquid

Nano-emulsions of the ionic liquid (loaded with extractant) in water were prepared using a low-energy emulsification phase inversion (EPI) method, which is essentially a titration of water into a constantly stirred surfactant-ionic liquid mixture. The EPI process consists of two stages – formation of a water-in-ionic liquid emulsion (on exposure to several of the very first droplets of water) and its inversion into an ionic liquid-in-water emulsion with the increase of the amount of added water[11]. Ionic liquid (0.110 g), surfactant (0.018g,

ionic liquid to surfactant ratio 6.1) and extractant (0.006 g) were stirred together (Stuart US152 Hotplate) at 900 rpm in a glass cylinder (1.5 cm, graded up to 10 ml) at constant temperature of 60°C in order to ensure complete dissolution of the surfactant and the extractant in the ionic liquid. After that deionized water was added to the mixture drop by drop at a rate of 0.45 ml/min (Watson Marlow 2-channel pump, 1.2 rpm setting, 3mm tubing) while maintaining the temperature at 60°C. During the first three minutes of adding the water stirring speed was gradually increased from 900 to 2000 rpm and kept at this setting for the rest of the experiment. When the volume of the liquid in a cylinder reached 10 ml it was sealed and the stirring continued for further 4 hours without a temperature change. After 4 hours the emulsion was gradually cooled down to the room temperature and left stirring for a further 16 hours.

2.3. Core nano-emulsion encapsulation

The resulting emulsion was not sufficiently stable on its own to be used as a core material for layer-by-layer process – it was opaque rather than transparent indicating droplet aggregation. It has been shown previously that in some cases oil-soluble surfactant could not stabilize an oil-in-water emulsion on its own, but could if paired with a polyelectrolyte of the opposite charge[47]. Therefore the same approach was considered viable for the case of ionic liquid-in-water emulsions, so the resulting emulsion was immediately encapsulated in polyelectrolyte shells via mixing with poly(sodium-4-styrenesulfonate) solution (4 g·L^{-1}) in a volume ratio of 1:10 respectively under the constant stirring (600 rpm) for 1 hour. The resulting capsule suspension was centrifuged for 10 minutes at 8000 rpm in order to remove the excess of polyelectrolyte from the system, the solute was replaced with equal volume of deionized water.

2.4. Continuous layering of polyelectrolytes onto the encapsulated emulsion

Multilayers of polyelectrolytes were deposited onto the encapsulated emulsion using a continuous flow tubular reactor consisting of a peristaltic pump and a set of silicone tubing, which is well described in our previous study[39]. Briefly, encapsulated emulsion, PDADMAC (polycation) and PSS (polyanion) simultaneously entered the reactor through three individual channels (at the same rate of 1.9 ml·min^{-1}). The emulsion was then consequently mixed with polyelectrolytes in separate tubing sections starting with polycation (as it is initially encapsulated in PSS shells making it negatively charged) creating one polyelectrolyte layer after another until the desired number of layers was achieved (in this study it was 8 layers). In this method, the possibility of continuous layering is provided by optimization of the polyelectrolyte concentrations meaning that the minimum amount of polyelectrolyte was used to ensure the complete coverage of the emulsion droplets and the creation of a stable polyelectrolyte layer onto them without any appreciable excess. Optimum polyelectrolyte concentrations were found by mixing the encapsulated emulsion with equal volumes of polyelectrolyte solutions of various concentrations followed by zeta potential measurements. The minimum concentrations that provided zeta potential readings ≥ 25 mV were taken to be the optimum concentrations for layering. The time allowed for mixing of the emulsion with polyelectrolytes was set to 3 minutes (based on our previous studies[39]). Zeta potential measurements were also taken for each deposition step to ensure the stability of each layer and the reversal of surface charge. The resulting multilayered capsules loaded with ionic liquid-extractant mixture were stored without any further treatment.

2.5. Preparation of Cd^{2+}, Ca^{2+}, and $Cd^{2+} + Ca^{2+}$ solutions

Solutions for extraction experiments were prepared form diluting stock 1000 ppm solutions of cadmium chloride, calcium nitrate and both calcium nitrate and cadmium nitrate.

2.6. Extraction of Cd^{2+} ions

In order to test the extraction efficiency of the multilayered capsules, the following experiments were performed. Generally, the experimental procedure consisted of adding the dispersion of multilayered capsules into solutions containing metal ions (prepared using cadmium chloride) and stirring it overnight followed by the removal of the capsules from the resulting system. In the first experiment, the efficiency of extraction was measured as a function of number of polyelectrolyte layers on capsules. Measurements for capsules with 2, 4 and 8 layers were compared (ratio 1:5 of capsule dispersion : Cd^{2+} solution). The second experiment was dedicated to measure the efficiency as a function of the amount of capsules added to ionic solutions (ratios 1:5, 2:5 and 4:5 of capsule dispersion : Cd^{2+} solution). In the third experiment, two techniques of a post-extraction removal of the capsules from the solution were compared – filtration and magnetic separation (on ratio 2:5

samples, capsules with 8 polyelectrolyte layers). The stock Cd^{2+} solution concentration was 6.578 ppm (±0.0269 ppm) throughout.

2.7. Extraction of Ca^{2+} ions

Additional experiments were conducted in order to check whether the capsules extract Cd^{2+} selectively, or are able to extract ions of another metal. Encapsulated emulsion was mixed with solution containing only Ca^{2+} ions (prepared using calcium nitrate) as well as to a solution containing both Ca^{2+} and Cd^{2+} ions (ratio 2:5 of capsule dispersion : Ca^{2+} or (Ca^{2+} + Cd^{2+}) solution prepared using calcium nitrate and cadmium nitrate). Stock Ca^{2+} concentration was 7.502 ppm (±0.1749 ppm), stock concentrations of (Ca^{2+} + Cd^{2+}) ions in solution were 7.341 ppm (±0.3140 ppm) and 6.719 ppm (±0.0507 ppm) respectively.

2.8. Post-extraction removal of capsules from solutions

Two methods were used to separate capsules from the solutions – double filtration (Millex-GS Syringe Filter Unit, 0.22 μm) and magnetic separation. The latter method consisted of mixing a suspension of magnetite nanoparticles that were fabricated using the method described by Das[48] (0.5 g·L⁻¹) with capsule-ionic liquid emulsion post-extraction dispersions (after overnight mixing) in a ratio of 1:1 magnetite suspension to capsule dispersion, stirring the resulting system for 2 hours and then separating the capsules fortified with the magnetite using a strong magnet (15x2 mm ultra-high performance N52 neodymium magnet) overnight. Magnetite nanoparticles exhibit negative charge when measured by zeta potential, allowing for their deposition on positively-charged capsules with 8 layers of polyelectrolyte (PDADMAC (cation) layer is the 8th layer).

2.9. Characterisation

Zeta potential measurements (Brookhaven ZetaPALS) were used to determine the optimum polyelectrolyte concentrations, as well as to check the stability of the capsules, at each step of layer-by-layer polyelectrolyte deposition. The zeta potential is the electrostatic potential at the boundary between the particle's diffuse layer of weakly associated ions and the dispersion medium[49]. Stability of the layered particles, meaning their zeta potential values are ≥±25 mV, does generally indicate their complete coverage with polyelectrolyte[50], thus utilizing zeta potential measurement as a tool for polyelectrolyte adsorption was considered reasonable.

Dynamic Light Scattering (Brookhaven ZetaPALS) was used to determine the size of the capsules of the core encapsulated nano-emulsion before and after the centrifugation. (Particle sizing of the un-encapsulated nano-emulsion was not undertaken since it was unstable before being treated with polyelectrolytes.

Transmission electron microscopy (JEOL 2100 Plus) was used to determine the morphology and the size of the multi-layered capsules, as well as to observe the distribution of the magnetite nanoparticles on the surface of the capsules.

Inductively coupled plasma atomic spectrometry, ICP, (PerkinElmer Optima 2000 DV) was used to determine the extraction efficiency of the capsules. As capsules were used in a form of a dispersion, all ICP measurements were recalculated accordingly to dilutions accompanied each experiment. The full details of this procedure can be found in section 3 of the supplementary materials to this study.

3. Results and discussion

3.1. Fabrication of the core nano-emulsion

After preparation of the initial emulsion of extractant-loaded ionic liquid it was mixed with poly(sodium-4-styrenesulfonate) solution (4 g·L⁻¹). The encapsulated emulsion was then centrifuged at 8000 rpm for 10 minutes. Zeta potential and DLS measurements were taken before and after the centrifugation in order to determine its impact on the stability and the particle size of the capsules. The comparison is presented in Table 1.

Table 1

Zeta potential and nano-emulsion droplet size values for before and after centrifuge samples

	Zav (average droplet size), nm	Zeta potential, mV

Before centrifugation	427±9	-103.7±1.5
After centrifugation	427±9	-67.2±0.8

Since the size of the capsules has not changed, and even though zeta potential value have decreased it was still ≫ – 25 mV, it was concluded that centrifugation had minor impact on the encapsulated nano-emulsion, hence indicating its high overall stability. Encapsulated nano-emulsion was stored under continuous stirring (100 rpm) in an air-tight container to prevent it from coalescence.

3.2. Layer-by-layer on the encapsulated nano-emulsion

Continuous layering of polyelectrolytes onto capsules was performed in two steps.

The first step was dedicated to the determination of the optimum concentrations of polyelectrolytes. Encapsulated emulsion was mixed with PDADMAC solutions of a range of concentrations (see supplementary information section 1) and left for 3 minutes to allow for polyelectrolyte deposition. Zeta potential measurements have shown that the very minimum concentration of stock PDADMAC that have exhibited strong positive readings (+49.52 ±1.12 mV) was 1.5 g·L^{-1}. Since electrostatic interactions between polyelectrolytes are believed to be the main mechanism behind layer-by-layer polyelectrolyte deposition[51], the concentration ratio between polyelectrolytes of opposite charges can be related to the amount of charge present in each solution[39]. In case of PDADMAC/PSS pair, considering that stock PDADMAC solution only contained 20% of an actual polymer, the theoretical ratio of PDADMAC to PSS is 3.3 (details of calculations can be found in section 2 of the supplementary information). Experimentally it has been shown to be appropriate to use the ratio of 1:3[39]. Therefore, a PSS concentration of 0.5 g·L^{-1} was used.

The second step was the layer-by-layer procedure itself conducted using pre-determined optimum polyelectrolyte concentrations. The schematic of the process is presented in Fig. 1. Zeta potential measurements were taken at each deposition step (with deposition of each new polyelectrolyte layer) in order to ensure stability of multi-layered capsules at each stage of the process. Encapsulated system exhibited surface charge reversal at each following deposition cycle, which can be seen from the zeta potential graph that has a distinctive "zig-zag" shape (Fig. 2). Zeta potential readings exceeded ± 25 mV at each stage.

A total of 8 layers were deposited onto the nano-emulsion ending with a positively charged PDADMAC layer. Further layering was not considered necessary taking into account major dilution of initial emulsion with each deposition step which would affect the extraction experiments (concentrating the capsules after layering was problematic as the emulsion have become almost transparent and it was impossible to centrifuge; evaporation of the liquid was also considered unacceptable as it would affect the emulsion in unpredicted ways). The concentration of multi-layered capsules was 1.9 g·L^{-1}. The morphology and the size of multi-layered capsules are presented in Fig. 3 a and b (capsule size being 150-220 nm).
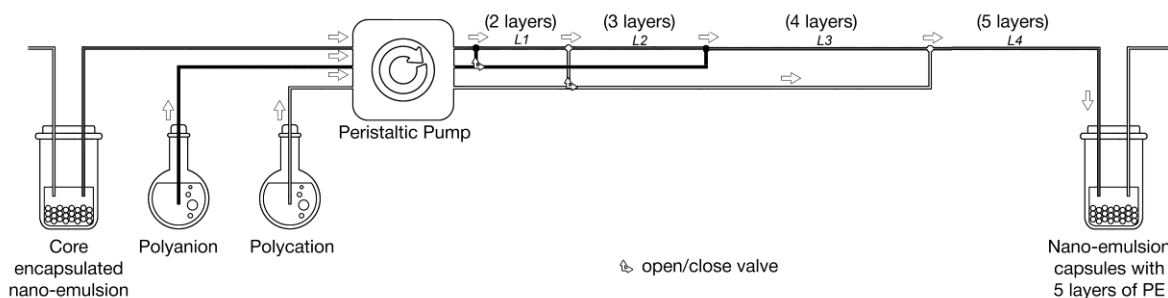

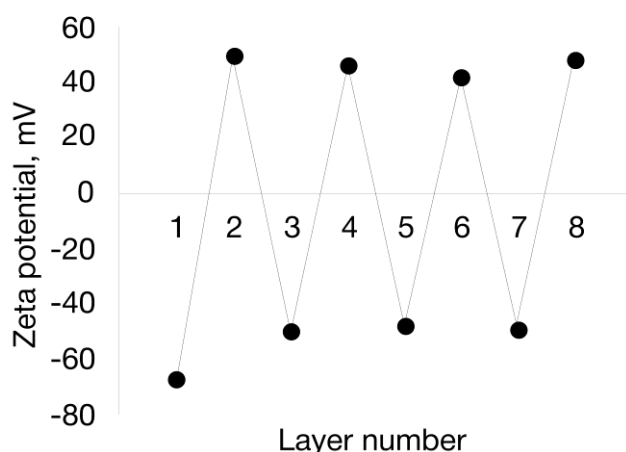**Fig. 1.** Schematic layout of continuous layer-by-layer setup

Fig. 2. Zeta potential as a function of number of layers on the encapsulated nano-emulsion. Unless visible, error bars are within the size of the data points.

3.3. Evaluation of extraction efficiency

The first set of experiments was to determine extraction efficiency on the number of polyelectrolyte layers of the capsules. As capsules were used in the form of dispersions, their initial concentrations were different, therefore, appropriate dilutions of 2 and 4-layered capsules were performed to ensure that the amount of capsules added was the same (as in 8-layered sample). 2 ml of the capsule dispersions were added to 10 ml of 6.578 ppm Cd^{2+} solution (making the actual Cd^{2+} initial concentration equal to 5.480 ppm). After stirring the samples, capsules were removed by filtration, ICP measurements were taken to determine concentrations of remaining Cd^{2+} ions. The results are presented in Table 2. As it can be seen, there is a clear trend of an extraction efficiency increase with the increase of the number of polyelectrolyte layers on capsules. This can be potentially explained by increased mechanical strength of capsule shells with the increase of a number of polyelectrolyte layers that makes them more resistant to stress accompanying the filtration process, making the probability of capsules breaking while going through filter and staying in the sample smaller.

Table 2

Extraction efficiency as a function of number of polyelectrolyte layers on capsules

Sample ID	Number of polyelectrolyte layers	Concentration of Cd^{2+} before extraction, ppm	Concentration of Cd^{2+} after extraction, ppm	Reduction of Cd^{2+} concentration, %
X2-2:10	2	5.482 ±0.027	3.846 ±0.032	29.8
X4-2:10	4	5.482 ±0.027	3.637 ±0.070	33.6
X8-2:10	8	5.482 ±0.027	3.066 ±0.007	44.1

A second set of experiments was performed in order to determine the dependency of extraction efficiency with the addition of a larger amount of capsules into Cd^{2+} solutions. The expectation of the potential increase of the amount of extracted cadmium ions was not met – as it can be seen from Table 3, the more capsules were added, the less reduction of Cd^{2+} was achieved. The authors believe that this was a case of poor filtration – for the purpose of consistency, all samples were filtered only twice. Further filtration would result in a significant loss of liquid in samples, making them unsuitable for measurements. Increasing the number of filtration steps was also considered counterproductive from time and labour intensity point of view, therefore, the decision was made to explore other options for post-extraction removal of the capsules from solutions.

Table 3

Extraction efficiency as a function of amount of the added capsules

Sample ID	Volume ratio of capsule dispersion to Cd^{2+} solution	Concentration of Cd^{2+} before extraction, ppm	Concentration of Cd^{2+} after extraction, ppm	Reduction of Cd^{2+} concentration, %
X8-2:10	1:5	5.482 ±0.027	3.066 ±0.007	44.1
X8-2:5	2:5	4.690 ±0.027	2.800 ±0.018	40.3
X8-4:5	4:5	3.654 ±0.027	2.446 ±0.004	33.1
X8-5:1	5:1	1.090 ±0.027	0.914 ±0.011	16.0

3.4. Post-extraction capsule removal

Third set of experiments was dedicated to investigate an alternative method of separation of capsules from solutions after Cd^{2+} extraction was completed. A new batch of 8-layered capsules was fabricated from the initial encapsulated nano-emulsion. As the new dispersion of multi-layered capsules was slightly less concentrated than a previous batch (1.04 g·L^{-1}), the volume of capsule dispersion that was needed to be added was increased to 3 ml in order to keep the amount of capsules (and the functional extractant material) the same as in previous experiments. 2 ml of magnetite nanoparticles (0.5 g·L^{-1}) were added to the capsule-cadmium solution system after the completion of extraction process. The resulting dispersions were stirred for 2 hours and left on magnets for magnetic separation process; as a control, filtered samples were fabricated for comparison. The results of this experiment are presented in Table 4.

A considerably large decrease of extraction efficiency of filtered samples can be noticed in comparison with experiments performed with the previous batch of multi-layered capsules. This may be explained by a reduction of capsules size (Fig. 3 c and d, average capsule size under 100 nm), that was facilitated by the decrease in droplet size of initial encapsulated emulsion, as a new set of multi-layered capsules was prepared when it was 3 weeks old. Nevertheless, some degree of extraction was achieved by filtration, making these samples eligible for comparison. A large increase of extraction efficiency is clearly observed when using magnetic separation in comparison with filtration, making this removal method more appropriate when working with multi-layered capsules fabricated for the current study.

The TEM images of capsules with magnetite nanoparticles on their surface are presented in Fig. 3c and d.

Table 4

Comparison of post-extraction capsule removal techniques (new batch of multi-layered capsules using the initial core dispersion)

Sample ID	Volume ratio of capsule dispersion to Cd^{2+} solution	Concentration of Cd^{2+} before extraction, ppm	Concentration of Cd^{2+} after extraction, ppm	Reduction of Cd^{2+} concentration, %
X8-6-F	3:5	3.824 ±0.027	3.275 ±0.075	14.45
X8-6-M	3:5	3.103 ±0.027	1.780 ±0.059	42.60
X8-12-F	3:5	7.069 ±0.027	5.874 ±0.122	16.9
X8-12-M	3:5	5.376 ±0.027	3.770 ±0.044	34.3

3.5. Extraction selectivity of the capsules

Multi-layered capsules (8 layers) were also tested on a subject of an extraction selectivity, i.e., in the presence of multiple ionic species, in particular, Ca^{2+} (since Ca^{2+} and Cd^{2+} have similar ionic radius[52] which leads to replacement of Ca^{2+} by Cd^{2+} in soft tissue and bones[53]), would they extract only Cd^{2+} or would they extract Ca^{2+} ions as well. Two different solutions were tested – one containing only Ca^{2+} cations (capsules removed by filtration), another – containing a mixture of Ca^{2+} and Cd^{2+} ions together (capsules removed by both filtration and magnetic separation).

The results of the first experiments are presented in Table 5. As it can be seen, there is no decrease in Ca^{2+} concentration, meaning capsules do not extract calcium ions.

Table 5

Ca^{2+} extraction efficiency

Sample ID	Volume ratio of capsule dispersion to Ca^{2+} solution	Concentration of Ca^{2+} before extraction, ppm	Concentration of Ca^{2+} after extraction, ppm	Reduction of Ca^{2+} concentration, %
X8-2:10-Ca	1:5	6.520 ±0.1349	6.589 ±0.189	-1.06
X8-2:5-Ca	2:5	5.540 ±0.1349	5.579 ±0.127	-0.70

But, considering that filtration was found to be not particularly effective, a second experiment was performed using two methods of post-extraction capsule removal in order to make sure that capsules that contained Ca^{2+} ions were not simply unable to be filtered. This experiment included mixing multi-layered capsules with solution containing both Cd^{2+} and Ca^{2+} ions. The results of this experiment are presented in Table 6. As it can be observed, neither filtration nor magnetic separation provided any evidence for Ca^{2+} extraction, while clearly showing the reduction in Cd^{2+} concentration.

An observation can be made that in this experiment that filtration provided a larger reduction results than in previous experiment using a new batch of capsules. The authors are unsure what may have facilitated this efficiency rise, but can hypothesise that the time taken between manufacturing of a new batch and performing this particular experiment (10 days) might have caused aggregation of capsules therefore making them more suitable for filtration.

Table 6

Extraction efficiency in presence of both Cd^{2+} and Ca^{2+} ions

Sample ID	Volume ratio of capsule dispersion to Cd^{2+} and Ca^{2+} solution	Concentration of Cd^{2+} and Ca^{2+} before extraction, ppm	Concentration of Cd^{2+} and Ca^{2+} after extraction, ppm	Reduction of Cd^{2+} or Ca^{2+} concentration, %
X8-Cd-F	3:5	4.327 ±0.051	2.894 ±0.0208	33.1 (Cd^{2+})
X8-Ca-F		4.268 ±0.314	4.304 ±0.311	-0.8 (Ca^{2+})
X8-Cd-M	3:5	3.440 ±0.051	1.530 ±0.029	55.5 (Cd^{2+})
X8-Ca-M		3.759 ±0.314	3.763 ±0.311	-0.1 (Ca^{2+})

3.6. Optimization of the Cd^{2+} extraction efficiency

Based on data presented in Table 4, the maximum extraction efficiency achieved so far was 42.6% for samples with initial Cd^{2+} concentration of $\simeq$ 6 ppm and with 3:5 volume (ml) ratio of capsule emulsion to sample solution while using magnetic separation for post-extraction capsule removal. Therefore, the assumption was made that in order to achieve extraction efficiency close to 100% one might use 100 (%) · 3 (ml) / 43 (%) $\simeq$ 7 milliliters of encapsulated emulsion to 5 ml of Cd^{2+} solution. The sample using these ratios was prepared and separated into separate samples of 4 ml, followed by addition of different amounts of magnetite – 50 and 250 µl. The concentration of stock magnetite used in these experiments was increased greatly in order to prevent further dilution of samples and was ___ g·L^{-1}. The results of experiments are presented in Table 7.

Table 7

Optimization of Cd^{2+} extraction efficiency

Sample ID	Volume ratio of capsule dispersion to Cd^{2+} solution	Concentration of Cd^{2+} before extraction, ppm	Concentration of Cd^{2+} after extraction, ppm	Reduction of Cd^{2+} concentration, %
X8-6-50	7:5	2.447 ±0.3604	0.066 ±0.0018	97.3
X8-6-250	7:5	2.447 ±0.3604	0.000 ±0.001	100

As can be seen, an efficiency of almost 100% can be achieved by using the stated amount of capsules coupled with magnetite separation which uses only 50 µl of magnetite nanoparticles, and a confident total extraction can be achieved by using 250 µl.
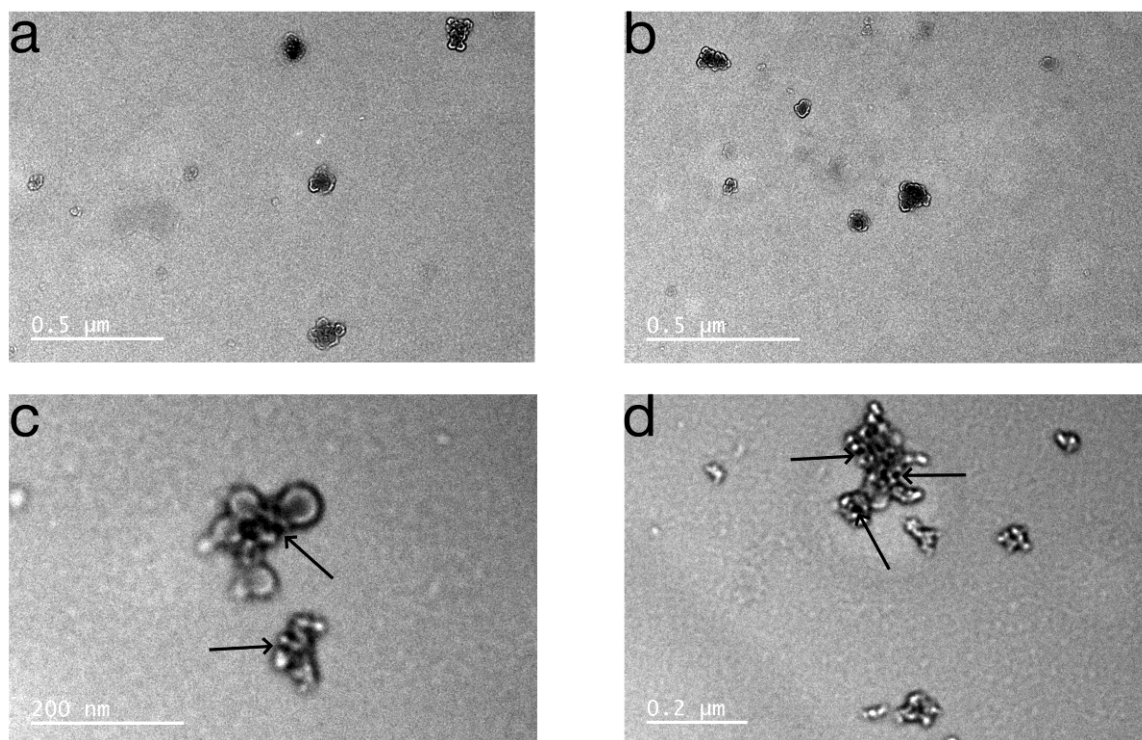
Fig. 3. TEM pictures of multi-layered capsules before extraction (a, b first batch) and after extraction (c,d second batch, size reduced). Arrows indicate magnetite nanoparticles attached to the capsules surface.

3.7. Long-term stability of multilayered nanocapsules

After four months of storage, the stability of the capsules was reassessed using zeta-potential measurements and was found to be 43.8±2.5 mV which is very close to the zeta-potential value at the moment of initial encapsulation (48.2±0.8 mV), suggesting kinetic stability of the encapsulated nano emulsion. Furthermore, DLS measurement of the same sample shows that the average size of the capsule is 85±3 nm, which is less than 100 nm, the average size of encapsulated nano-emulsions approximated from TEM images at the time of initial encapsulation, which justifiably indicates colloidal stability as well.

4. Summary and conclusion

The nano-capsule based system for extraction of Cd^{2+} ions from aqueous solutions was created using emulsified encapsulated ionic liquid (Trihexyl(tetradecyl)phosphonium-bis(trifluoromethylsulfonyl)imide) as a medium for active extractant material (1-(2-Pyridylazo)-2-naphthol). Nano-capsules were created in three steps: emulsification of extractant-loaded ionic liquid also containing cationic surfactant in water using low-energy emulsification phase inversion (EPI) method, initial encapsulation of nano-emulsion in poly(sodium-4-styrenesulfonate) shells by means of electrostatic interactions between the surfactant and polyanions, and finally continuous layer-by-layer fabrication of multi-layered nano-dispersion of functional capsules using poly(diallyldimethylammonium chloride) and poly(sodium-4-styrenesulfonate) polyelectrolyte solutions. These nano-capsules were mixed with aqueous solutions containing Cd^{2+}, Ca^{2+} and both Ca^{2+} and Cd^{2+} ions, then removed by filtration or magnetic separation (for capsules surface-fortified with magnetite nanoparticles). The efficiency and selectivity of extraction provided by capsules were tested using inductively coupled plasma atomic spectrometry. The efficiency of Cd^{2+} removal was 14.5% if capsules were removed from solutions via filtration and 100% using magnetic separation. Ca^{2+} concentration didn't change either in experiments with only Ca^{2+} ions being present in solution, or in ones where solution contained both Ca^{2+} and Cd^{2+} ions (while there was significant reduction of Cd^{2+} content), meaning that capsules are selective. Multi-layered nano-capsules

didn't exhibit any loss of stability in four months, which suggests that they are suitable for a long-term storage. The reported system can be used on its own, but it is not limited to the particular materials used in this study. Method used for the initial emulsion encapsulation and continuous layer-by-layer technique can in principle be used for any charge-stabilized emulsion, while the magnetic separation strategy can also be applied to any other encapsulated system of electrostatic nature. Therefore, this study can serve as a guide for creation of different multi-layered emulsion-based systems for a variety of applications, including extraction systems for other elements (assuming the appropriate choice of extractant).

With the extraction efficiency of the optimized system as high as of previously reported emulsion-based extraction systems[13–15], the use of the layer by layer ionic liquid-core capsules is preferable to using emulsions since they are more stable[47,54] and easier to remove from aqueous solutions than non-encapsulated emulsion droplets, while being suitable for performing the extraction in cases when *in-situ* emulsification is not possible. Future work, therefore, will focus on finding a way to safely concentrate multi-layered capsules in order to add more polyelectrolyte layers onto them to further increase their mechanical strength thus making filtration a viable option for post-extraction capsule removal, as well as to make them suitable for efficient extraction of Cd^{2+} from more concentrated solutions.

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