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Droplet Microfluidic Device for Rapid and Efficient Metals Separation Using Host-Guest Chemistry

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Abstract

Metals are pivotal elements in our daily life and industrial processes, to produce electronic devices, catalysts, smart materials and so on. However, they are mostly present as a mixture in the environment that makes their separation challenging over the past decade. Host-guest chemistry principle thoroughly has been used to design and synthesize thousands of organic receptors with high complexation ability and selectivity to certain metal ions. On the other hand, the droplet microfluidic device is well-known for its unique characteristics of fluid dynamics, such as large specific surface area and short diffusion distance making the process robust and efficient. Therefore, many reports of research employ host-guest chemistry of the droplet microfluidic system for the effective metal separation process. This chapter deals with up-to-date examples of the droplet microfluidic system application for separation of base and alkali metals, recovery of rare-earth and precious metals and removal of heavy metals either from the competitive metal system or from the real waste solution sample through solvent extraction techniques utilizing host-guest chemistry principle.

Keywords: droplet microfluidic device, host-guest chemistry, solvent extraction, recovery, metal separation

1. Introduction

Nowadays, smart and advanced technology researches have infiltrated on all aspects of human daily activities [1]. For example, smart devices containing metal elements have massively been applied in pharmaceutical and electronic fields [2]. In general, based on their properties and usage, metal elements can be divided into four groups, *i.e.* alkali and base metals (lithium, iron, cobalt, nickel, zinc, etc.), precious metals (silver, gold, palladium, platinum, rhodium, iridium, osmium and ruthenium), rare-earth metals (lanthanum, neodymium, europium, holmium, etc.) and heavy metals (cadmium, lead, mercury, chromium, etc.). Silver materials have been applied as an antimicrobial agent while lithium ones as well-known energy storage materials [3]. The demands for these smart materials have kept increasing,

therefore, their supply has been depleting day-by-day. Global maldistribution of metals, furthermore, is worsened by the metal supplies in several countries. Over the past several years, researchers are putting their continuous efforts on metal recycling and recovery process from wastewater and other secondary resources [4].

Metal recycling is a process to recover metals either from generated solid waste/ liquid metal waste or spent home appliances using several techniques for a constant supply to meet the demand. Many kinds of research have been conducted to evaluate the metal recycling process; however, the metal recycling is quite complicated due to the presence of other metals with similar physicochemical properties in varying concentrations [1]. Additionally, heavy metals removal from the environment is difficult because they usually exist in trace amounts compared with other elements [5]. Therefore, versatile techniques which exhibit high metal selectivity and high recovery percentage are highly required [6].

Solvent extraction or liquid-liquid extraction is one of the metal separation techniques where the metal extraction efficiency mainly depends on the nature of the extraction reagents used. For example, di(2-ethylhexyl)phosphoric acid (D2EHPA) extracted lead(II) from chloride aqueous solution, however, the selectivity against iron(III), zinc(II) and copper(II) ions is unsatisfied [7]. Meanwhile, a complete separation of lead(II) ions from iron(III), zinc(II) and copper(II) successfully achieved using an amide derivative of calix[4]arene due to its high and suitable host-guest interaction [8].

On the other hand, droplet microfluidic devices are popular in biology and analytical chemistry areas because of their unique characteristics and advantages [9–15]. Numerous research papers related to rapid and efficient metal separations reported recently, and their numbers keep increasing with time [16–20]. This chapter serves an up-to-date review on the application of the droplet microfluidic system for separation and recovery of metal elements using a combination of host-guest chemistry principle and solvent extraction technique.

2. Host-guest chemistry

Host-guest chemistry is one of the chemistry fields studies various non-covalent interactions between host and guest molecules [21]. Host molecule defined as a molecular entity that forms complexes with organic or inorganic guests, or a chemical species that can accommodate guests within cavities of its crystal structure. The guest molecule is a molecule having a complementary structure to the binding site of the host compound, thus generating a selective and strong interaction between them [22]. The non-covalent interactions between host and guest molecules are including size effect, hydrophobic, cation-π, π-π, electrostatic, and hard-soft acid-base interactions as well as hydrogen bonding. Because of these specific interactions, a selective complexation between host and guest molecules could be achieved [23].

Thousands of host molecules are being prepared and evaluated to find out the best suitable host candidate for metal separations. Among them, calixarenes are found to be interesting host molecules and they attracted a lot of attention for research works due to their special inclusion phenomena [24]. Calixarenes are macrocyclic compounds that are prepared from formaldehyde and *p*-alkylphenol as the repeating units. A single step preparation of calixarenes was firstly introduced by Prof. C.D. Gutsche in 1978, subsequently, it has grown rapidly due to some merits, such as large-scale synthesis, rigid structure, easy modification and stable host compound [25]. It is also interesting to note that, the ring size and conformation of calixarenes are controlled by using template and reaction temperature.
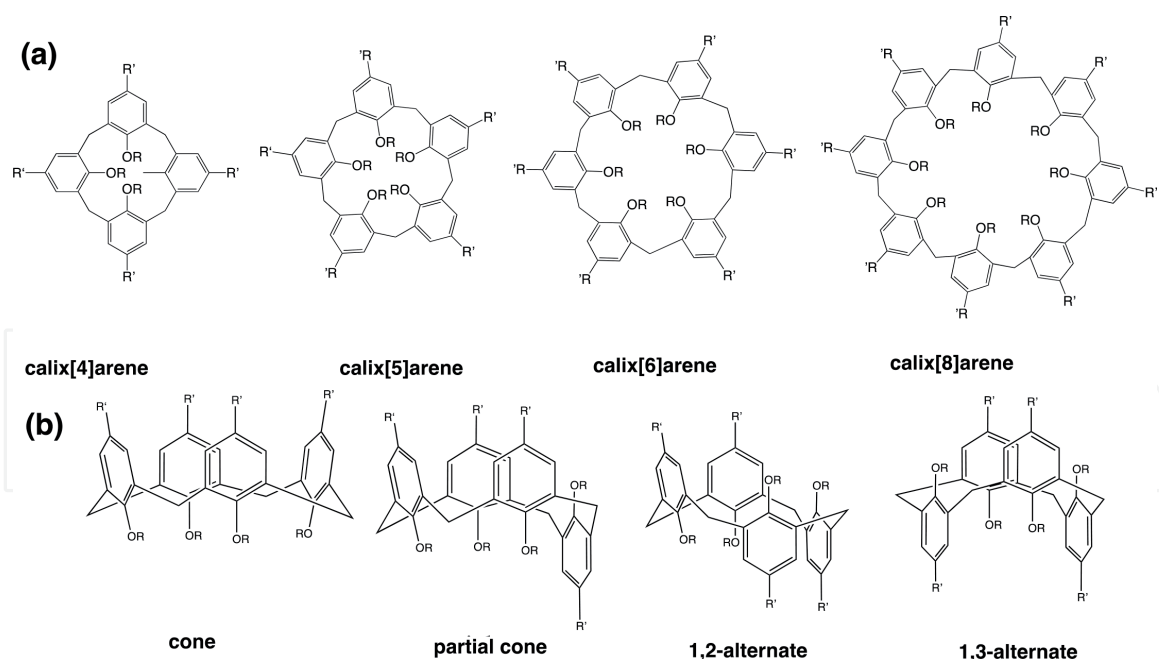
Figure 1.
(a) The structures of calix[n]arenes and (b) the conformations of calix[4]arene.

So far, there are four main subfamilies of calixarenes based on their ring size, *i.e.* calix[4]arene, calix[5]arene, calix[6]arene and calix[8]arene as displayed in **Figure 1(a)**. By increasing the ring size of calixarenes, their conformation could not easily be adjusted because of weaker hydrogen bonding on the calixarene structure [26].

Calix[4]arene is the most simple and special subfamily of calixarenes because it serves the most stable conformations. In general, there are four available conformations of calix[4]arene, *i.e.* the cone, partial cone, 1,2-alternate and 1,3-alternate conformations as shown in **Figure 1(b)**. Calix[4]arenes offer ideal frameworks for metal separation because of their size discrimination and chelating effects that contributed to high selectivity and high complexation ability with certain metal ions [27]. Furthermore, it is possible to change its sequence of metal selectivity by modifying their upper and lower rims [28]. Therefore, it is reasonable to understand that a lot of research works utilized calix[4]arenes for metal extraction, metal adsorption, and as chemosensor of metal ions, etc. [29–31].

3. Droplet microfluidic device

Microfluidic system is a miniaturized device that manipulates and controls fluids, usually in the range of microliters to femtoliters, in the channels with dimensions from tens to hundreds of micrometers [14]. The earliest microfluidic system was reported by Hodgson and Charles in 1963 while they investigated droplet generation when oil and water phases were introduced into the microchannel [32]. In 2001, Burns and Ramshaw firstly reported that the mass transfer of acetic acid from kerosene to aqueous phase was significantly enhanced by using droplet microfluidic device [33]. As of today, there are many types of microfluidic devices, such as continuous microfluidic devices, droplet microfluidic devices, paper microfluidic devices, and digital microfluidic devices have been fabricated and applied for many applications [34, 35]. Each of them serves as a unique platform for certain applications. Continuous microfluidic devices have been widely applied to particles and cell separation due to density differences. Droplet microfluidic devices serve as an ideal platform for metal separation, nanoparticle fabrication, drug delivery, and

cell assay. Paper microfluidic devices have also been reported for routine chemical analysis and biochemical assays, while digital microfluidic devices are employed for immunoassays and chemical synthesis, etc. [36].

As the name indicates, the droplet microfluidic device generates droplets of two immiscible liquids such as organic and aqueous phases in the microchannel. Based on the liquids' intersection, there are 2 types of droplet microfluidic devices, *i.e.* T-type and Y-type of droplet microfluidic devices [9, 12]. A schematic representation of a droplet microfluidic device is shown in **Figure 2**. When the liquid is introduced into the microchannel through an inlet which is perpendicular to the main microchannel of a T-type droplet microfluidic device, it was defined as the dispersed phase, while, the continuous phase liquid that has introduced through an inlet which is in line with the main microchannel of a T-type droplet microfluidic device. However, both phases are equal to the Y-type of droplet microfluidic devices [13].

Kashid *et al.* have observed the droplets generation on both T-type and Y-type droplet microfluidic devices in 2010 [37]. For example, on the T-type droplet microfluidic device, first, the dispersed phase is entered the main microchannel and starting to block the flow of the continuous phase by exerting the pressure. The generated pressure squeezes the neck of the dispersed phase and the droplet of the dispersed phase is formed. Since both phases are immiscible, each droplet has a role as an individual reactor with a short diffusion distance. Furthermore, each droplet serves a large specific surface area. The combination of a short diffusion distance and a large specific surface area contribute to boosting the mass transfer process of chemicals from one phase to another phase [38].

Even though solvent extraction offers a selective and efficient technique for metal separation, the extraction kinetics rate in some processes is slow and time-consuming [38]. For comparison, **Figure 3** shows the obtained parameters and experimental data for silver(I) extraction using a tetramethylketonic derivative of calix[4]arene in batch-wise and microfluidic systems. In the batch-wise system, the extraction was carried out in a small glass vial with a diameter of 4 cm and height of each phase is about 1 cm. The extraction using a continuous microfluidic device was performed in a microchannel with 20 mm of length and 200 μm in depth and width while the extraction in a droplet microfluidic device was carried out in a microchannel with 73 mm of length and 200 μm of depth and widths. As shown in **Figure 3**, the diffusion distance of chemicals using batch-wise (20,000 μm) was a hundred times farther than both the microfluidic devices (200 μm). Furthermore, the total specific surface area of the droplet microfluidic device employed was ~550 times larger than that of the continuous microfluidic system while ~55,000 times larger than that of the batch-wise system. Because of that, it is reasonable to know that the required extraction time to reach an equilibrium state is 259,200 s (72 h), 15.0 s and 1.00 s for the batch-wise system, continuous microfluidic system, and droplet microfluidic system, respectively. This result demonstrates the remarkable advantage of using the droplet microfluidic device for metal extraction and separation process [39].
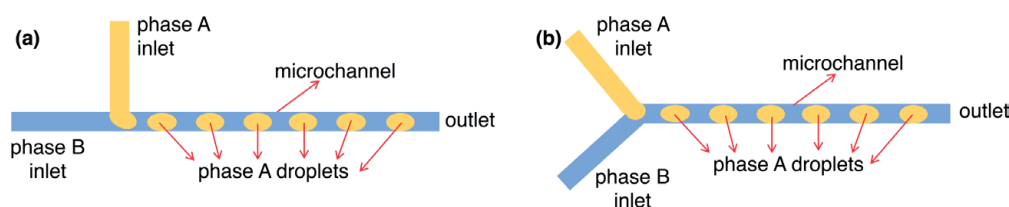

Figure 2.
(a) T-type and (b) Y-type of droplet microfluidic devices.
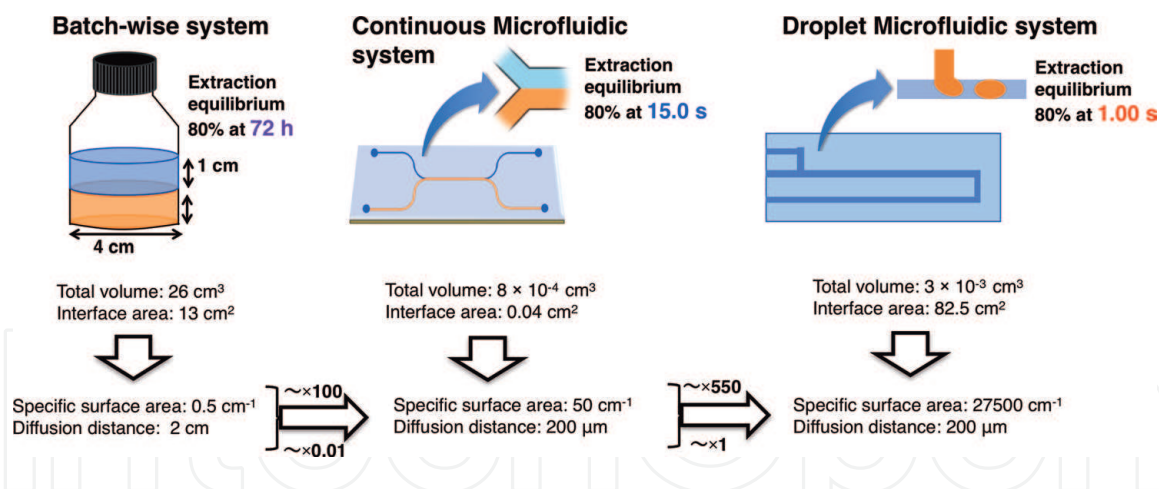
Figure 3.
Comparison of batch-wise, continuous and droplet microfluidic systems for silver(I) extraction using a tetramethylketonic derivative of calix[4]arene [38].

4. Metal separations using the droplet microfluidic device

Due to the significant enhancement of the extraction process, droplet microfluidic devices have been employed for metal ion separations through a solvent extraction technique [18–20]. The chemical structures of several extraction reagents employed in metal separations are shown in **Figure 4**. In general, metal ion concentrations were measured using either atomic absorption spectroscopy (AAS) or induced coupled plasma-atomic emission spectroscopy (ICP-AES) or induced coupled plasma-mass spectrometry (ICP-MS). The measured metal ion concentrations were further used to calculate extraction percentages (%E), distribution ratio (D) and separation factor (β) as mentioned in Eqs. (1)–(3) whereas *[metal ion]$_{aqueous,0}$* is initial metal ion concentration in the aqueous phase before solvent extraction process, *[metal ion]$_{aqueous,t}$* is the metal ion concentration in the aqueous phase after *t* extraction time, and *[metal ion]$_{organic,t}$* is the metal ion concentration in the organic phase after *t* extraction time [26]. The metal extraction and separation processes are summarized and listed in **Table 1**.

$$\%Extraction = \frac{[metal\ ion]_{aqueous,0} - [metal\ ion]_{aqueous,t}}{[metal\ ion]_{aquoeus,0}} \times 100 \qquad (1)$$

$$D = \frac{[metal\ ion]_{organic,t}}{[metal\ ion]_{aqueous,t}} \qquad (2)$$

$$\beta = \frac{D_{metal\ ion\ A}}{D_{metal\ ion\ B}} \qquad (3)$$

4.1 Alkali and base metals

Alkali and base metals are non-precious metals which are abundantly found in nature [40]. In this part, the example of utilization of droplet microfluidic system for extraction and separation of copper(II), iron(III), indium(III), calcium(II), cesium and lithium ions were discussed.

Evaluation of copper(II) extraction using Y-type microreactor was carried out by Yang *et al*. The commercially available extractant, AD-100 which consists of 70–75% (w/w) of 2-hydroxy-5-nonylbenzaldehyde oxime as the active reagent in 260# solvent oil as the organic diluent was used. The concentrations of AD-100 used influenced the copper(II) extraction percentage. Higher AD-100

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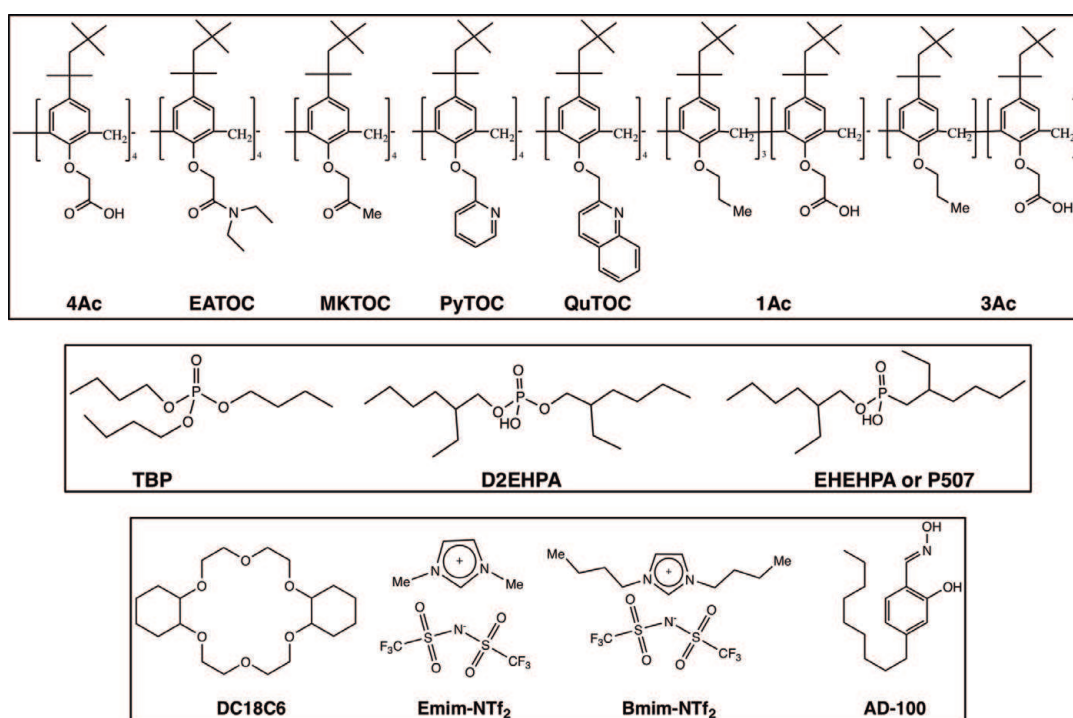
Figure 4.
Host compounds and extraction reagents used for metal separations in this chapter.

concentration gave higher extraction percentage while a higher concentration of copper(II) gave lower extraction percentage. The extraction percentages were also increased at longer extraction time, lower Reynolds number, higher pH of the aqueous phase, and higher temperature. Using the T-type of droplet microfluidic device, 96.0% copper(II) ions were extracted in 32.0 s extraction time [41]. On the other hand, Jiang *et al*. employed a Y-type microfluidic device to achieve an effective separation of copper(II) over iron(III) and zinc(II) with a mixture of 2-hydroxyl-5-nonyl acetophenoneoxime and 5-nonylsalicyladoxime in 1:1 volume ratio, called as DZ988N, as the extraction reagent. Using the microfluidic device, as much as 80.6% of copper(II) extracted at 0.78 s extraction time. While as much as 98.9% of copper(II) was stripped at 3.92 s by using 1.84 M of sulfuric acid solution in 2:1 organic to aqueous phase ratio. In a comparison of the microfluidic device to the batch-wise system, the separation factors of copper(II) over iron(III) and zinc(II) were significantly enhanced from 86.2 to 466 and 123 to 1089, respectively [42].

Iron(III) extraction kinetics using D2EHPA was investigated in a Y-type microfluidic device. The experimental results showed that the extraction of iron(III) was controlled by mixed reaction-diffusion resistance regime on a second-order extraction rate equation. Moreover, since the required extraction times for iron(III) and cobalt(II) are different, iron(III) could be separated from the cobalt(II) in the metal mixture solution, which may contribute to the real hydrometallurgical process [43].

Indium(III) separation from a metal mixture solution has been successfully achieved using a T-type of droplet microfluidic device. The metal mixture contains 23.0 mM of indium(III), 35.8 mM of iron(III), 44.2 mM of zinc(II), 153.8 mM of aluminum(III) and 141.5 mM of magnesium(II) ions [44]. It was found that indium(III) was extracted in 98.8%, while the other metal ions were hardly extracted (<5.00%). The separation process yielding that the separation factors of indium(III) over iron(III), zinc(II), aluminum(III) and magnesium(II) ions were 18,720, 266,373, 41,955 and 11,809, respectively, demonstrating that a high selective indium(III) separation was achieved within a minute.

Sl. No	Metal ions	Extraction reagents	Microchannel			%E	β	t (s)	Ref
			Length (mm)	Width (mm)	Type				
Base metals									
1	Cu(II)	AD-100	900	0.6	T	96.0	—	32.0	[41]
2	Cu(II)	DZ988N	131	0.2	Y	80.6	$466^{Fe(III)}$ $1250^{Zn(II)}$	0.78	[42]
3	Fe(III)	D2EHPA	3	0.1	Y	32.0	—	—	[43]
4	Co(II)	D2EHPA-Na	500	1.0	Y	92.0	$3.54^{Li(I)}$	15.0	[50]
5	In(III)	D2EHPA	2000	0.8	T	98.8	$18720^{Fe(III)}$ $266373^{Zn(II)}$ $41955^{Al(III)}$ $11809^{Mg(II)}$	60.0	[44]
Alkali metals									
6	Ca(II)	DC18C6	20	0.5	Y	98.2	—	5.70	[45]
7	Ca(II)	EMIMNTf$_2$ + BMIMNTf$_2$	130	0.4	Y	52.0	—	6.00	[46]
8	Cs(I)	D2EHPA	22	0.7	Y	100	—	40.0	[47]
9	Li(I)	D2EHPA + TBP	500	1.0	Y	50.0	—	5.00	[49]
10	Li(I)	1Ac	73	0.2	T	100	> 1000	4.00	[51]
Precious metals									
11	Ag(I)	MKTOC	73	0.2	T	100	—	4.00	[52]
12	Pd(II)	QuTOC	73	0.2	T	100	—	4.00	[52]
13	Pt(IV)	PyTOC	73	0.2	T	100	—	4.00	[52]
Rare-earth metals									
14	La(III)	P507	120	0.1	Y	99.5	—	0.37	[55]
15	La(III)	Phosphorus reagent	100	1.0	T	90.0	$3.50^{Eu(III)}$	10.0	[56]

Sl. No	Metal ions	Extraction reagents	Microchannel			%E	β	t (s)	Ref
			Length (mm)	Width (mm)	Type				
16	Nd(III)	P507	125	0.3–1.0	Y	88.0	2.23$^{Pr(III)}$	12.0	[58]
17	Ce(III)	P507	125	0.3	Y	76.5	3.25$^{Pr(III)}$	12.0	[57]
18	Sm(III)	P507	125	0.3	T	75.1	—	45.0	[59]
19	U(IV)	TBP	13	0.5	T	100	—	1.50	[65]
Heavy metals									
20	Pb(II)	4Ac	73	0.2	T	96.0	14.2$^{Fe(III)}$ 324$^{Cu(II)}$ 296$^{Zn(II)}$	4.00	[66]
21	Pb(II)	EATOC	73	0.2	T	100	> 1000	2.00	[8]

Table 1.
Summary of reports on metal ion extractions and separations carried out in the microfluidic devices at t extraction time.

Jahromi *et al.* separated calcium(II) isotopes, [48]calcium(II) and [40]calcium(II) ions using dicyclohexano-18-crown-6 in a Y-type microfluidic device. Using a combination of the dicyclohexano-18-crown-6 and microfluidic device, [40]calcium(II) was selectively extracted in 98.2% within 5.70 s. By using a continuous cycle extraction process, the amount of [40]calcium(II) becomes lower in the aqueous phase, therefore, the concentration of [48]calcium(II) ion was enriched [45]. Another experiment on calcium(II) extraction was carried out by using ionic liquids as the extraction reagent, named as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM NTf2) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM NTf2) in a Y-type of droplet microfluidic device. The pH value of the aqueous phase did not affect the extraction percentage because the main extraction mechanism is not an ion-exchange mechanism. Even though some parameters were optimized, the highest extraction efficiency was only 52.0%, which was still unsatisfied [46].

On the other hand, cesium(I) extraction in a Y-type of droplet microfluidic system was studied by Tamagawa *et al.* Stable droplet generation was observed when the total flow rate of both phases is less than 100 mL h^{-1}. By using D2EHPA as the extraction reagent, the required times to reach the quantitative amount of extraction percentage (100%) were shortened 25 times from 1000 to 40.0 s using batch-wise and droplet microfluidic system, respectively [47].

Lithium metals are widely used as the main part of lithium-ion batteries and aircraft alloys, the continuous supply of lithium may become critical over time. Urban waste, especially from lithium-ion batteries and seawater, may serve as the potential secondary resource in the future. However, lithium-ion batteries contain lithium, cobalt(II) and manganese(II) ions, while seawater contains lithium and other metal ions, such as sodium, potassium, magnesium, and calcium ions in different concentrations, the lithium recovery from these resources poses to be a tough work [48].

Muto and co-workers investigated the extraction process of lithium using D2EHPA in a droplet microfluidic device. They found that a glass substrate gave higher extraction efficiency as well as the mass transfer coefficient due to stronger convection rate and larger specific surface area of the organic droplets. When 2.0 M D2EHPA was used as the extraction reagent for 1.0 mM of lithium ions in the aqueous phase, around 0.3 mM of lithium ions were extracted in 5.00 s as the extraction time. Furthermore, by the addition of 0.18 M tributyl phosphate (TBP), the amount of the extracted lithium can be improved to 0.5 mM at 5.00 s extraction time. Even though the extraction efficiency was only around 50%, the droplet microfluidic device serves as a potential platform for quick metal extraction compared with the conventional extraction process [49].

Hirayama *et al.* evaluated the separation of cobalt(II) over lithium from a model solution of lithium-ion battery waste. The mixture of 0.20 M of D2EHPA and 0.01 M of NaOH, called as D2EHPA-Na in cyclohexane was used as the organic phase while the model solution containing 1.0 mM of cobalt(II) and 1.0 mM of lithium ions was used as the aqueous phase. From the model solution, the extraction reagent extracted around 50 ppm of cobalt(II) and 1.5 ppm of lithium ions giving 3.54 as the separation factor for cobalt(II) over lithium ions. Furthermore, using the droplet microfluidic device, 98% purity of cobalt(II) solution was obtained within 4.50 s extraction time [50].

In our previous study, we investigated the possibility to extract lithium ions with monoacetic acid derivative of calix[4]arene using T-type of droplet microfluidic system [51]. At first, the droplet microfluidic device was fabricated from Tempax glass and the microchannel was produced utilizing a diamond-coated needle through a micromilling process. The microchannel dimensions were 73.0 mm in length and 200 μm in width and depth as confirmed by laser reflection microscope. The top

and bottom parts of the T-type droplet microfluidic device were permanently bonds through a thermal fusion technique [52]. To prevent any disturbance of leaked sodium ions from the glass substrate, the microchannel was coated with SFE-X008 coating agent (1% of *m*-bis(trifluoromethyl)benzene in 94% of the ethyl perfluorobutyl ether). After coating, the wettability of the glass substrate was significantly changed from 20 to 120°, demonstrating a successful coating of the microchannel. From the preliminary investigation on lithium extraction using the monoacetic acid derivative of calix[4]arene (shown in **Figure 4** as 1 Ac) on the individual metal extraction, it was found that 100% of lithium ions were quantitatively extracted just within 2.00 s as the extraction time. Moreover, the complete stripping of lithium ions from the organic phase was easily achieved using 0.10 M HCl as the stripping agent.

Since the monoacetic acid derivative of calix[4]arene completely recovered (extraction and stripping efficiencies were 100%) the lithium ions, the competitive metal extraction was carried out using a mixture of metal ions as the aqueous phase. In a mixture of all alkali and alkaline earth metals (lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium ions) in 10.0 mM concentration each, the 5.00 mM of the monoacetic acid derivative of calix[4]arene extracted 4.99 mM of lithium ions showing a quantitative (99.8%) extraction percentage of lithium ions. By using 1.00 M of HCl, as much as 99.5% of lithium ions were successfully stripped from the ligand, which is remarkable. The results demonstrated that the lithium separation from seawater which mainly contains sodium, potassium, magnesium and calcium ions was successfully achieved using the monoacetic acid derivative of calix[4]arene in the droplet microfluidic system.

Seawater was sampled from Minatohama, Karatsu, Japan and filtered using Millipore membrane to prevent any blockage on the microchannel during the extraction process. The lithium concentration in the seawater was 0.03 mM while the sodium, potassium, magnesium and calcium ions concentration was 495, 10.1, 47.4 and 12.8 mM, respectively. Using a droplet microfluidic system, it was found that 31.6% of lithium (0.01 mM) and 1.00% of sodium ions (4.95 mM) were extracted from seawater, however, other metal ions were not extracted at all and remained in the aqueous phase. In this case, sodium ions were extracted due to the huge amount of existing sodium (~19,000 times higher) compared to lithium ions.

To achieve complete extraction of lithium ions from seawater, 20.0 mM of the monoacetic acid derivative of calix[4]arene in chloroform was used as the extraction reagent. As expected, 100% of lithium ions were successfully extracted. However, since the higher concentration of the extraction reagent was used, as much as 2.56% of sodium ions were also extracted. Both metal ions were completely stripped using HCl to obtain an aqueous phase containing 0.03 mM of lithium and 12.2 mM of sodium ions. To obtain a pure lithium solution, another type of calix[4]arene, named as triacetic acid derivative of calix[4]arene was used because it exhibits high sodium selectivity over lithium ions at the acidic condition. When the 10.0 mM of triacetic acid derivative of calix[4]arene (shown in **Figure 4** as 3Ac) was employed, 100% of the remained sodium ions were completely extracted leaving pure lithium ions in the aqueous phase. Similar to monoacetic acid derivative, triacetic acid derivative of calix[4]arene was also recycled. The scheme of recovery of lithium ions from seawater is shown in **Figure 5(a)**. From this experiment, a rapid and efficient lithium-ion recovery from the seawater was successfully achieved in the three-step process using calix[4]arene derivatives as the extraction reagents in a droplet microfluidic device [51].

4.2 Precious metals

Precious metals, *i.e.* silver, gold, palladium, platinum, rhodium, iridium, osmium and ruthenium metals are indispensable metals because of their high economic value
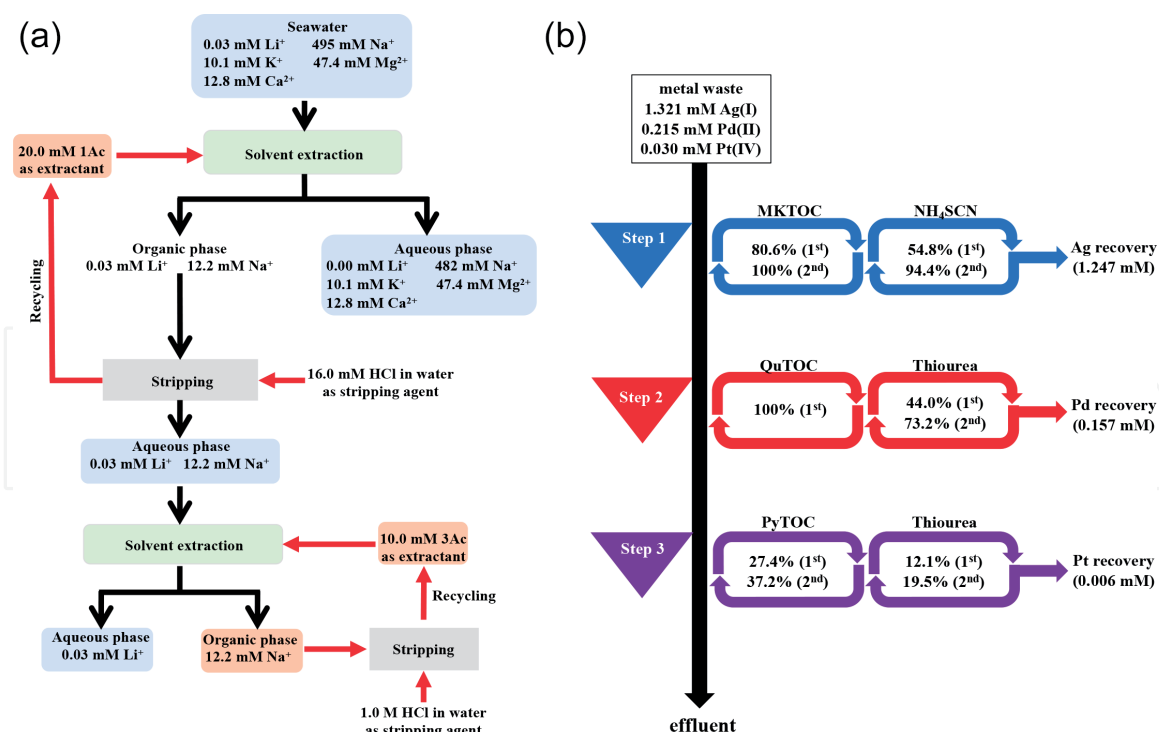
Figure 5.
(a) A process of lithium separation from seawater [51] and (b) precious metals separation from a real metal waste [52] using the droplet-based microfluidic system.

and their application for smart materials [53]. Bizzo *et al.* reported that silver(I), palladium(II) and platinum(IV) ions were found in the electronic waste serving as the secondary resource for precious metal ions [40]. Stepwise recovery of precious metals from electronic waste, therefore, must be established as an untapped resource for future precious metals supply. Even though the recovery process is complicated because of the presence of other metal ions with similar physicochemical properties, a stepwise recovery of precious metals from real metal waste using neutral type of calix[4]arene derivatives in a T-type of droplet microfluidic device was established [52]. Silver(I), palladium(II) and platinum(IV) ions extraction were carried out employing tetramethylketonic, tetraquinoyl and tetrapyridyl derivatives of calix[4] arene, respectively, as the extraction reagents. The chemical structure of tetramethylketonic, tetraquinoyl and tetrapyridyl derivatives of calix[4]arene were shown in **Figure 4** as MKTOC, QuTOC and PyTOC, respectively.

From the individual metal extraction experiment, it was found that as much as 99.9% of silver(I) was extracted at 2.00 s of extraction time from 0.10 mM of $AgNO_3$ solution in 0.10 M HNO_3 media using 5.0 mM of the tetramethylketonic derivative of calix[4]arene in a droplet microfluidic device. However, it required 72 h to achieve a similar extraction percentage of silver(I) using a batch-wise system showing that the droplet microfluidic device enhanced the required extraction time 130,000 times faster to reach the equilibrium stage of silver(I) ion extraction compared with the conventional batch-wise system. On the other hand, as much as 96.2% of palladium(II) ions was extracted at 4.00 s extraction time from 0.10 mM of $Pd(NO_3)_2$ solution in 0.10 M HNO_3 media using a tetraquinolyl derivative of calix[4]arene, and as much as 93.1% of platinum(IV) ions were extracted at 4.00 s extraction time from 0.10 mM of H_2PtCl_6 solution in 0.10 M HCl media using a tetrapyridyl derivative of calix[4]arene. The stripping of silver(I), palladium(II) and platinum(IV) ions were obtained in medium percentages using 2.00 M ammonium thiocyanate in water, 1.00 M thiourea in 1.00 M HCl and 1.00 M thiourea in water, respectively, from the metal-laden organic phase within 2.00 s only.

The evaluated real metal waste, mainly consisted of silver(I), palladium(II), platinum(IV), iron(III), copper(II), and nickel(II) ions at 1.32, 0.22, 0.03, 0.01, 0.82, and 0.01 M, respectively. To prevent any metal precipitations, the real metal waste was diluted 1000 times using 1.0 M HNO_3. Since the concentration of silver(I) was higher than palladium(II) and platinum(IV) ions, the silver(I) ions were extracted first and followed by palladium(II) and platinum(IV) ion extraction. The scheme of stepwise recovery of those precious metal ions from real metal waste is shown in **Figure 5(b)**. All extractions and stripping processes using a droplet microfluidic device were conducted at 4.00 s extraction time. Silver(I) ion extraction was carried out in two-cycle process due to high existed concentration. On the first cycle, 80.6% of silver(I) ions (1.064 mM) were extracted using 20.0 mM of the tetramethylketonic derivative of calix[4]arene. A complete extraction of silver(I) ions were achieved in the second cycle. Even though only 54.8% of silver(I) ions were stripped from the first cycle using 2.0 M ammonium thiocyanate, as much as 94.4% of silver(I) ions were recovered on the second cycle.

A complete palladium(II) ions recovery was achieved within a single cycle extraction process using 5.00 mM of the tetraquinolyl derivative of calix[4]arene, while the stripping percentages of palladium ions were 44.0 and 73.2% on the first and second cycle of stripping process using 1.00 M thiourea in 1.00 M HCl. On the other hand, 27.4 and 37.2% of platinum(IV) ions were extracted in the first and second cycles of extraction process using a tetrapyridyl derivative of calix[4] arene. Meanwhile, low stripping percentages of platinum(IV) ions, 12.1 and 19.5% of the first and second cycles of the stripping process, respectively, were obtained using 1.00 M thiourea in the water as stripping reagent. Even though platinum(IV) recovery still needs to be optimized, a stepwise and complete recovery of silver(I) and palladium(II) ions from real waste was established using a droplet microfluidic system at 4.00 s extraction time [52].

4.3 Rare-earth metals

Rare-earth metal separations leave a serious challenge due to astounding properties as well as their extensive applications in electronic and advanced materials [1]. Rare-earth metals including lanthanide and actinide groups which are classified as 4f and 5f elements in the Periodic Table. Their physicochemical properties are quite similar to each other, thus challenging many researchers to find the optimum separation process for hydrometallurgy field [30, 54]. In this part, lanthanum(III), praseodymium(III), neodymium(III), samarium(III) and uranium(VI) extraction and separation processes are described and discussed.

Lanthanum(III) extraction from a chloride solution was studied in a Y-type microfluidic device by Yin et al. By using phosphonic acid (2-ethylhexyl)-mono(2-ethylhexyl) ester (P507) as an extractant, high extraction percentage of lanthanum(III) ions was achieved within only 0.37 s [55]. Furthermore, the separation of lanthanum(III) and europium(III) ions using a T-type of droplet microfluidic device has been carried out. The separation factor of lanthanum(III) over europium(III) is in the range of 1.50 to 3.50 depends on the flow rate of the liquids [56].

Separation of praseodymium(III) and cerium(III) in a Y-type microfluidic device employing P507 as the extraction reagent was also investigated. At 12.0 s extraction time, as much as 75.0% of praseodymium(III) and 42.9% of cerium(III) ions were extracted into the organic phase yielding 3.25 as the separation factor. Even though the separation was not satisfied enough, the process could be recycled further to obtain pure cerium(III) ions as the remained aqueous phase [57].

On the other hand, neodymium(III) separation over praseodymium(III) was studied by He et al. using a Y-type droplet microfluidic device [58]. One and a

half molar of P507 in sulfonated kerosene was used as the organic phase while praseodymium(III) and neodymium(III) in HCl and lactic acid media were used as the aqueous phase. At 12.0 s extraction time, it was found that P507 extracted 88.0% of neodymium(III) and 75.0% of praseodymium(III) yielding 2.23 as the separation factor of neodymium(III) over praseodymium(III). The similar separation factor was obtained using microfluidic at 12.0 s extraction time while the batch-wise system required 560 s extraction times. These findings initiated a rapid enrichment of neodymium from the wastewater sample within less than 600 s. From the wastewater containing 30–90 ppm of neodymium(III) ions, the neodymium(III) ions were enriched 200–450 times higher which is remarkable [58].

He et al. also investigated the extraction process of samarium(III) using P507 as the extraction reagent in a Y-type of droplet microfluidic device. Within 45.0 s, as much as 75.1% of samarium(III) can be extracted compared with the batch-wise system that requires 600 s to reach a similar extraction percentage [59]. Meanwhile, using a T-type of droplet microfluidic device, samarium(III) was extracted in 82.5% within 14.8 s, shorter than Y-type device. This phenomenon was caused by shorter diffusion distance and a larger specific surface area of T-type than Y-type of droplet microfluidic device [60].

Uranium(VI) extraction process was studied in a microfluidic device using several extraction reagents, such as phosphorus reagent, ionic liquids, and so on [61–64]. Among them, tributyl phosphate (TBP) exhibited as the best extraction reagent for uranium(VI) extraction process due to stable fluid dynamics, as well as, a possibility for large scale process through numbering-up the device. Darekar and coworkers investigated the extraction of uranium(VI) in 1.0 M HNO_3 using 30% v/v TBP in dodecane as the organic phase. It was found that quantitative (100%) extraction percentage was achieved at 1.50 s extraction time, however, the separation of uranium(VI) over other metal ions has not been reported yet [65].

4.4 Heavy metals

Heavy metals, especially lead(II) ions have been used in several industrial processes over the past several years and they get released into environment causing serious effects on environment and human health. A serious control monitoring of heavy metal ion concentration at industrial wastewater effluents should be comprehensively managed. So far, a lot of heavy metal removal techniques have been evaluated for wastewater treatment, however, they were unsatisfied because of heavy metals existed in trace amounts together with huge concentrations of base metal ions [5, 6]. In this part, two examples of a selective removal process of lead(II) removal using two derivatives of calix[4]arene, *i.e.* tetraacetic acid derivative (4Ac) and tetrakis(diethylamide) derivative of calix[4]arenes (EATOC) will be discussed.

In a conventional batch-wise system, the equilibrium state of lead(II) extraction using 4Ac reached after 24 h, however, it was shortened to 6.00 s using a droplet microfluidic device. The significant enhancement was observed by shorter diffusion distance and larger specific surface area aforementioned above. The lead(II) extraction percentages were increased from 73, 89 and 100% at 8.00 s for pH 2.00, 2.25 and 2.50, respectively, however, the separation of lead(II) and other metal ions was unsatisfied. As shown in **Figure 6(a)**, the extraction percentages of iron(III), copper(II), and zinc(II) were 60, 6.9 and 7.5%, respectively. This low selectivity of lead(II) extraction over Fe(III) was caused by the ion exchange mechanism in which the acetic acid groups of calix[4]arene were deprotonated and Fe(III) ions were easily extracted due to strong electrostatic interactions [66].

Another neutral calix[4]arene host molecule, EATOC was also evaluated to obtain a selective lead(II) separation from other metal ions mixture solution.
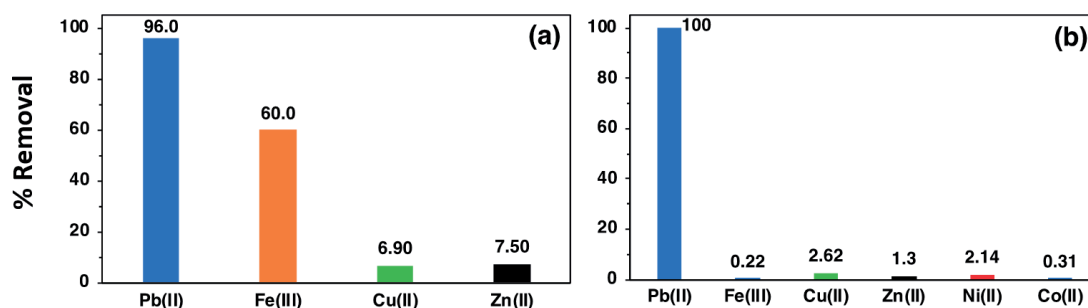
Figure 6.
Lead(II) separation from other metal ions from a competitive metal mixture solution using (a) 4Ac [66] and (b) EATOC [8] as the extraction reagents in a droplet microfluidic systems.

In this case, a neutral host molecule was used to achieve high metal selectivity. In 1.00 M HNO_3 media, one molecule tetrakis(diethylamide) derivative of calix[4]arene formed a 1:1 complex with one lead(II) ion revealed from the Job's plot experiment [8]. Using FTIR and ^{1}H-NMR titration studies, it was elucidated that the lead(II) ion was chelated by EATOC through phenoxy oxygen atoms and carbonyl oxygen moieties. Since the lead(II)-EATOC complex was stable enough, a selective lead(II) extraction (100%) was achieved from a competitive metal system containing copper(II), zinc(II), nickel(II), iron(III) and cobalt(II) ions at 0.10 mM concentration of each metal ion [8]. A complete lead(II) removal was also successfully performed from a simulated wastewater effluent containing 0.10 mM of lead(II), 45.0 mM of iron(III), while copper(II), zinc(II), nickel(II) and cobalt(II) was in 30.0 mM concentration, respectively as shown in **Figure 6(b)**. Furthermore, the lead(II) ions was easily stripped in 98% using distilled water as the stripping reagent, which is a convenient and low-price process. These finding demonstrated that droplet microfluidic system is a promising device for a complete and efficient lead(II) removal from environmental samples [8].

5. Conclusions

Several successful reports on optimized separation and recovery of alkali and base metals, precious metals, rare-earth metals, and heavy metals using the droplet microfluidic system have been published. By employing the host-guest chemistry in a droplet microfluidic system offers a rapid and efficient metal separation from binary metal mixtures or real samples either from nature or industrial activities. In order to realize the true potential of droplet microfluidic devices for renewable metallurgical applications, the improved design of microfluidics addressing larger volumes with continuous operation along with effective utilization of host-guest chemistry are greatly needed to become a step forward in building a novel metallurgical technique for selective metal separations from a real sample, which otherwise not technically feasible to extraction using the conventional batch-wise system.

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Conflict of interest

The authors declare that there is no conflict of interest.

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