

Microfluidic extraction of copper from particle-laden solutions

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ABSTRACT

Microfluidic solvent extraction (SX) of metal ions from particle-laden aqueous solutions is demonstrated as an alternative to conventional solvent extraction for a system of industrial interest: extraction of Cu^{2+} using 2-hydroxy-5-nonylacetophenone. In the presence of silica nanoparticles, bulk SX suffers from prolonged phase separation and, for hydrophobic particles, the formation of particle-stabilised emulsions, which can be indefinitely stable, leading to significant losses of valuable materials to the emulsion phase. In contrast, non-dispersive microfluidic SX can process fluids containing high particle concentrations (e.g. 61 g/L, 80 nm hydrophilic silica and 5 g/L, and 13 nm moderately hydrophobic silica). The SX was operated continuously for more than 7 h without blockage or failure of the microfluidic chip, in part due to the very short residence time of the silica nanoparticles in the aqueous phase. The microfluidic method is also able to access extraction kinetics for particle-laden systems, which cannot be obtained otherwise due to delayed phase separation.

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1. Introduction

Microfluidics has transformed the way we handle small volume, high value chemical and biological materials (Squires and Quake, 2005; Teh et al., 2008; Whitesides, 2006). Tailored microchannel networks can rapidly and efficiently host a variety of chemical and physical processes, realising the “lab-on-a-chip” concept (Evans et al., 2009; Kralj et al., 2006; Priest et al., 2008; Takagi et al., 2005; Tan et al., 2004; Yamada et al., 2008). As microfluidic technologies advance, higher throughput applications are being added, driven by process intensification (Yole Développement, 2007). Process intensification refers to the drive towards higher efficiency, cleaner, and faster processing through substantial changes to methodology and/or equipment. The microfluidic approach is generally associated with small-scale chemical and biomedical processes; however the significant advantages of dispensing (Anna et al., 2003; Priest et al., 2006b), handling (Huang et al., 2006; Surenjav et al., 2008), mixing (Song et al., 2003; Tice et al., 2003, 2004), and analysing (Kitamori et al., 2004) liquids at the microscale are non-specific to a particular industry.

The ability to substantially increase throughput via “numbering-up” (i.e. parallel processing) has opened new possibilities at scales traditionally out-of-reach for microfluidic processing. Microfluidics now extends to large-scale gas processing, chemical synthesis, and

particle synthesis, which can generate tonnes of product per year, while maintaining key attributes (2007), e.g. rapid mixing, ease of handling hazardous materials, and greater yields. The synthesis of heterogeneous (Janus) particles (and homogeneous particles) has also been demonstrated at throughputs of several 100 mL/h using parallel processing (Nisisako and Torii, 2008). However, the potential for microfluidics to impact solvent extraction in the minerals industry has not been explored and is the focus of this study.

Large-scale solvent extraction (SX) is a major technique used in mineral processing to extract valuable metals from mineral leach solutions, which is carried out in a two stage vessel called a mixer-settler (Coulson et al., 1996). The immiscible phases are dispersed in the form of droplets in turbulent flow created by an impeller. The target solute forms a complex with an extractant and diffuses into the organic phase. The dispersed liquids are then allowed to phase separate *via* droplet coalescence (Binks, 1998). For a more detailed description of SX, see Coulson et al. (1996). While dispersion is rapid due to energetic mixing, phase separation is governed by the rate of coalescence and tends to proceed slowly for complex systems, such as particle, certain metal ions, or surfactant containing systems. In particle-laden systems, phase separation can be completely arrested due to the formation of particle-stabilised (PS) emulsions (referred to as “crud” in the industry), in which particles adsorb as a protective layer at the liquid–liquid interface (Aveyard et al., 2003). The energy required to remove a particle from the interface is large (Aveyard et al., 2003). For a 10 nm particle at the water/toluene interface the desorption energy is 100 kT (where k is Boltzmann's constant, T is temperature) or more for contact angles between 35 and 145°.

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In some cases, the generated emulsions cannot be broken, even when using electrocoalescence—a method that is highly effective in surfactant systems (Kralj et al., 2005; Priest et al., 2006a) and commonly used in the petroleum industry (Eow et al., 2001). Persistent dispersion of the organic phase traps the extracted species for long periods or, worse still, indefinitely, and the liquids cannot be recovered for recycling. Where the liquids or their contents are costly, e.g. in biomedical applications, or the volumes are large, e.g. industrial applications, total phase separation is crucial. Therefore, handling of particle-laden systems would benefit from an alternative SX technique in which dispersion is eliminated.

SX has been demonstrated using microfluidic chips (μ SX), which achieve high surface-to-volume ratios using microscopic streams (Aota et al., 2006; Minagawa et al., 2001; Tokeshi et al., 2002) or dispersions (Castell et al., 2009; Choi et al., 2010; Kralj et al., 2007; Kralj et al., 2005; Mary et al., 2008). The latter, dispersed phase μ SX, suffers the same drawbacks of bulk extractions in the presence of particles (or surfactants), i.e. poor phase separation, although the consequences are more serious, e.g. channel blockage. Alternatively, μ SX using microscopic streams, for which liquid–liquid dispersions are not generated and therefore PS emulsions cannot form, may allow SX of complex liquids that are otherwise difficult to handle by dispersive methods. The potential for microfluidic solvent extraction (μ SX) techniques to handle particle-laden liquids has received almost no attention to date.

In this study, we investigate a microfluidic route for the recovery of copper from complex leach solutions, in which particulates that inhibit phase separation are present. The presence of silica particles was found to have a negligible influence on the extraction kinetics, while separation of the organic and aqueous phases was achieved immediately under continuous flow conditions. This finding stands in stark contrast to comparable conventional extractions in this work, for which phase separation was either hindered or arrested by the particles. The proposed microfluidic extraction technique is relevant not only to mineral processing, but also to chemical synthesis and analysis, catalysis, biological assay and separation, nanoparticle synthesis and purification.

2. Experimental

Aqueous copper solutions (5.1 g/L) were prepared using AR grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Chem-Supply) and pure water (18.2 M Ω cm, Barnstead), adjusted to pH 1.5 using H_2SO_4 . Cu^{2+} was extracted using 15% v/v LIX84-IC (2-hydroxy-5-nonylacetophenone oxime, Cognis) in Shellsol 2046 (Shell Chemicals). Two types of particles were added to the aqueous phase: (i) Hydrophilic silica particles, SNOWTEX-ZL (Nissan Chemical Industries), as a 40 wt.% dispersion in water at pH 9 ($\theta_{\text{water-air}} < 10^\circ$, primary size 80–100 nm) and (ii) moderately hydrophobic silica particles (Aerosil® R816, Degussa) with primary size of 12 nm and $\theta_{\text{water-air}} = 23^\circ$ (Degussa-Huls, 2004). Moderately hydrophobic silica was dispersed in the aqueous phase by sonicating for 30 min. Moderately hydrophobic and hydrophilic silica particles formed 200–300 nm and 140–180 nm aggregates within 30 min of dispersion, according to light scattering measurements (Malvern Nano Zetasizer).

Bulk extractions were carried out in a 200 mL round bottom flask stirred at 1100 rpm. The pH was fixed at 1.5 for all experiments (whether or not particles were added). Within 2 s, 67 mL of 5.1 g/L CuSO_4 solution was added to 43.3 mL of the stirred organic phase (15% v/v LIX84-IC in Shellsol 2046). The volumetric ratio $R = 0.65$ was fixed near to the viscosity ratio, ~ 0.62 , which gives the most stable microfluidic flow. One second before the sampling time t_c , a 5 mL aliquot of emulsion was removed using a large bore sampling tube and transferred to a glass vial. After phase separation, the aqueous phase was analysed by UV–vis spectroscopy. Samples were collected from 5 to 300 s. The rate of phase separation was determined only for $t_c = 300$ s. Sampling for phase separation experiments was carried out

as above, except aliquots were transferred to a 10 mL measuring cylinder for analysis. The height of the aqueous phase, h_t , was monitored until phase separation was complete or the initial (pre-mixing) height of the aqueous phase, h_0 , was reached. The ratio of h_t to h_0 , denoted as h in Fig. 1(a), represents the recovery of aqueous phase from the emulsion (complete phase separation is achieved at $h = 1$).

Microfluidic extractions were carried out in Pyrex™ microchips (Institute of Microchemical Technology, Japan). Two microchannels (100 $\mu\text{m} \times 40 \mu\text{m}$) merge at a Y-junction to form a single microchannel (160 $\mu\text{m} \times 40 \mu\text{m}$) that is divided into two by a guide structure which maintains the co-flow of the two liquids. This is where extraction takes place. The length of the channel varied from 80 to 480 mm. Phase separation occurred downstream, at a second Y-junction. Liquid flow was driven by a precision syringe pump (KDS210P, KD Scientific) fitted with Hamilton gas tight syringes. The flow rate of the aqueous phase ranged from 0.1 to 8 mL/h at a fixed organic/aqueous flow rate ratio of 0.65. Flow stability in the microchip was monitored using optical microscopy (Olympus, BH2-UMA). For experiments with particles present, the aqueous phase was spun at 22 000 rpm in a centrifuge (Hermle Labortechnik, Z36HK) for 30 min.

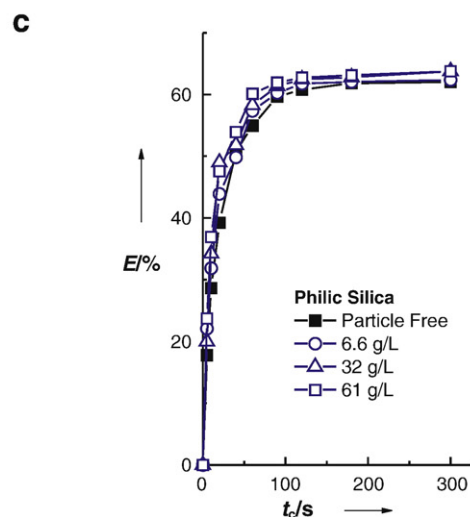
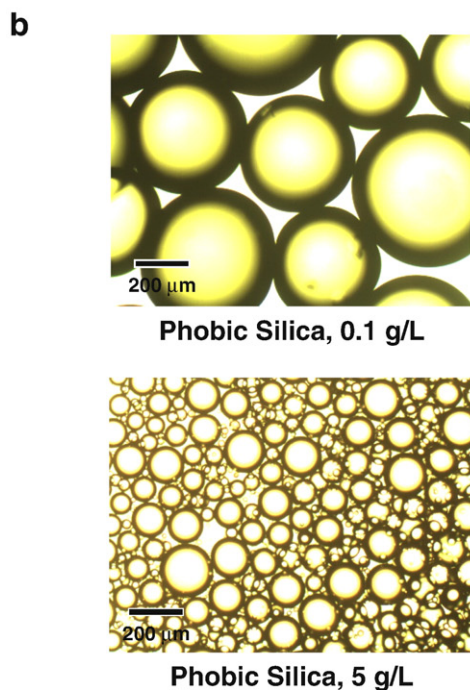
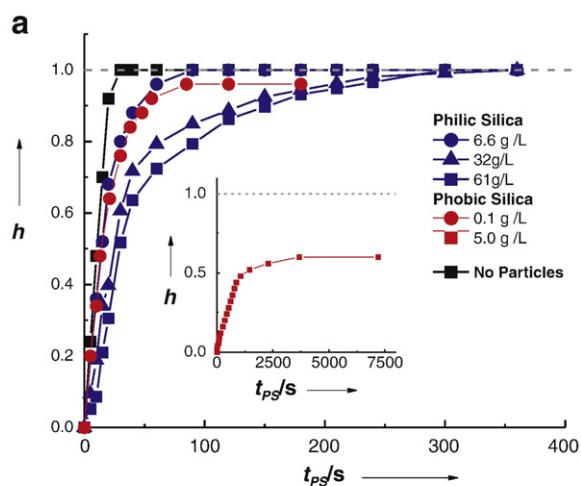
UV–vis absorption (Ocean Optics QE65000) was used to determine the concentration of Cu^{2+} , $\text{Cu}(\text{LIX})_2$, or silica particles. Silica suspensions were diluted 10-fold for UV–vis analysis. A Z-Flow Cell (2.5 or 10 mm path length, quartz windows) was directly connected to the outlet of the microchip using PEEK tubing. The tubing contained a T-junction (Upchurch Scientific) to flush the flow cell with solvent to check the baseline of the spectra. Absorbances measured at 750 nm (i.e. at the shoulder of the 796 nm peak), 656 nm, and 300 nm for the Cu^{2+} , $\text{Cu}(\text{LIX})_2$, and silica, respectively, were used according to Beer's law.

3. Results and discussion

Extraction of copper is often carried out in industry using oximes in a petroleum-based organic phase. The oxime chosen in this study, 2-hydroxy-5-nonylacetophenone oxime (referred to in this article as LIX), is able to rapidly extract 90% of the copper into the organic phase within 60 s, while spontaneous phase separation follows within approximately 30 s in the absence of particles (Cognis Group, 2007). Fig. 1(a) shows the progress of phase separation for conventional bulk extractions with and without silica particles present; hydrophilic particles ($\theta_{\text{water-air}} < 10^\circ$, 80 nm) and moderately hydrophobic particles ($\theta_{\text{water-air}} = 23^\circ$, 12 nm) in the aqueous phase at pH 1.5. The normalised height of the aqueous phase, h , is plotted against time after mixing cessation, t_{ps} . Phase separation is greatly inhibited by the presence of silica particles in the aqueous phase, irrespective of their wettability. However, the magnitude of the effect differs significantly for the two different particle types. Hydrophilic particles delayed phase separation from 30 s (particle-free solution) to ~ 300 s (61 g/L hydrophilic particles)—a ten-fold increase. In contrast, moderately hydrophobic particles (5 g/L) totally arrested phase separation at 60% recovery of the aqueous phase and the particle-stabilised (PS) emulsion was stable for >6 months. The time taken to arrive at the final state (incomplete separation) was two orders of magnitude longer when the highest concentration of hydrophobic particles (5 g/L) was used. Optical microscopy revealed a PS emulsion of decreasing droplet size with increasing silica particle concentration, as expected from classical studies (Aveyard et al., 2003), cf. Fig. 1(b).

The bulk extraction kinetics was determined using a standard procedure, described in Section 2. In brief, the organic and aqueous phases were dispersed and aliquots of emulsion were removed at various extraction times. The emulsion was allowed to phase separate before UV–vis analysis of the emulsion free aqueous phase. Fig. 1(c) shows the extraction efficiency as a function of contact time (excluding the time required for phase separation). The results are generally consistent, with only a minor increase in extraction efficiency with increasing particle concentration. This slight increase

is due to the increase in phase separation time in the presence of the hydrophilic particles. Thus, the presence of the hydrophilic particles did not slow down the transfer kinetics. When the hydrophobic



particles were considered, the long phase separation times (and incomplete separation) dominate the extraction efficiency results. Therefore, the transfer efficiency for aqueous solutions containing moderately hydrophobic particles could not be followed due to the inability to rapidly and completely separate the liquids after dispersion. The extraction efficiency for hydrophobic particles is reconsidered later in the context of microfluidic SX.

In this study, the bulk SX formed oil-in-water (O/W) emulsions irrespective of the type of particles present. This is consistent with the PS emulsion theory, which predicts that adsorbed particles will prefer to be wet by the continuous phase (Aveyard et al., 2003; Binks and Clint, 2002) (all particles were relatively hydrophilic, $\theta_{\text{water-air}} < 30^\circ$). For the SX of solute from aqueous to organic phase, O/W emulsions are particularly unfavoured due to the entrapment of both the extracted species and the organic phase (which is usually recycled) in the droplets. Furthermore, the effect of silica particles presents significant challenges in industrial phase separations, e.g. mineral processing. Therefore, these particle dispersions were used as a bench-mark for this investigation of μ SX from complex fluids.

The microchip used in this study is shown in Fig. 2. The microchip was fabricated in Pyrex™ glass using a combination of photolithography, wet-etching and thermal bonding. The aqueous and organic phases converge at a Y-junction and flow parallel for a given contact time, t_c , which is determined by the length of the main channel, L , and the flow rate of the liquids. The optimal flow rate ratio (organic/aqueous), $R = 0.65$, was fixed by the viscosity ratio (the cross-sections of the aqueous and organic streams were similar), and flow was laminar in all cases (Reynolds number < 50). The cross-section of the extraction channel includes a guide structure which helps to pin the three-phase contact line and, therefore, maintains the position of the liquid-liquid interface, cf. Fig. 2(b). The extraction channel terminates at a second Y-junction at which the two phases are separated and flow out of the device for online UV-vis analysis. Solvent extraction requires high surface-to-volume ratios (S/V) to enhance the rate of transfer. In bulk SXs, this is achieved by dispersing the liquids as small (sub-millimetre) droplets. In μ SX, the liquids are contacted in the form of microscopic streams. For our experiments, we have estimated S/V for bulk SX (based on 200 μm droplet radius) and μ SX. The ratios were similar ($S/V \sim 15000 \text{ m}^{-1}$), which permit a direct comparison of the transfer kinetics.

Fig. 3(a) shows the transfer kinetics for the bulk and microfluidic methods. Very little difference was detected between the two methods, as one might expect for the similar S/V and R ratios. The observed behaviour is consistent with that determined elsewhere (via bulk extraction) for the $\text{Cu}(\text{LIX})_2$ system (Cognis Group, 2007). It is well-known that the addition of particles to solvent extraction systems can prevent efficient phase separation, as demonstrated earlier. The inhibition of phase separation also prevents an appropriate study of the extraction kinetics due to the ambiguity of the actual contact time (and contact area) because of the slow or incomplete phase separation process. Fig. 1(c) shows extraction kinetics data for aqueous phases laden with hydrophilic particles. Now we turn our attention to the particle-laden systems in the microchannel extraction. The presence of both hydrophilic and moderately hydrophobic particles in the aqueous phase had a negligible influence on the rate of transfer, which was consistent with our bulk experiments with hydrophilic particles, cf. Fig. 1(c). This was expected for hydrophilic particles, as they are not readily adsorbed at the liquid-liquid

Fig. 1. Bulk solvent extraction: phase separation and extraction efficiency, E , for solutions containing silica particles. The particles are hydrophilic, "phobic", ($\theta_{\text{water-air}} < 10^\circ$, 80 nm) or moderately hydrophobic, "phobic", ($\theta_{\text{water-air}} \sim 23^\circ$, 12 nm). (a) Phase separation with time after cessation of mixing, t_{PS} , with and without particles present (results for 5 g/L moderately hydrophobic particles plotted in the inset). (b) Images of particle-stabilized emulsions formed in the presence of moderately hydrophobic particles. (c) Extraction efficiency of Cu^{2+} , E , from aqueous phases containing hydrophilic particles with mixing (contact) time t_c .

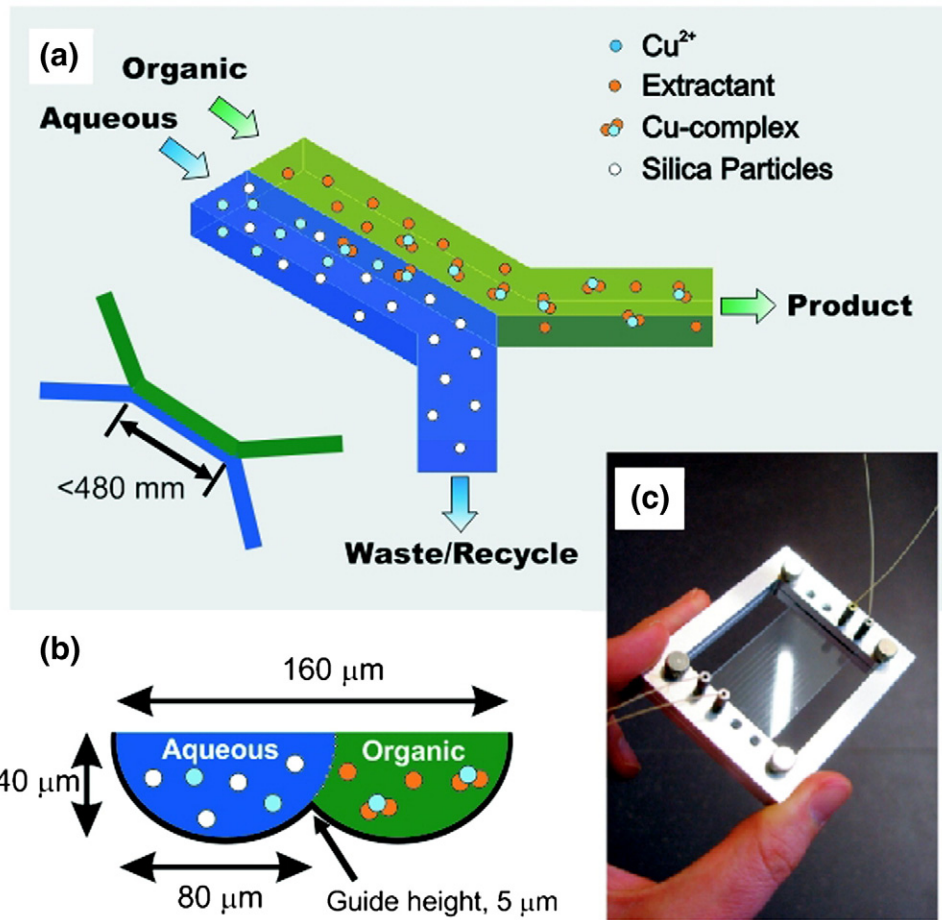


Fig. 2. (a) Schematic of the solvent extraction microchip. Two liquids meet, flow in parallel through the extraction channel, and separate at a Y-junction. (b) Cross-section of the extraction channel, showing the channel dimensions and the liquid–liquid interface. Flow is partly stabilized by a guide structure. (c) Image of microchip mounted in an aluminium chip holder with fluid connections.

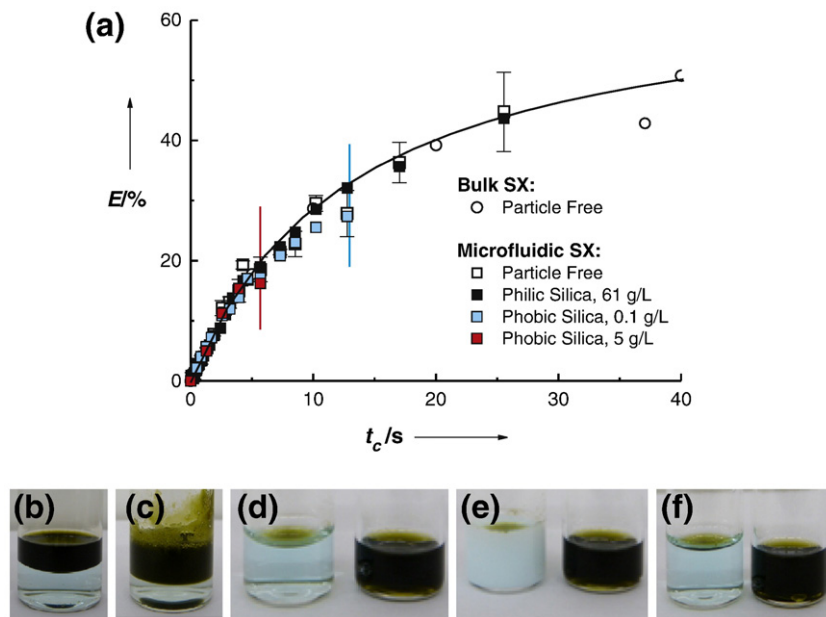


Fig. 3. Microfluidic extraction performance. (a) Bulk SX and μSX efficiency, E , against contact time t_c in the absence of particles (bulk SX and μSX) and with particles (μSX only). The maximum t_c accessible with moderately hydrophobic particles present is marked by the vertical lines: red, 5 g/L, and blue, 0.1 g/L. This is due to droplet formation during flow initialization only. The solid line is a guide only. (b–f) Bulk and microfluidic phase separation: Bulk SXs with (b) no particles and (c) 5 g/L moderately hydrophobic particles. Microfluidic SX with (d) no particles, (e) 61 g/L hydrophilic particles, and (f) 5 g/L moderately hydrophobic particles present, showing no PS emulsion.

interface (they are preferentially wet by water). In contrast, moderately hydrophobic particles will adsorb at the liquid–liquid interface and reduce the interfacial area available for extraction. Despite this, the rate of extraction in the presence of moderately hydrophobic particles was comparable to that for the particle-free experiments, suggesting that transfer through the interface was uninhibited by the particles present at the interface. Thus, one must question as to what extent the particles adsorb at the liquid–liquid interface during microfluidic extraction.

Now we consider the behaviour of particles in the microfluidic environment. As they flow through the microchip, particles may be transported from the bulk aqueous phase to the liquid–liquid interface, solid–liquid interface (microchannel walls), or the bulk organic phase. Therefore, with the addition of particles, one could intuitively expect major problems with fouling of the channels or disruption of the flow stability. For low flow rates and in the presence of hydrophobic particles, initialization was interrupted by flow fluctuations as the streams stabilized, causing particle-stabilized droplets to persist in the microchannel during the experiment. Thus, only data for the stable regimes are plotted in Fig. 3(a); $t_c \leq 6$ s for 0.1 g/L and $t_c \leq 13$ s for 5 g/L. However, after initializing the concurrent flow, no particle-induced disturbances were observed, regardless of the hydrophobicity or concentration of the particles. Fig. 4(a–b) provides a quantitative analysis of the aqueous phase pre- and post-SX in the microchip, showing no significant loss of particles during

extraction. In addition, the silica particles (61 g/L) can be observed flowing exclusively in the aqueous stream in Fig. 4(c), courtesy of scattered light. Thus, the behaviour of the particles in the microchip differs greatly from that in the bulk, where the silica particles were taken up into the crud phase (emulsion), where they prolonged or arrested phase separation. The main difference between the two methods is the flow behaviour, which is likely to play a significant role in determining the particle behaviour. In bulk SX, the turbulent mixing of the two phases promotes transport of particles to the liquid–liquid interface. In contrast, microfluidic flow is laminar and the contact time available for diffusion of the nanoparticles to the interface is relatively short. Thus, it appears that the majority of particles travel through the chip without sufficient time to adsorb at the liquid–liquid interface; however, factors other than diffusion, e.g. the induction time required for particle attachment at an interface (Dai et al., 1999), may also play a role.

Flow stability was tested for endurance under the most challenging conditions studied; 61 g/L hydrophilic and 5 g/L moderately hydrophobic silica, Fig. 4(d). The endurance test revealed negligible particle adsorption on the microchannel walls and no detrimental effect on phase separation after more than 7 h of continuous extraction. Similarly, phase separation was unhindered by the presence of particles. Compared with the formation of indefinitely stable PS emulsions in our bulk SXs, cf. Fig. 1(b), μ SX significantly outperforms bulk SX for particle-laden systems.

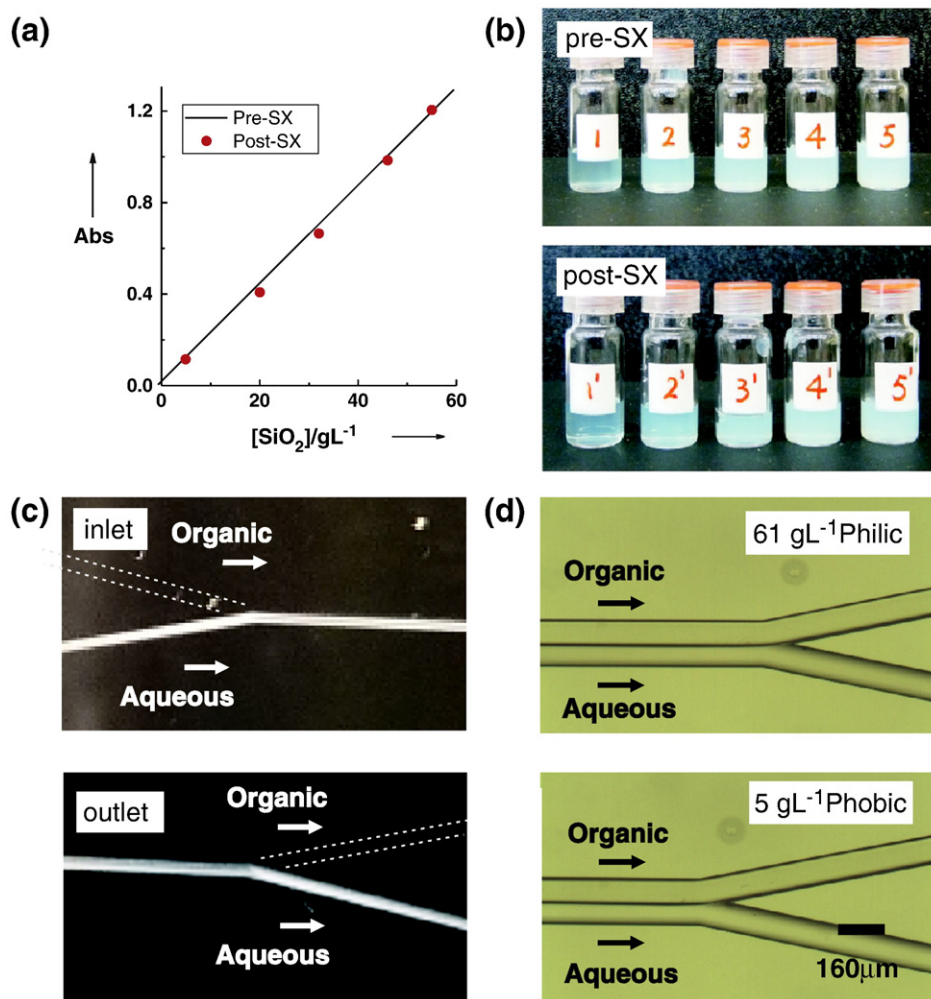


Fig. 4. (a) UV-vis absorption spectroscopy of silica suspensions before and after μ SX ($\lambda = 300$ nm). (b) Images of the aqueous phase (containing silica) pre- and post-SX; from left to right, 4.9, 20, 32, 46, and 55 g/L, diluted 10-fold for analysis. (c) Microfluidic SX for aqueous phase containing hydrophilic silica (61 g/L), showing merging and diverging of aqueous and organic streams. (d) Images of the microflow for 61 g/L hydrophilic and 5 g/L moderately hydrophobic particles after >7 h continuous operation.

4. Conclusion

Microfluidic SX shows great promise for handling particle-laden solutions of industrial relevance. Complexation and extraction of Cu^{2+} using LIX proceed without hindrance in the presence of high concentrations of hydrophilic (61 g/L) and moderately hydrophobic (5 g/L) silica particles. The latter causes conventional bulk extractions to completely fail. Particle-stabilized emulsions, which have a major effect on industrial SX, do not form in μSX due to the absence of liquid–liquid dispersion. This unique behaviour is well-suited to launch a step-change in the way complex leach solutions, particulate biomaterials, and environmental samples are handled. It can also assist synthetic chemistry *via* particulate catalysts in microfluidic platforms. The SX performance demonstrated here may be accompanied by reduced footprints for SX unit operations. As the microchannels are closed systems, there is greater potential for recycling of volatile liquids and reduced human exposure to potentially hazardous chemicals.

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