The extraction and process optimization of Cu (II) and Cd (II) using Pickering emulsion liquid membrane

P. Murugan, S. Bhuvaneshwari and D. Vidhyeswari

ABSTRACT

In the present study, the extraction of divalent heavy metals like copper [Cu (II)] and cadmium [Cd (II)] using a Pickering Emulsion Liquid Membrane (PELM) has been investigated by using three different surfactants such as Amphiphilic silica nanowires (ASNWs), Aluminum oxide nanoparticles (Alumina) and Sorbitan monooleate (SPAN 80). The influence of the process parameters such as pH, the stripping phase concentration, the agitation speed, and the carrier concentration on the extraction efficiency have been examined to find the optimum conditions at which the maximum recovery of Cu (II) and Cd (II) could take place. At optimum conditions, the extraction efficiency of 89.77% and 91.19% for Cu (II) and Cd (II) ions were achieved. Non-edible oils were used as diluent in this present study to reduce the need for toxic organic solvents in preparing PELM. The impact of each process factor on the extraction efficiency of Cu (II) and Cd (II) ions has been verified using analysis of variance (ANOVA). The higher values of F and lower values of P (less than 0.05) indicate pH is the most significant parameter on the percentage extraction of Cu (II) and Cd (II) using the Taguchi design approach.

Key words | Cd (II), Cu (II), extraction, PELM, stripping phase, Taguchi design approach

P. Murugan
Department of Petrochemical Engineering,
SVS College of Engineering,
Coimbatore, Tamilnadu 642109,
India

S. Bhuvaneshwari (corresponding author)
D. Vidhyeswari
Department of Chemical Engineering,
National Institute of Technology Calicut,
Kozhikode, Kerala 673 601,
India
E-mail: *sbuvana@nitc.ac.in*

HIGHLIGHTS

- Removal of Cu (II) and Cd (II) using PELM.
- Extraction performance has been compared for the three different surfactants such as ASNWs, Alumina and SPAN 80.
- Non-edible oil such as Pungai oil was used as diluent.
- Effect of various parameters on Cu (II) and Cd (II) removal were studied and optimized using the Taguchi approach.
- Probable interactions between each parameter and efficiency have been studied.

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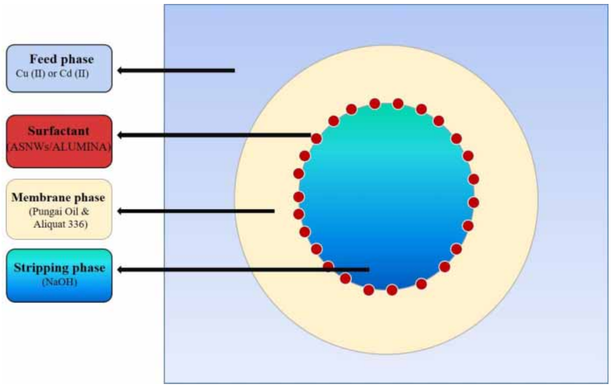
GRAPHICAL ABSTRACT



INTRODUCTION

Divalent copper, Cu (II) ions are toxic above the concentration of 2 mg/L as per the general standards for the discharge of the environmental pollutants. Cu (II) ions are being discharged in larger quantities to water bodies from many industries such as plating, metallurgy, fertilizer, paper and pulp, mining, steel works, circuit printing, wood preservatives, petroleum refining, and so on. Cu (II) ions accumulate and biomagnify in the human body and cause certain serious health issues like kidney damage, stomach disorders, intestinal problems, anaemia, coma and can even lead to death. Therefore, it is necessary to develop economically innovative techniques for an effective removal of Cu (II) ions from wastewater (Tofighy & Mohammadi 2015).

Naturally, cadmium is found in the Earth's crust. Divalent cadmium, Cd (II) ions are toxic even at an extremely low concentration. World Health Organization (WHO) has set the standard as 0.05 ppm for Cd (II) release to water bodies. Cd (II) ions are found in industrial wastewater due to manufacturing processes, such as nickel-cadmium batteries, cadmium alloys, cadmium plating, ferrous metallurgy, and so on. (Awual *et al.* 2013). Excessive Cd (II) exposure could result in health risks like kidney damage, lethargy, headache, vomiting, nausea, ataxia, renal disorder and increased thirst (Mortaheb *et al.* 2013). Hence, it is the responsibility of the research community who work in the heavy metal toxicity to find a feasible and an effective method for the removal of Cu (II) and Cd (II) from the industrial effluents before discharging them to surface water (Ahmad *et al.* 2017).

The Emulsion liquid membrane (ELM) is an effective technique for the recovery of the various toxic organic and inorganic compounds from wastewater when compared to the conventional methods like liquid – liquid extraction, solid – liquid extraction, and so on. The ELM system consists of three phases: (i) wastewater as in the feed phase, (ii) a diluent along with an extractant and a surfactant as in the membrane phase and (iii) NaOH, as in the stripping phase. The ELM is a double emulsion type membrane with either water in oil in water (w/o/w) emulsion, or oil in water in oil (o/w/o) emulsion. The surfactants are repeatedly adsorbed and desorbed at the interface of the ELM, which leads to phase separation (Zeng *et al.* 2016). The pioneering work of Ramsden, which resulted in Pickering emulsion, has opened a new window to emulsion science, and it is now renowned that the solid colloid particles would be the best alternative for conventional emulsion stabilizers. The emulsions formulated using micro and nano-sized solid particles as stabilizers are called Pickering emulsions (Hedjazi & Razavi 2018). Pickering Emulsion Liquid Membrane (PELM) stabilized by the solid particles has received great attention in areas like wastewater treatment, food science, drug delivery, biphasic catalysis, and in the preparation of porous materials (Xie *et al.* 2018).

Until now, to the best of our knowledge, the removal of Cu (II) and Cd (II) from aqueous solution by the PELM technique has not been reported by the research community. So, a comprehensive and detailed study on PELM preparation and its application for extraction of Cu (II) and Cd (II) from aqueous solution has been carried out and, additionally, an experimental design for multivariable optimization by Taguchi design had also been investigated. Genichi Taguchi developed the Taguchi experimental design method to evaluate the effect of the process parameters and to determine the optimal process conditions in order to achieve the maximum efficiency with minimal experimental runs (Hsu *et al.* 2015). Taguchi suggested that the orthogonal arrays for controlling the parameters should be applied in order to determine the level of factors for the experimental design (Nagpal *et al.* 2016). This method reduces the experimental cost and enhances the reliability of the results. S/N ratios have been used to analyse the contribution of each and every experimental factor. S/N ratios have been calculated for the batch process optimization by using three methods, namely – nominal-the-better, smaller-the-better and larger-the-better (Shahavi *et al.* 2015). The contribution level of each of these process parameters and its significance have been analysed using analysis of variance (ANOVA) (Reyhani & Meighani 2015).

In the present study, the extraction of Cu (II) and Cd (II) from the aqueous solution using a Pickering emulsion liquid membrane and the optimization of the process parameters using the Taguchi experimental design method have been investigated. The influence of the various parameters like pH, the stripping phase concentration, the agitation speed, the initial feed concentration, the treat ratio, the surfactant concentration, the carrier concentration and the M/S (Membrane to Stripping) ratio on the percentage extraction of Cu (II) and Cd (II) have been studied in detail and the optimum values for each and every factor has been identified. The experiments have been performed at optimised conditions to find out the deviation between the experimental and predicted values.

MATERIALS AND METHODS

Materials used

Polyvinylpyrrolidone (PVP, analytical grade) and aluminium oxide nanoparticles (alumina) were purchased from Himedia whereas 1-pentanol (99%), tetraethylorthosilicate (TEOS, 98%), methyltrioctylammonium chloride (Aliquat 336) and hexadecyltrimethoxysilane (HDTMOS, 85%) were purchased from Sigma-Aldrich. Ethanol had been procured from MP Biomedicals. Sodium citrate and ammonium hydroxide were procured from Merck. Sorbitan monooleate (SPAN 80) was purchased from SRL Chemicals, India. Pungai oil (*Pongamia Pinnata*) was bought from the local market. The deionized water was used without any further purification.

Preparation of amphiphilic silica nanowires (ASNWs)

The ASNWs were prepared by wet chemical process. 15 g of PVP was dissolved in 150 ml 1-pentanol and sonicated for 35 min. To this solution, 5 ml of deionized water, 1 ml of 0.18M of the sodium citrate aqueous solution, 1.15 ml of ammonium hydroxide solution and 30 ml of ethanol were added, and immediate gentle shaking was provided to the mixture for 30 sec to keep all the components well mixed. 2 ml of TEOS was added to introduce the hydrophilic character to the prepared surfactants. The mixture was undisturbed overnight at ambient temperature for the hydrolysis of TEOS. For the synthesis of ASNWs, 0.4 ml of HDTMOS was added and 12 h of reaction time was provided for hydrolysis of HDTMOS. The obtained reaction mixture was washed five times with ethanol and centrifuged at 5,000 rpm for 15 min. Prepared ASNWs were taken in Petri dishes, dried in hot air oven at 80 °C and stored in closed containers. The average particle size of ASNWs were 172–238 nm (Perumal *et al.* 2019).

Preparation of PELM

The membrane phase was prepared by mixing an appropriate ratio of the carrier (Aliquat 336) and surfactant with the diluent, Pungai oil. The extraction studies have been conducted individually for each surfactant, namely ASNWs/alumina/SPAN 80. 3 ml of 0.3 M NaOH solution has been added as a stripping phase to the membrane phase consisting of 6.5 ml of Pungai oil, 0.5 ml of the carrier and 25 mg of surfactant. The mixture was homogenized by using a high-speed homogenizer (Ultra-Turrax T10 basic, IKA) at an agitation speed of 8,000 rpm for 1 min (Yan *et al.* 2015). Thus, the water-in-oil (w/o) emulsion was obtained with a membrane phase to stripping phase ratio of 7:3 (Perumal *et al.* 2019).

Extraction of Cu (II) and Cd (II)

The individual PELM extraction studies were carried out for 10 ppm Cu (II) and 10 ppm Cd (II) as feed solutions. The mixture (PELM and feed solution) was continuously stirred at an agitation speed of 400 rpm to provide an intimate contact between the two phases for a contact time of 2 minutes and transferred into a separating funnel. It was left undisturbed until the separation of the two product phases was obtained. The product phases were analysed for the residual concentration of Cu (II) and Cd (II) by using an atomic absorption spectrophotometer (AAS; Thermo Fisher Scientific, Model AA 303).

RESULTS AND DISCUSSION

Extraction of Cu (II) using three different surfactants

Effect of pH on percentage extraction of Cu (II)

The effect of pH on Cu (II) extraction was studied in the pH range from 1 to 6. Cupric hydroxides began to precipitate at pH above 6, which was the reason for the selection of pH range from 1 to 6. From the experimental results, it has been observed that the percentage extraction efficiency of Cu (II) decreases from 85.88% to 56.63% with an increase in pH from 2 to 6 for ASNWs. Likewise, the percentage extraction efficiency of Cu (II) decreases from 67.74% to 49.84% and from 79.68% to 51.49% for alumina and SPAN 80 as surfactants respectively, and has been represented in Figure 1(a). This is due to the larger difference in hydrogen ion concentration between the stripping phase and the feed phase, which increases the driving force. Hence, Cu (II) extraction is reduced when the pH of the feed solution increases, but it retards the accumulation of Cu (II) – Aliquat 336 complex in the membrane phase at pH 1 (Leon *et al.* 2017).

Effect of the agitation speed on the percentage extraction of Cu (II)

The higher stirring rate would induce the formation of smaller sized emulsion droplets, thereby increasing the interfacial mass transfer area in the membrane phase and leading to the intensification of the mass transfer rates. The higher agitation speed might result in swelling of the membrane and rupturing of the emulsion droplets. The significance of the agitation speed on extraction of Cu (II) ions is shown in Figure 1(b). It has been clear from the results that a rise in the agitation speed from 100 to 400 rpm increases the extraction efficiency of Cu (II) ions from 66.69% to 82.51%, 47.23% to 62.98%, and 54.72% to 75.34% for ASNWs, Alumina and SPAN 80 as surfactants respectively. Further, the increase in the stirring speed had resulted in the reduction of the extraction efficiency of Cu (II) ions (Alaguraj *et al.* 2009). It has confirmed that the higher shear rates ruptured the membrane and reduced the extraction efficiencies of Cu (II) ions.

Effect of the initial feed concentration on the percentage extraction of Cu (II)

The effect of the initial feed phase concentration has been studied by varying the concentration of Cu (II) ions' range from 10 to 50 ppm as shown in Figure 1(c). From the results, it has been observed that the extraction efficiency of Cu (II) ions decreases with an increase in the initial concentration of Cu (II) ions in the feed phase. When the initial concentration of Cu (II) ions was very high, the internal droplets in the emulsion globule at the boundary and would easily become saturated. As a result, the metal-carrier complex did not have proper chances to migrate from the membrane phase to the inner region of the stripping phase so as to release the metal ions into the stripping phase (Alaguraj *et al.* 2009). The PELM process would be more significant at the lower concentration of Cu (II) ions in the aqueous/feed solution.

Effect of the treat ratio on the percentage extraction of Cu (II)

The effect of the treat ratio on the extraction efficiencies of Cu(II) ions has been studied for a constant volume of the Pickering emulsion of 10 ml by varying the feed volume from the range of 10 to 50 ml, whereas the feed concentration was maintained constant (10 ppm Cu (II)). The appropriate ratio of the feed phase and the Pickering emulsion has been stirred at an agitation speed of 400 rpm for 2 minutes. From the experimental results, the percentage extraction efficiencies of Cu (II) ions decrease with an increase in the treat ratio and is shown in Figure 1(d). The higher degree of the extraction is possible at the lower treat ratio, due to the high emulsion volume with a large surface area. The volume of the emulsion utilized could be low which is economically favoured, but the removal efficiency of Cu (II) ions were found to be high for high emulsion volumes. Therefore, the higher extraction efficiency occurs at lower treat ratio (Alaguraj *et al.* 2009). The treat ratio of 1:1 has been found to be optimum for the maximum extraction of Cu (II).

Effect of carrier concentration on the percentage extraction of Cu (II)

Aliquat 336 used as a carrier which varied from the range of 0.014 to 0.129 vol. % in the membrane phase. The extraction efficiency of Cu (II) ions has been determined for each carrier concentration by keeping the constant feed volume

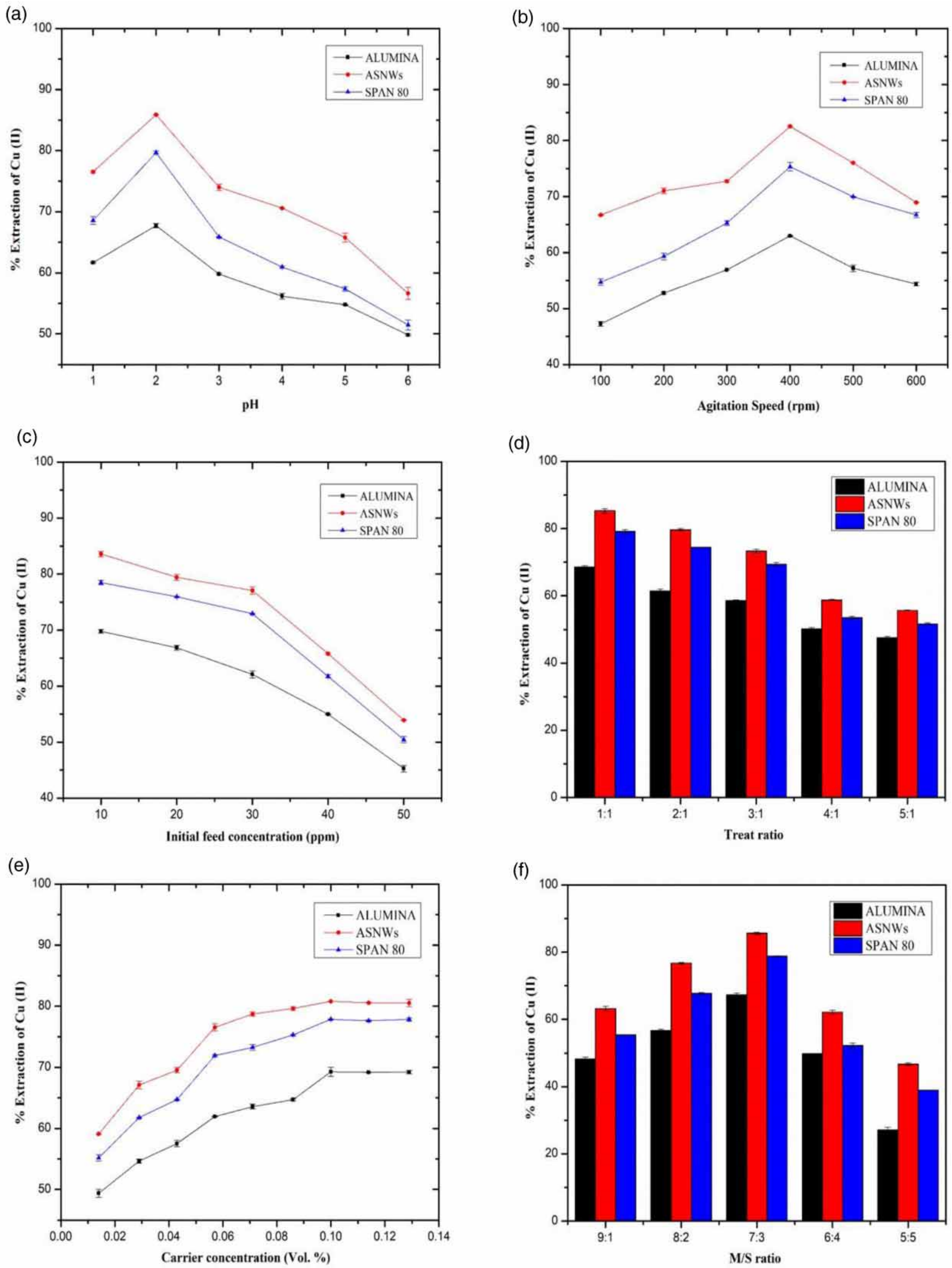


Figure 1 | Effect of various parameters on percentage extraction of Cu (II) (a) pH, (b) agitation speed, (c) initial feed concentration, (d) treat ratio, (e) carrier concentration and (f) M/S ratio.

of 10 ml. The 6.5 ml diluent and the 25 mg surfactant in the membrane phase were maintained constant throughout the experiments. The significance of the carrier concentration on the extraction efficiency of Cu (II) ions are represented in Figure 1(e). The extraction efficiency increases with an increase in the carrier concentration, since the carrier would facilitate the transportation of the solute from the feed phase to the membrane phase. It is also inferred from the literatures that the carrier concentration would significantly affect the emulsion stability as well (Lu *et al.* 2015).

Effect of the membrane to the stripping phase (M/S) ratio on the percentage extraction of Cu (II)

The membrane to the stripping phase ratio (v/v) has been studied (Figure 1(f)) at 9:1, 8:2, 7:3, 6:4, and 5:5 and their effects on the extraction of Cu (II) ions have been investigated by adding 10 ml of Cu (II) solution into it. From the results, it is inferred that the percentage extraction of Cu (II) ions increases with the increase in the volume of the membrane phase to up to 7. This is actually due to the reason that the increase in the emulsion volume not only increases the number of emulsion globules and the surface area of PELM, but also increases the number of active sites for the carriers in the membrane phase which could increase the total number of Cu (II)/Aliquat 336 complexes in the feed/membrane interface (Lu *et al.* 2015). Further, the increase in the volume of membrane phase decreases the extraction efficiency, since the heavy metal ions cannot migrate effectively in the highly viscous membrane phase.

Effect of the stripping phase concentration on the percentage extraction of Cu (II)

The effect of the stripping phase concentration on the extraction efficiency of Cu (II) ions has been studied by changing the NaOH concentration from 0.1 to 0.5 M. It is clear from the results that an increase in NaOH concentration from 0.1 to 0.3 M increases the percentage extraction efficiency of Cu (II) ions from 74.81% to 86.63%, 62.23% to 69.65% and from 71.55% to 79.52% for ASNWs, Alumina and SPAN 80 respectively. However, an increase in the concentration of NaOH in the stripping solution from 0.4 M reduces the percentage removal efficiency of Cu (II) ions as represented in Figure 2(a)–2(c). The stability of the emulsion decreases at a higher concentration of NaOH, as the alkalinity of the stripping phase may affect the properties of the surfactant and leads to the destabilization of PELM (Dass & Hamdaoui 2010). The optimum stripping concentration for the extraction of Cu (II) ions has been found to be at 0.3 M (Mohamed & Ibrahim 2012).

Effect of the surfactant concentration on the percentage extraction of Cu (II)

The surfactant concentration has played a crucial role in the emulsion stability. For ASNWs and alumina, the concentration of the surfactant has shown a variation from 5 to 30 mg per 7 ml of the membrane phase, and for SPAN 80, it varied from 0.0143 to 0.0857 vol. % per 7 ml of the membrane phase. Individual extraction studies have been performed for all the emulsions by varying the surfactant concentration. The extraction percentage of Cu(II) ions has been found to increase with an increase in the surfactant concentration (up to 20 mg for ASNWs and alumina and up to 0.0572 vol. % for SPAN 80) as shown in Figure 3(a) and 3(b). On further increase in the surfactant concentration, the percentage extraction of Cu (II) ions remains nearly constant (Alaguraj *et al.* 2009). Hence, the surfactant concentrations of 20 mg for ASNWs and alumina and 0.0572 vol. % for SPAN 80 have been chosen for further studies.

Extraction of Cd (II) using the three different surfactants

Effect of pH on the percentage extraction of Cd (II)

The effect of pH on the extraction of Cd (II) ions has been studied within the range of pH 1 to 6. From the results, it has been inferred that at higher pH values, the rate of association of Cd (II) ions with Aliquat 336 decreases. The Figure 4(a) shows that pH 1 is the most appropriate pH in the feed phase for transferring the solute. On comparing the different experiments studied in the pH range of 1 to 6, the removal efficiency at pH 1 has been found to be optimum (Mortaheb *et al.* 2013). Hence, it is reported that the percentage extraction of Cd (II) ions decreases with an increase in the pH of the feed solution (Coelhoso *et al.* 2000).

Effect of the agitation speed on the percentage extraction of Cd (II)

The effect of the agitation speed on the percentage extraction of Cd (II) ions is shown in Figure 4(b). From the results, it is conclusive that the extraction efficiency of Cd (II) ions increases with an increase in the agitation speed up to a certain point. An increase in the agitation speed results in smaller emulsion globules, which in turn enhances the surface area for mass transfer, and thereby the percentage extraction of Cd (II) ions increases (Ahmad *et al.* 2017). It is found that a speed of 400 rpm could achieve the maximum removal efficiency of Cd (II); 88.99%, 85.49%, and 73.38% for ASNWs, alumina, and SPAN 80 respectively.

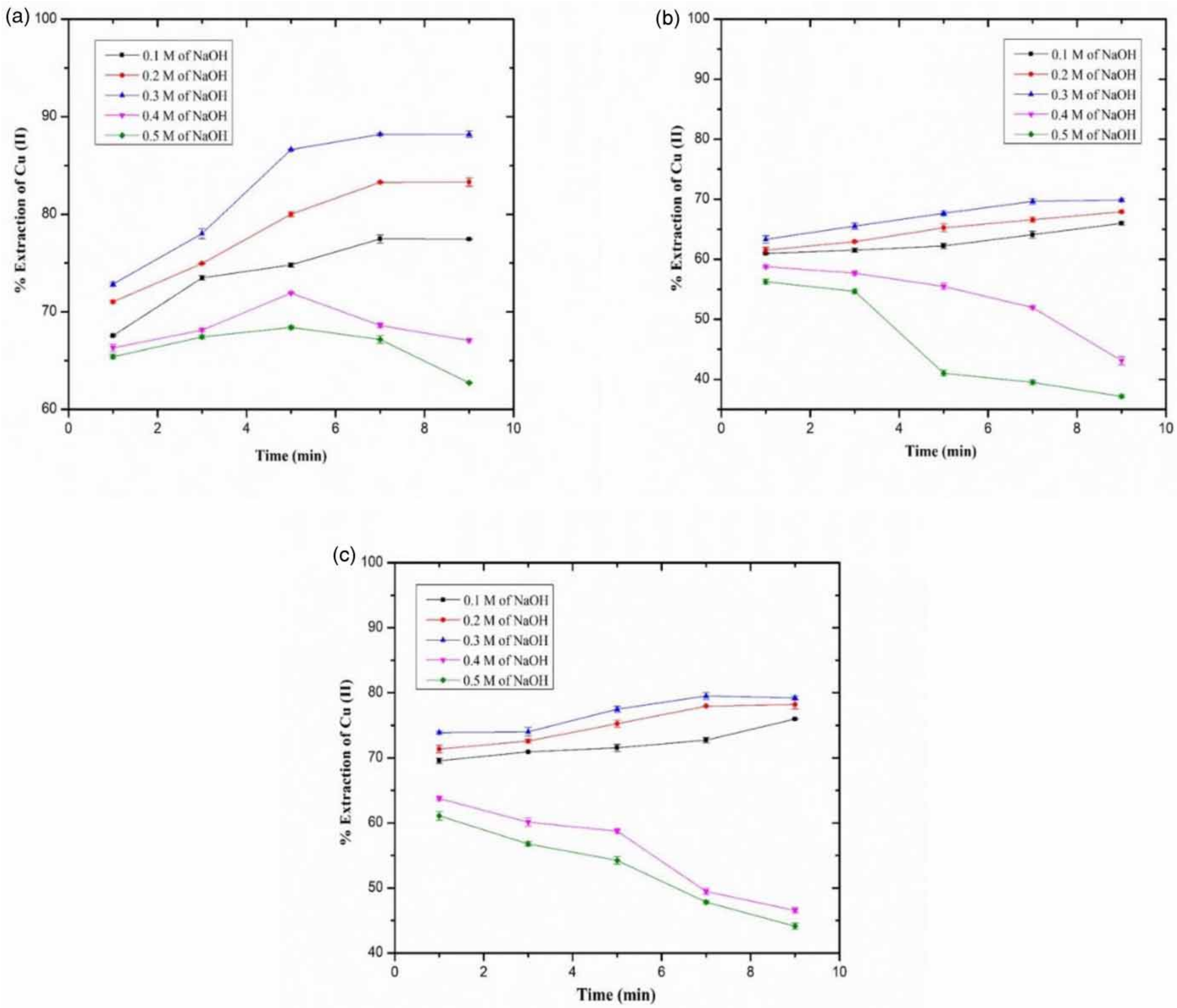


Figure 2 | Effect of stripping phase concentration on percentage extraction of Cu (II) using various surfactants (a) ASNWs, (b) alumina and (c) SPAN 80.

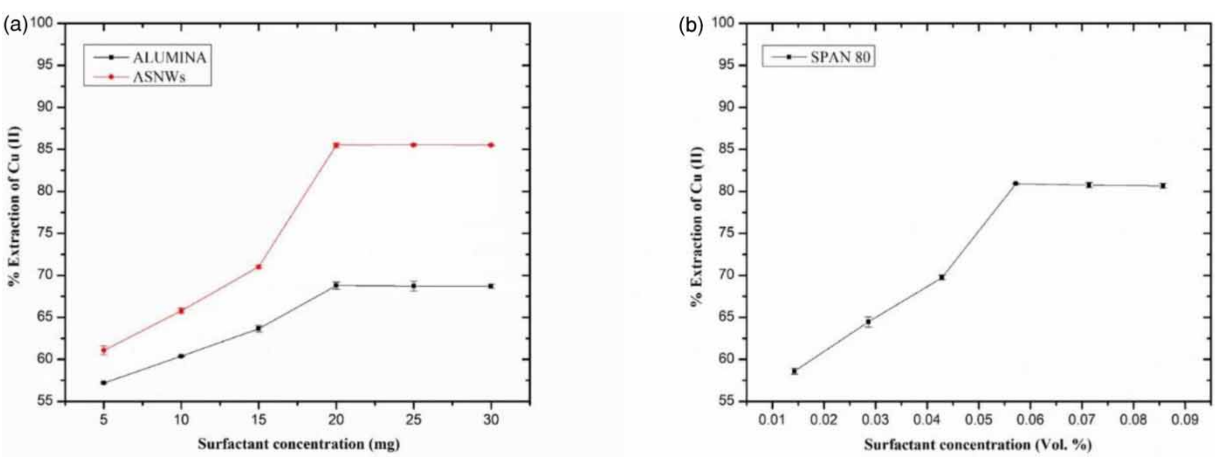


Figure 3 | Effect of surfactant concentration on percentage extraction of Cu (II) using various surfactants (a) ASNWs and alumina and (b) SPAN 80.

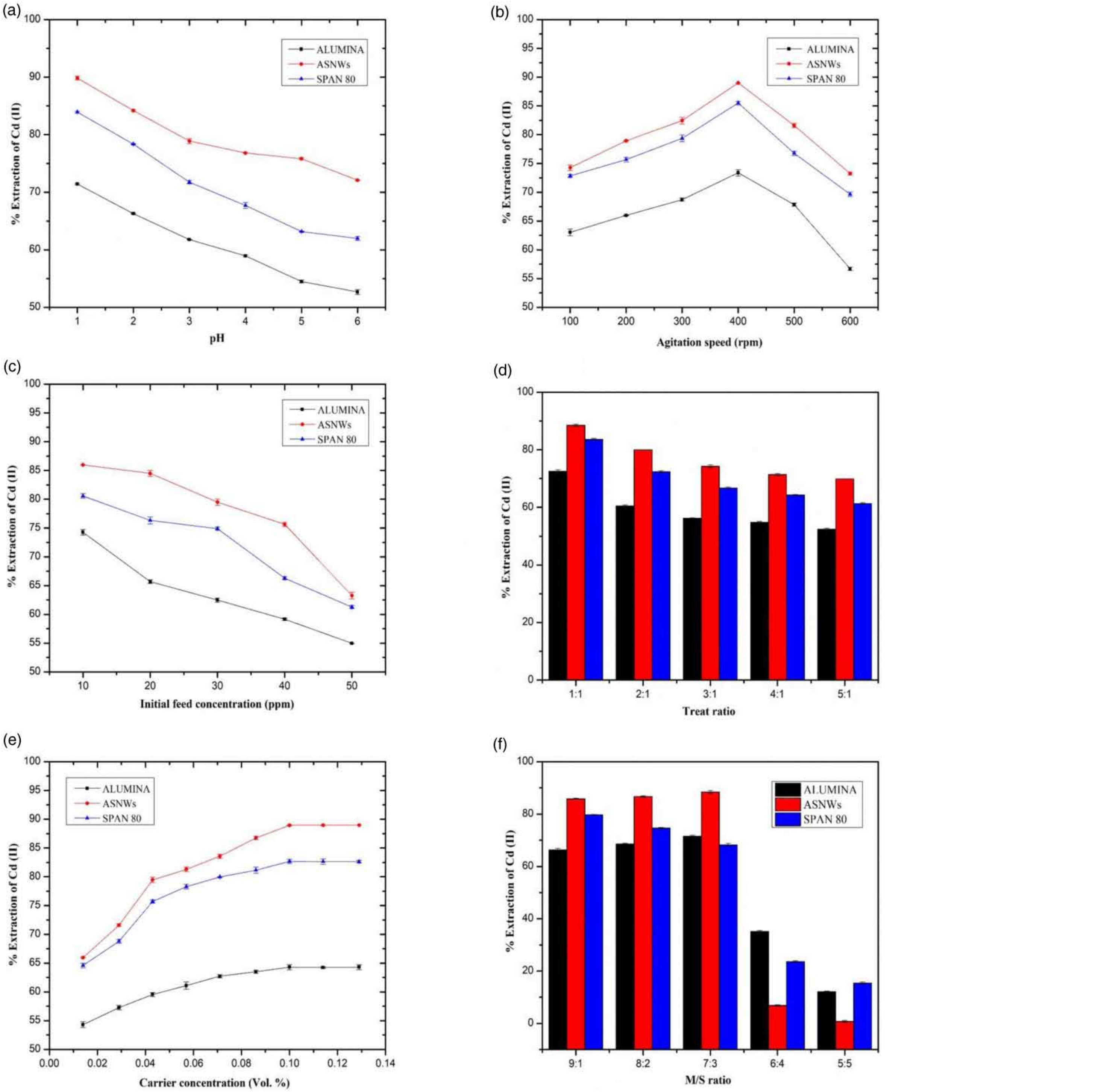


Figure 4 | Effect of various parameters on percentage extraction of Cd (II) (a) pH, (b) agitation speed, (c) initial feed concentration, (d) treat ratio, (e) carrier concentration and (f) M/S ratio.

On the other hand, increasing the agitation speed beyond 400 rpm reduces the extraction performances. The extraction efficiency has gradually decreased from higher speeds as the membrane gets ruptured due to the excessive shear induced by the impeller tip during the extraction process.

Effect of the initial feed concentration on the percentage extraction of Cd (II)

Figure 4(c) represents the effect of the initial Cd (II) concentration on the extraction efficiency of Cd (II) and it is evident from the results that the feed phase containing 10 ppm of Cd (II) concentration yields the highest percentage removal for all three surfactants examined. The extraction efficiency of Cd (II) ions was found to be 85.96%, 74.26%, and 80.57% for ASNWs, alumina, and SPAN 80 respectively for a contact time of 2 minutes. As the concentration increases beyond 10 ppm, the percentage extraction of Cd (II) ions decreases due to the saturation of the active sites. At a higher concentration of solute in the feed phase, the stripping phase needs to strip the targeted solute very quickly; otherwise, the membrane-stripping interface undergoes saturation. This phenomenon also reduces the driving force of a system that is exploited by the reactions with the stripping agent at the membrane-stripping interface, thereby resulting in a low performance (Ahmad *et al.* 2017).

Effect of the treat ratio on the percentage extraction of Cd (II)

The impact of the treat ratio on the extraction efficiency of Cd (II) ions has been studied by varying the feed volume within the range of 10 to 50 ml. A constant volume of Pickering emulsion (10 ml) was added in different volumes to the feed solution. The appropriate ratio of the feed phase and the Pickering emulsion has been stirred at an agitation speed of 400 rpm for 2 minutes. Figure 4(d) shows that the percentage extraction of Cd (II) decreases at higher treat ratios. At the treat ratio of 1:1, the volume of the emulsion is sufficient with a larger surface area for the mass transfer. As a result, higher extraction performances were possible (Ahmad *et al.* 2017). At higher treat ratios, less emulsion is used for the extraction of Cd (II). Even though it is desired from an economic point of view, however, extraction performance decreases (Medjahed *et al.* 2017). Hence, a treat ratio of 1:1 has been found to be the optimum for the extraction of Cd (II) from the synthetic Cd (II) solutions.

Effect of the carrier concentration on the percentage extraction of Cd (II)

The impact of the carrier concentration on the percentage extraction of Cd (II) ions is represented in Figure 4(e). Several experiments have been carried out for the metal transport through PELM by varying the carrier concentration within the range of 0.014 to 0.129 vol. %. If there is an increase in the carrier concentration, the extraction efficiency increases too. It is also seen that when the extent of the metal transport through PELM is enhanced, the content of extractant also increases in the membrane phase. An increase in the carrier concentration from 0.014 to 0.129 vol. % resulted in an increase of the percentage extraction of Cd (II) from 65.94% to 88.96%, 54.27% to 64.27%, and 64.58% to 82.62 for ASNWs, alumina and SPAN 80 as surfactants respectively. However, an increase in the carrier concentration beyond 0.10 vol. % showed no significant difference in the percentage extraction of Cd (II). The results of Medjahed *et al.* (2017) also had the same trend.

Effect of the membrane to stripping phase (M/S) ratio on the percentage extraction of Cd (II)

The mesoscale structure and the performance of the emulsion strongly depend on the nature of the emulsifier and its proportion in the mixture. By increasing the M/S ratio, the percentage extraction of Cd (II) increases. On the other hand, increasing the M/S ratio would also increase the mass transfer resistance. The impact of the M/S ratio on extraction efficiency of Cd (II) ions is studied in a series of experiments and reported in Figure 4(f). The result shows that for the M/S ratios of 9:1, 8:2, and 7:3, the removal efficiency increased (Ahmad *et al.* 2017). However, the extraction efficiency of Cd (II) ions decreased for the M/S ratios of 6:4 and 5:5. Hence, the M/S ratio of 7:3 has been found to be optimum for the present studies.

Effect of the stripping phase concentration on the percentage extraction of Cd (II)

The influence of the stripping phase concentration on Cd (II) extraction was studied at different NaOH concentrations ranging from 0.1 to 0.5 M. The result shows that 0.3 M NaOH was best for Cd (II) extraction, as illustrated in Figure 5(a)–5(c). It is evident from the results that an increase in the stripping concentration from 0.1 to 0.3 M has increased the Cd (II) removal from 79.35% to 88.16% for ASNWs, and 61.81% to 71.37% for Alumina and 68.39% to 79.38% for SPAN 80. On increasing the NaOH concentration in the stripping solution beyond 0.3M, the extraction efficiency of Cd (II) was reduced. Increasing the stripping phase concentration does not provide better Cd (II) extraction as the number of moles of NaOH

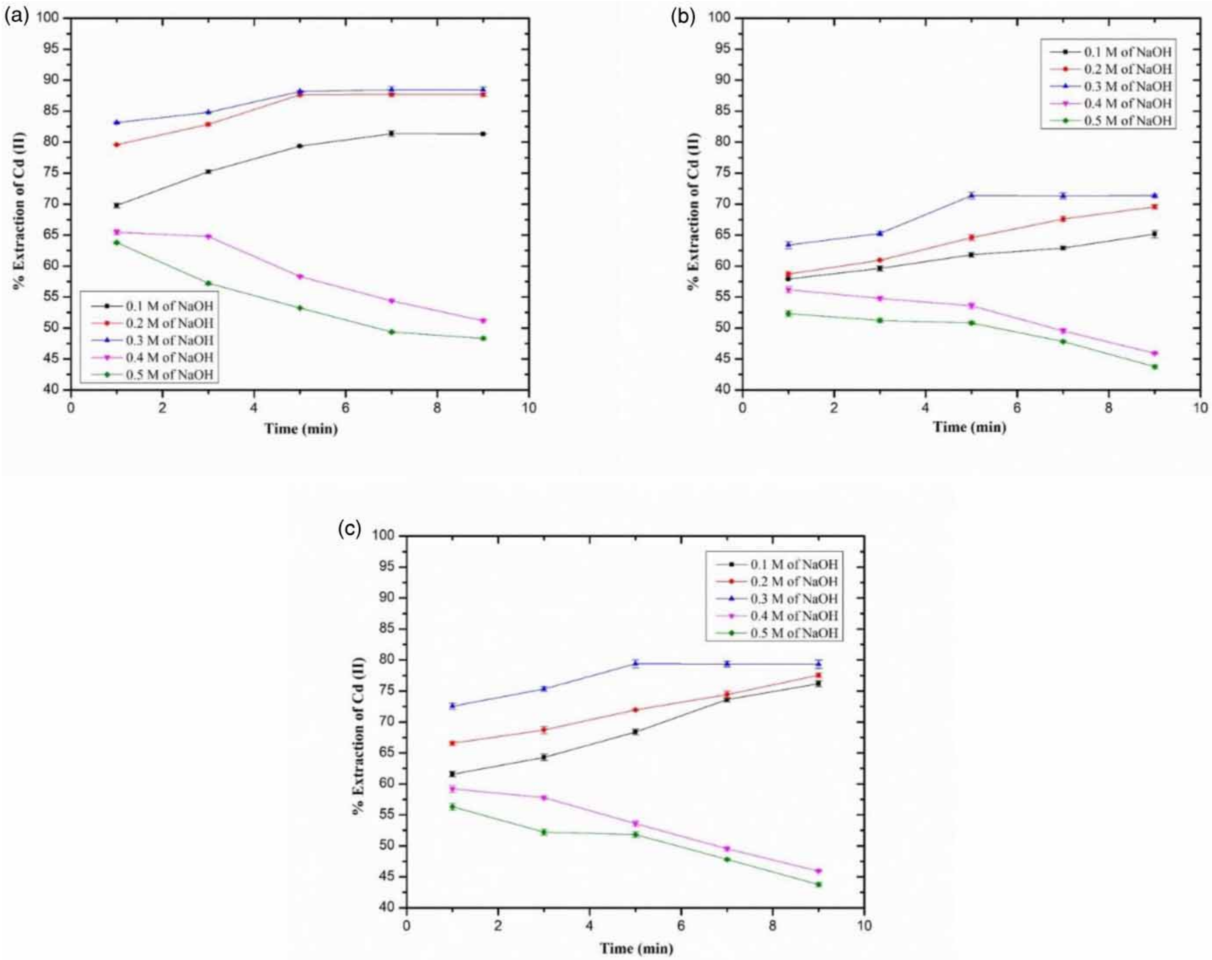


Figure 5 | Effect of stripping phase concentration on percentage extraction of Cd (II) using various surfactants (a) ASNWs, (b) alumina and (c) SPAN 80.

needed to react during the stripping process has proved to be in excess beyond 0.3 M of NaOH (Ahmad *et al.* 2017). Hence, it is not necessary to use high concentration of the stripping phase as it benefits neither the emulsion stability nor the extraction efficiency.

Effect of the surfactant concentration on the percentage extraction of Cd (II)

The surfactant concentration varied from 5 to 30 mg per 7 ml of the membrane phase, for ASNWs and alumina. However, for SPAN 80, the surfactant concentration varied from 0.0143 to 0.0857 vol.% per 7 ml of the membrane phase, and the extraction studies have been carried out for each emulsion. The percentage extraction was found to increase along with an increase in the surfactant concentration, as shown in Figure 6(a) and 6(b). It has been noted that the emulsion was stable, and the percentage extraction remained almost constant beyond 20 mg for ASNWs and alumina. Similar effects were observed for SPAN 80 beyond 0.06 vol. % (Mortaheb *et al.* 2013). From the experiments carried out, it is understood that the high interfacial area, high stability and good regeneration possibility of Pickering Emulsion Liquid Membrane (PELM) made from non-edible oil are advantages of the present system. At optimum conditions, the extraction efficiency of Cu (II) and Cd (II) was 89.77% and 91.19% respectively. Improvement of existing formulations and identification of new fields of application are the latest challenges.

Optimization and extraction of the heavy metals using Taguchi method

The Taguchi method has been employed for the extraction of Cu (II) and Cd (II) ions from the wastewater by ASNWs stabilized PELM. The optimization of controllable

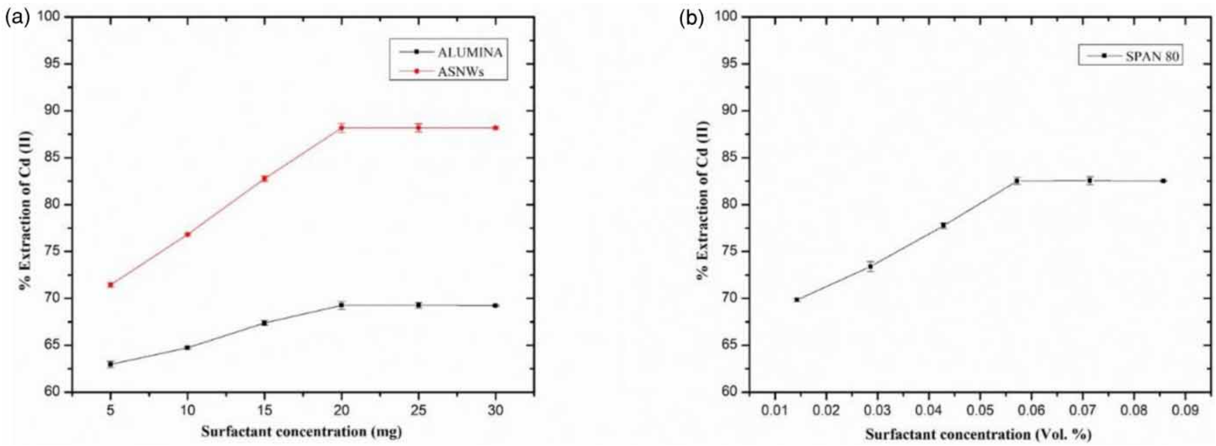


Figure 6 | Effect of surfactant concentration on percentage extraction of Cd (II) using various surfactants (a) ASNWs and alumina and (b) SPAN 80.

factors, including the initial pH of the solution, the agitation speed, the carrier concentration and the stripping phase concentration, have been investigated at three levels (Hsu *et al.* 2015), as shown in Table 1.

From Taguchi's results, the number of experiments has been reduced to nine while assigning all the three levels to each of all the four factors (Deepanraj *et al.* 2017). The L9 orthogonal array of Taguchi's design is represented in Tables 2 and 3.

Nine experiments have been performed as per the design by neglecting the interactions between the main factors. The S/N ratios have been figured out for all the nine trials, and their values are given in Tables 4 and 5.

The main effects' plot for S/N ratios on the percentage extraction of Cu (II) and Cd (II) ions are shown in Figure 7.

Table 1 | Design of experiments: factors and their level

	Levels		
Factors	**1**	**2**	**3**
pH	1	2	3
Sc (Stripping concentration (NaOH), M)	0.2	0.3	0.4
N (Agitation speed (300–500), rpm)	300	400	500
Cc (Carrier concentration (Aliquat 336), vol. %)	0.071	0.114	0.129

Table 2 | L_9 orthogonal array and response values on Cu (II) extraction

Run	pH	Sc (mol/l)	N (rpm)	Cc (vol. %)	% Extraction	S/N Ratio
1	1	0.2	300	0.071	77.26	37.76
2	1	0.3	400	0.114	79.51	38.01
3	1	0.4	500	0.129	77.82	37.82
4	2	0.2	400	0.129	89.77	38.42
5	2	0.3	500	0.071	77.50	37.79
6	2	0.4	300	0.114	79.88	38.05
7	3	0.2	500	0.114	76.77	37.70
8	3	0.3	300	0.129	75.40	37.55
9	3	0.4	400	0.071	74.76	37.47

Table 3 | L_9 orthogonal array and response values on Cd (II) extraction

Run	pH	Sc (mol/l)	N (rpm)	Cc (vol. %)	% Extraction	S/N Ratio
1	1	0.2	300	0.071	82.45	38.32
2	1	0.3	400	0.114	91.19	38.99
3	1	0.4	500	0.129	78.92	37.94
4	2	0.2	400	0.129	78.12	37.86
5	2	0.3	500	0.071	81.59	38.23
6	2	0.4	300	0.114	76.55	37.68
7	3	0.2	500	0.114	79.08	37.96
8	3	0.3	300	0.129	73.24	37.30
9	3	0.4	400	0.071	74.27	37.42

Table 4 | Response table for S/N ratios of Cu (II) extraction

	Levels			
Factors	**1**	**2**	**3**	**Optimum values**
pH	37.86	38.08	37.79	2
Sc (stripping concentration (NaOH), M)	37.96	37.78	37.78	0.2
N (agitation speed (300–500), rpm)	37.79	37.97	37.77	400
Cc (Carrier concentration (Aliquat 336), vol. %)	37.67	37.92	37.93	0.129

Table 5 | Response table for S/N ratios of Cd (II) extraction

Factors	Levels 1	2	3	Optimum values
pH	38.42	37.92	37.56	1
Sc (stripping concentration (NaOH), M)	38.05	38.17	37.69	0.3
N (agitation speed (300–500), rpm)	37.77	38.09	38.05	400
Cc (carrier concentration (Aliquat 336), vol. %)	37.99	38.21	37.70	0.114

Analysis of variance (ANOVA) for the extraction of Cu (II) and Cd (II) using PELM

Analysis of variance (ANOVA)

The ANOVA procedure was used to determine the percentage contribution of each of the factors studied.

Degree of freedom (DOF)

The DOF denotes the number of independent variables. The degree of freedom for each factor is the number of its levels minus one. The total degree of freedom is the total number of trial number of repetition minus one.

Contribution factor

The percentage of contribution factor was calculated using Equation (1).

$$\text{Contribution factor } (\%) = \frac{SS}{MS} \times 100 \quad (1)$$

where, SS is the sum of squares of factor and MS is the mean (total sum) of squares of all factors. In addition, the Fischer test (F – value) was used to determine the significant effect of factors on the performance characteristics (Patel & Murthy 2010).

F – test

This is the ratio of the sum of squares of each trial sum result involving the factor, divided by the error or pooled error (P_e). The F value was calculated using Equation (2)

$$\text{F value} = \frac{SS}{P_e} \quad (2)$$

The actual impact of each process factor on the extraction efficiency of Cu (II) and Cd (II) ions has been verified using ANOVA and represented in Tables 6 and 7. In this study, the degree of freedom is consumed by all factors and has no left over information for error calculation. Therefore, the error variance was found to be zero. The impact of each factor could be estimated by comparing the factor variances (Reyhani & Meighani 2015). From Table 6, the variance for stripping concentration (Sc) has been observed to be the lowest and recognized as an insignificant one because of the lowest contribution during the Cu (II) extraction. Therefore, the variance and the degree of freedom of carrier concentration have pooled error to estimate the error variance. The F – test has been performed for the extraction of heavy metals, and the higher values of F indicate the greater effect on the percentage extraction of these metals. Table 6 provides the F values for the four factors (pH, N, Sc, and

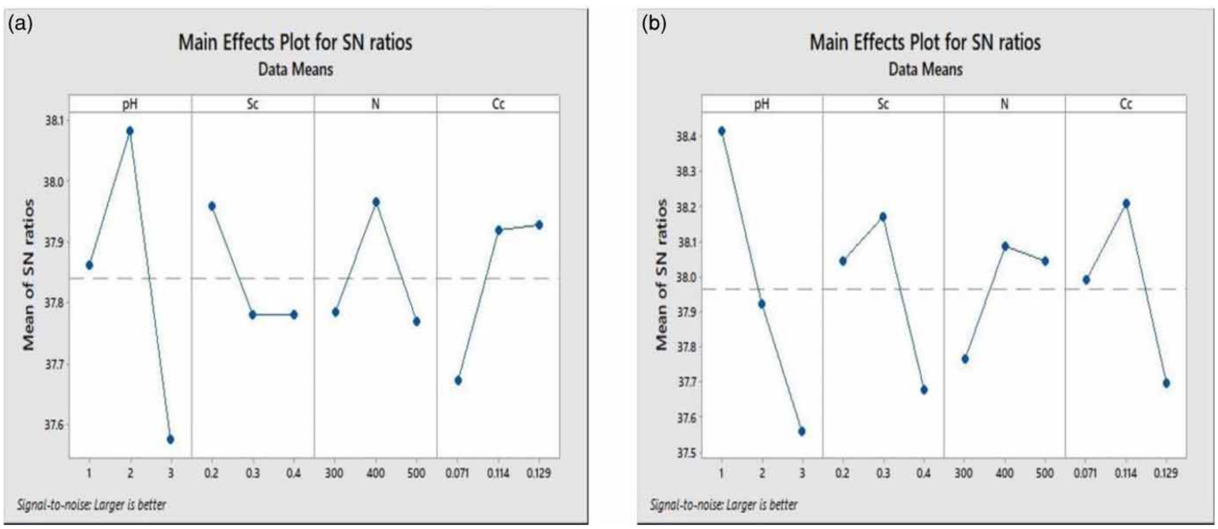


Figure 7 | Main effects plot for S/N ratios of extraction. (a) Cu (II) and (b) Cd (II).

Table 6 | ANOVA with pooled error of Cu (II) extraction

Factors	DOF	SS	MS	F-value	*p*-value	% Contribution of factor
pH	2	0.31736	0.15868	5.91	0.068	59.09
Sc (stripping concentration (NaOH), M)	2	0.05369	0.02684	1	0.194	9.99
N (agitation speed (300–500), rpm)	2	0.06217	0.03109	1.16	0.225	11.58
Cc (carrier concentration (Aliquat 336), vol. %)	2	0.10390	0.05195	1.94	0.291	19.34
Error	0	0	0	–	–	–
Total	8	0.53712	0.26856	–	–	100
Pooled error	2	0.05369	0.02684	–	–	–

Table 7 | ANOVA with pooled error of Cd (II) extraction

Factors	DOF	SS	MS	F-value	*p*-value	% Contribution of factor
pH	2	0.95260	0.47630	6.09	0.083	52.86
Sc (stripping concentration (NaOH), M)	2	0.34870	0.17436	2.23	0.284	19.35
N (agitation speed (300–500), rpm)	2	0.15640	0.07820	1	0.204	8.68
Cc (carrier concentration (Aliquat 336), vol. %)	2	0.34440	0.17218	2.20	0.229	19.11
Error	0	0	0	–	–	–
Total	8	1.8021	0.9011	–	–	100
Pooled error	2	0.15640	0.07820	–	–	–

Cc) and the percentage contribution of each factor were as follows: pH (59.09%) > Cc (19.34%) > N (11.58%) > Sc (9.9%) for the extraction of Cu (II) ions.

It is observed that pH is the most significant contributing factor for the extraction performances of Cu (II) ions when compared to the other factors. The optimum extraction efficiency of 89.77% for Cu (II) has been obtained at pH 2, the carrier concentration – 0.129 vol% and agitation speed – 400 rpm. Similarly, the DOF, F-value, and the percentage contribution of the four factors towards Cu (II) and Cd (II) extraction have been calculated and shown in Table 7. In the case of Cd (II) extraction, the percentage contribution of each factor was in the order: pH (52.86%) > Sc (19.35%) > Cc (19.11%) > N (8.68%). It is observed that pH has the most significant contribution for the extraction of Cd (II) ions when compared to the other factors. The optimum extraction efficiency of 81.59% for Cd (II) ions has been obtained at pH 2, stripping concentration – 0.3 M and carrier concentration – 0.073 vol%.

Interactions in the Cu (II) and Cd (II) for the extraction process

The probable interactions among the four parameters have been studied using the interaction plots and are depicted in Figure 8(a) and 8(b).

Figure 8(a) shows the interaction matrix plot for the extraction efficiency of Cu (II) ions. The interactions between pH and the stripping phase concentration are shown in Row 1 and 2. The interactions between the stripping phase concentration and the agitation speed are indicated in Rows 2 and 3, whereas the interactions between the agitation speed and the carrier concentration can be witnessed in Row 3 and 4. Similarly, rows 1 and 4 indicate the interactions between pH and the carrier concentration. Rows 1 and 3 indicate the interactions between pH and the agitation speed. And the interactions between the stripping phase concentration and the carrier concentration are indicated in rows 2 and 4. The likely interactions among the process parameters were studied by Sohrabi *et al.* (2017). Patel and Murthy in 2010 also supported the present study (Patel & Murthy 2010).

From the matrix plot of Cu (II) extraction, it could be confirmed that the interactions among pH with the stripping phase concentration, the agitation speed and the carrier concentration are strong at pH 2 and 1, whereas the interactions between the stripping phase concentration and pH and the agitation speed along with the carrier concentration are found to be strong at 0.2 and 0.4 M. But, the interactions between the agitation speed and pH and between the stripping phase concentration and the carrier concentration are found to be strong at 300 and 400 rpm. The interactions

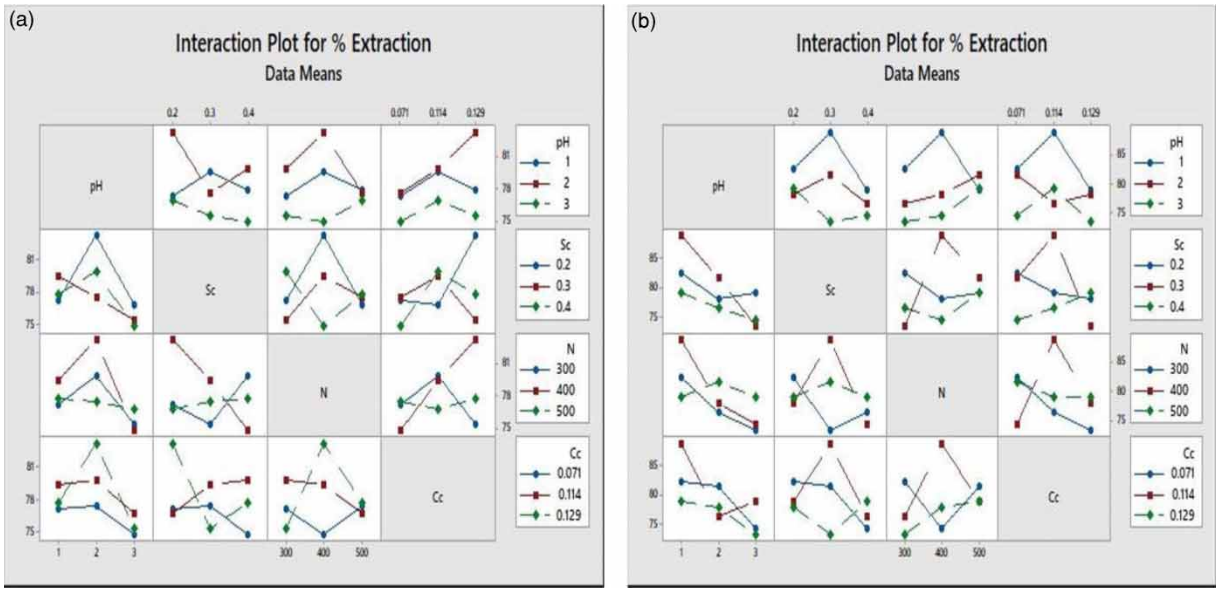


Figure 8 | Interaction matrix plot for % extraction. (a) Cu (II) and (b) Cd (II).

of the carrier concentration with pH and the stripping phase concentration with the agitation speed were strong at 0.114 and 0.129 vol. %. Similarly, from the matrix plot (Figure 8(b)) for Cd (II) extraction, it can be concluded that the interactions between pH with the stripping phase concentration, the agitation speed and the carrier concentration are strong at pH 1 and 2. Whereas the interactions between the stripping phase concentration and pH, the agitation speed and the carrier concentration are found to be strong at 0.3 and 0.2 M and, in addition, the interactions between the agitation speed and pH, the stripping phase concentration and the carrier concentration are found to be strong at 400 and 500 rpm. The interactions of the carrier concentration with pH and the stripping phase concentration with the agitation speed were strong at 0.114 and 0.071 vol. %.

CONCLUSIONS

In this study, the PELM process has been used for the extraction of Cu (II) and Cd (II) ions from the synthetic wastewater solution. Taguchi design approach was employed to determine the optimal conditions for extraction of Cu (II) and Cd (II) ions from wastewater. The ANOVA results confirmed that pH has the most significant effect on the extraction efficiency of Cu (II) and Cd (II) ions. At optimum conditions, the extraction efficiency of Cu (II) and Cd (II) ions was found to be 89.77% and 91.19% respectively. The relative errors between the predicted and the experimental values have been estimated as 9.99% and 3.01% for the extraction of Cu (II) and Cd (II) ions respectively. The results revealed that the contributing parameter for the extraction efficiency of Cu (II) and Cd (II) ions have been found to be in the order: pH (59.09%) > Cc (19.34%) > N (11.58%) > Sc (9.9%) and pH (52.86%) > Sc (19.35%) > Cc (19.11%) > N (8.68) respectively. The results confirmed that there were probable interactions among the operating parameters that influenced the extraction efficiencies.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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