

A Novel Use of Imidazole-based Ionic Liquid as Supporting Electrolyte on the Electrogenenerative Process of Copper(II) Ions

Nora Shahidah Shaharif, Syed Fariq Fathullah Syed Yaacob, Rabia Tasaduq Hussain, Norita Mohamed and Faiz Bukhari Mohd Suah*

Green Analytical Chemistry Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia

*Corresponding author (e-mail: fsuah@usm.my)

An electrogenerative process has acquired interest among scientists due to its feasible functioning to recover the heavy metals in polluted water. But due to its long-time recovery due to obstruction of ohmic resistance in conventional supporting electrolytes makes it less preferable. To conquer this issue, ionic fluids were acquainted to function in as a supporting electrolyte that accelerate conductivity of the application. This short article investigated the impacts of different kinds of imidazole-based ionic fluids such as 1-Butyl-3-methylimidazolium chloride (Bmim[Cl]), 1-Butyl-3-methylimidazolium bromide (Bmim[Br]) and 1-Ethyl-3-methylimidazolium chloride (Emim[Cl]) as supporting electrolytes in the electrogenerative process. This electrogenerative process utilizes a batch cell comprising of a reticulated vitreous carbon as the cathode and pure zinc plate as the anode. The results show Emim[Cl] is the best performing supporting electrolyte to recover 99.9% of copper(II) from a copper(II) sulphate solution after 90 minutes of operation compared to 240 minutes in the use of conventional supporting electrolyte of ammonium chloride. The Emim[Cl] has a high conductivity and mobility characteristics which contribute to total recovery of copper(II) ions.

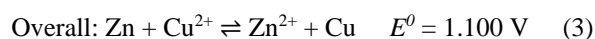
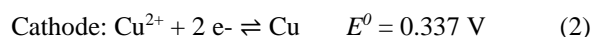
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Currently, water pollution is a considerable issue due to growing industrial discharge from various sources such as mining, chemical industries, plantation and industrial discharge [1–3]. This industrial discharge consists of toxic substances that are not biodegradable such as heavy metals. Prolonged exposure to very high levels of heavy metals can affect living organisms badly [4–6].

There are numerous methods for removing heavy metals from wastewater such as solvent extraction, precipitation, adsorption, ion exchange, membrane and filtration [1,7–9]. However, all of these technologies have advantages and disadvantages. So, there is a need to introduce a system that is not only cost-effective but also simple to operate. Electrochemical treatments are proven to be a suitable approach to prevent pollution. Electrochemical treatments have two types such as electrolytic and electrogenerative processes. Between them, the electrolytic treatments are not cost effective due to poor performance in extracting metal ions it needs high electrical power input. Therefore, electrogenerative process is a better choice for removing metal ions from wastewater [9,10].

In this study, the electrogenerative process is introduced to remove copper(II) ions using reticulated vitreous carbon (RVC) as a cathode and zinc foil as an anode. The electrogenerative process involves a spontaneous chemical reaction in which a more noble metal is reduced at the cathode and a less noble metal is oxidized at the anode [11,12]. Due to the spontaneous chemical reaction, this technology is cost-effective because no external supply of energy is required. The electrogenerative reactions all have a negative Gibb's free energy, indicating spontaneous redox reactions. The equations below represent the galvanic reaction of copper and zinc:



The positive cell potential in the overall equation (Eq. (3)) for this galvanic reaction implies that the process will occur spontaneously when the cell is short-circuited. In previous work, the electrogenerative system had been demonstrated successfully to remove copper from aqueous solutions by [1,13,14].

The functions of supporting electrolyte are to increase the conductivity of the solution and to eliminate the electrical field from the electrolyte. The use of conventional supporting electrolyte such as NaCl, KCl, NaClO₄ and KF in the electrogenerative process have been reported [15,16]. However, the generation of resistance from the extremely high concentration of supporting electrolyte raised the operating costs of the experiments [16]. This phenomenon occurs when supporting electrolyte used has an extremely high salt concentration and the analysis take a long time to complete. The high salt concentration of supporting electrolyte resulting an uncompensated ohmic resistance of the electrolyte, which requires an extra electrical energy to complete the electrogenerative process. This subsequently contributes to an increase of operating costs of the experiments. Thus, it is appropriate to utilize other potential supporting electrolyte, for instance, ionic liquids.

Ionic liquids are raising much interest in the study area of electrochemistry to overcome the drawbacks of traditional supporting electrolytes. Several studies have been carried out on the application of ionic liquids in electrochemistry [17–19]. It was found that ionic liquid provides a system with intrinsically high ionic conductivity and a relatively sizeable electrochemical stability window. Other reports claimed ionic liquids as promising green reaction media, and it gained an interest in sustainable chemistry to overcome waste issues associated with traditional supporting electrolytes [20–24]. In addition, it is discovered that ionic liquids are desirable because of its high conductivity, wide electrochemical window, and unique chemical and physical properties. In addition, ionic liquids possess high thermal stability, low toxicity, low volatility, non-flammable and extremely low negligible vapor pressure [20]. Furthermore, Jonsson (2020) also added that ionic liquids are appealing supporting electrolyte for energy storage's application [19].

This work aims to study the recovery of copper(II) ions using an electrogenerative process by varying different types of imidazole ionic liquids as supporting electrolytes. The selected ionic liquids are 1-Butyl-3-methylimidazolium chloride (Bmim[Cl]), 1-Ethyl-3-methylimidazolium chloride (Emim[Cl]) and 1-Butyl-3-methylimidazolium bromide (Bmim[Br]). In addition, the effect of physicochemical properties and concentrations of each ionic liquids used during the electrogenerative process will be investigated too.

EXPERIMENTAL

Chemicals and Materials

All solutions were prepared from analytical grade-reagents which are copper(II) sulphate, CuSO₄ (QreC) (Malaysia), ammonium sulphate (NH₄)₂SO₄ (QreC) (Malaysia), Bmim[Cl] (Ionictech) (Germany), Emim[Cl] (Ionictech) (Germany) and Bmim[Br] (Ionictech) (Germany). The materials used throughout the

experiment were ion exchange membrane Neosepta® AM-01 (Tokuyama Corp.) (Japan), electrodes such as RVC 80 porous per inch (ppi) (The Electrosynthesis Co.) (USA), and zinc foil (R&M) (United Kingdom). 1000 mg L⁻¹ copper standard solution (Merck) (Germany) was used as the standard copper solution.

Characterization Methods

The electrogenerative setup used in this study is similar to the reported literature [14]. The batch cell has two electrolyte compartments (cathode and anode) separated by an anion exchange membrane (Figure 1). The cell was prepared by sandwiching two cell compartments together with rubbers, a membrane and six pairs of bolts and nuts. The RVC (cathode) was cut into rectangular shapes with dimensions of 2.0 cm × 5.5 cm × 0.4 cm. A pure zinc plate with a purity of 99% was used as the anode material with dimensions of 2.0 cm × 5.5 cm × 0.07 cm. Electrodes were adhered to current collectors using a small piece of parafilm. The current collector used in this experiment was copper plate. The cell was completed using crocodile clip wires to connect the current collectors to the anode and cathode terminals on a multimeter (model Sanwa CD800). A magnetic stirring bar is placed in the cathode compartment to flutter the electrolyte.

Distilled water was utilized to prepare all reagents. The supporting electrolytes utilized were Bmim[Cl], Emim[Cl] and Bmim[Br] and the concentration utilized were 1%, 3%, 5% and 10%. For catholyte, 100 mL of a mixture of copper sulphate (CuSO₄) and the ionic liquid was utilized. An amount of 99 mL of water was mixed with 1 g of ionic liquid. Glass rod was utilized to stir the solution until the ionic liquid was dissolved. Then, 0.03 g of copper sulphate (CuSO₄) was weighed and added into the mixture of water and ionic liquid. The mixture was stirred until dissolved. Then the mixture was poured into a 100 mL volumetric flask. The preparation of catholyte was repeated with different proportions of copper sulphate (CuSO₄): ionic liquid ratio of 99:1, 97:3, 95:5 and 90:10, with respect to different concentrations of ionic liquids. For anolyte, ammonium sulphate was weighed and dissolved in water to make a 0.5 M ammonium sulphate (NH₄)₂SO₄ solution. Experimental details of the batch cell are listed in Table 1.

A 0.5 mL (500 μL) of the catholyte solution was pipetted from the catholyte compartment using a micropipette. The sample was then pipetted into a 25 mL volumetric flask and was filled with distilled water to level. Then, the sample was transferred into a 25 mL labelled plastic bottle. After that, to ensure that both electrolytes were in the same quantity as the initial volume, 0.5 mL of distilled water was added back into the catholyte compartment of the batch cell. The sample was collected every 30 minutes again during a four-hour operation. All experiments were conducted at room temperature.

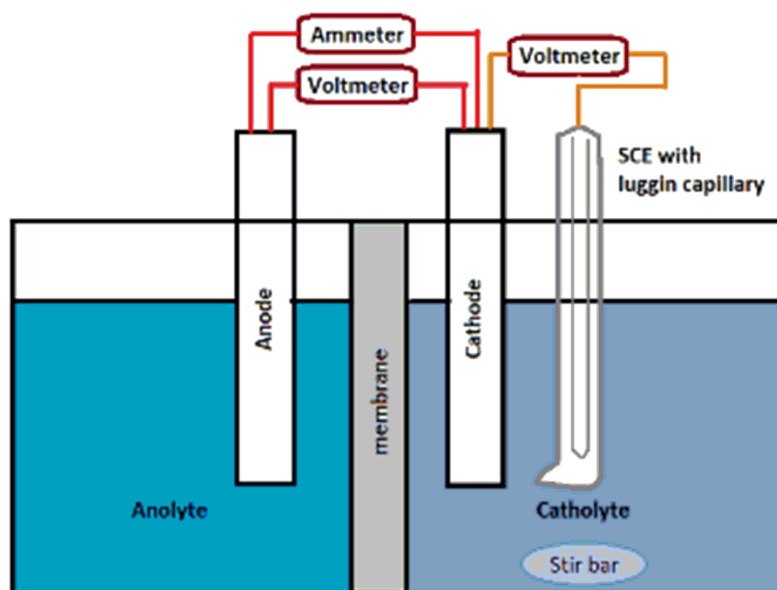


Figure 1. Experimental setup consisting the static batch cell.

Table 1. Experimental condition for the batch cell.

| Cathode compartment | Anode compartment |
|--|--|
| 5 mg L⁻¹ Copper (II) ions concentration (CuSO₄): ionic liquid ratio = 99:1, 97:3, 95:5 90:10 Cathode: RVC (Dimensions 2.0 cm × 5.5 cm × 0.4 cm) | 0.5 M ammonium sulphate (NH ₄) ₂ SO ₄ Zinc plate (Dimensions 2.0 cm × 5.5 cm × 0.07 cm) |

The amount of copper(II) ions left in catholyte solutions was monitored from the samples taken at every 30 minutes. Atomic Absorption Spectroscopy (AAS), Perkin Elmer Analyst 200, was used to determine the copper ion concentrations. The AAS used was set up at a wavelength of 324.8 nm with an air acetylene flame. The percentage of copper ions recovered was calculated mathematically with equation (4):

$$\text{Percentage of copper(II) ions recovery} = [1 - (C_t / C_{0 \text{ min}})] \times 100 \% \quad (4)$$

With C_t is the concentration of copper(II) ions at a specific time (mg L^{-1}) while $C_{0 \text{ min}}$ is the initial concentration of copper(II) (mg L^{-1}).

Finally, the influence of difference concentration of the best performance supporting electrolyte was investigated by varying its concentration with 1, 3, 5 and 10% of ionic liquid.

RESULTS AND DISCUSSION

An electrogenerative process was utilized to study the recovery of copper(II) ions. The experiment was

conducted for 240 minutes. Three sets of operations were performed three times for each supporting electrolyte used. A layer of red-brown copper was observed to be deposited on the RVC surface area of the cathode. The mass transfer has driven the electrode rate reaction. Diffusion occurred as the dissolved reactant from the bulk solution diffused to the surface of the electrode [25]. The diffusion of the bulk solution moved down the gradient from higher to lower concentration areas [26].

Figure 2 shows the graph of logarithm of normalized copper(II) ions versus time using three different supporting electrolytes. The concentration of copper(II) ions decreased over time. It can be observed that the use of Emim[Cl] as the supporting electrolyte was able to recover copper(II) faster than Bmim[Cl] and Bmim[Br]. The result obtained also verified that the use of ionic liquids as the supporting electrolyte have enhanced the copper(II) ions recovery time (90 minutes) as opposed to the reported literature (240 minutes) [11]. In addition, the linear concentration-time relationship also proves that the copper(II) reduction on the cathode was a mass transport-controlled process [27].

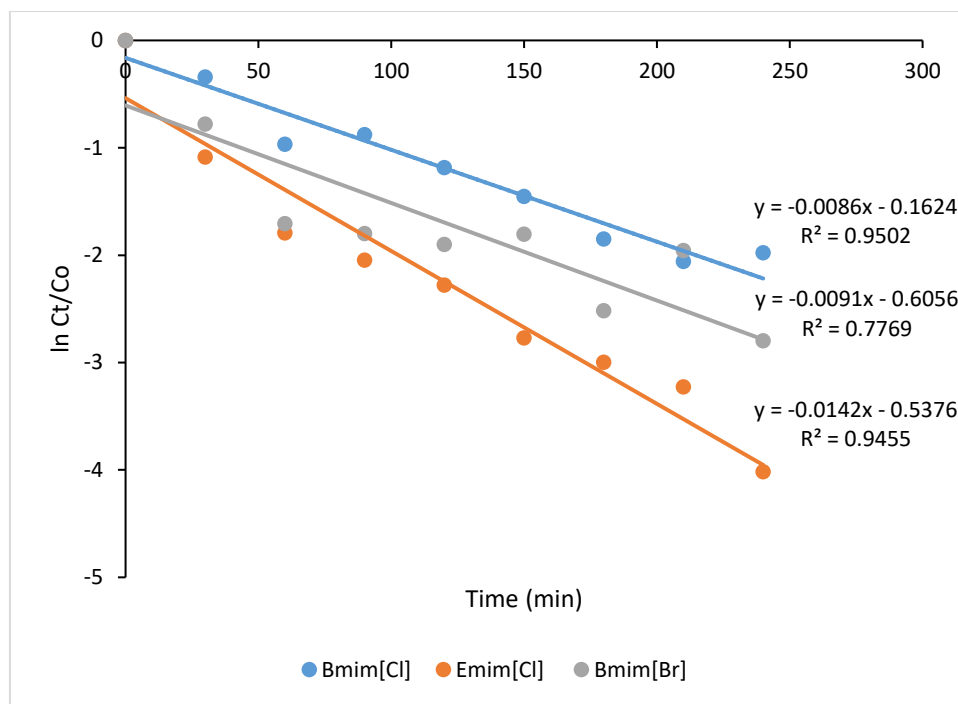


Figure 2. Graph of the logarithm of normalized copper(II) concentration versus time using 3% Bmim[Cl], 3% Emim[Cl] and 3% Bmim[Br] as the supporting electrolytes for the recovery of 5 mg L⁻¹ CuSO₄ solution.

Table 2. Current efficiencies of different supporting electrolytes in recovery of copper(II) ions via an electrogenerative process. (time= 240 minutes, temperature 25 °C).

| Type of supporting electrolyte | Current efficiency (%) | Reference |
|--------------------------------|------------------------|------------|
| None | 15.20 | [11] |
| 0.1 M NH ₄ Cl | 32.40 | [12] |
| 1% Bmim[Cl] | 48.60 | This study |
| 1% Bmim[Br] | 46.30 | This study |
| 1% Emim[Cl] | 61.30 | This study |

Table 2 displays the influence of supporting electrolytes on the current efficiency of an electrogenerative process under different concentration of supporting electrolytes. It can be seen that the absence of supporting electrolyte, the current efficiency is very low, which is less than 15%. The presence of a supporting electrolyte has increased the current efficiencies two-fold [12]. While the use of ionic liquids have raised the current efficiencies tremendously. This can be explained by the ability of the ionic liquids to accelerate the mass transfer process, depress the production of CuO₂ and significantly reduce the hydrogen evolution reaction (HER) side reaction [16, 19].

Figure 3 shows the comparison of copper(II) ions recovery using different types of supporting electrolytes. From the results obtained, Emim[Cl] as the supporting electrolyte produced the best copper(II) ions recovery in 90 minutes of operation, followed by

Bmim[Cl] and Bmim[Br]. The recorded copper(II) ions recovery using Emim[Cl] as the supporting electrolyte is 99.9%.

In the electrogenerative process, the hydronium adsorption and hydrogen gas desorption occur at the same time. In order to minimize HER, the protonated imidazolium molecules are electro-statically adsorbed in competition with the catholyte [28, 29]. The ionic liquid cation, on the other hand, is larger than the conventional supporting electrolytes molecules that cause molecular water to be displaced from the metal surface. Due to the electrons present in the imidazolium ring and nitrogen atom with a free electron pair available to be donated, the ring covers a substantial part of the metal surface by donation. Thus, adsorption promotes the protection of the metal surface. This show ionic liquids influence the diffusion process and facilitate the ion transfer in the electrogenerative process [21, 30, 31].

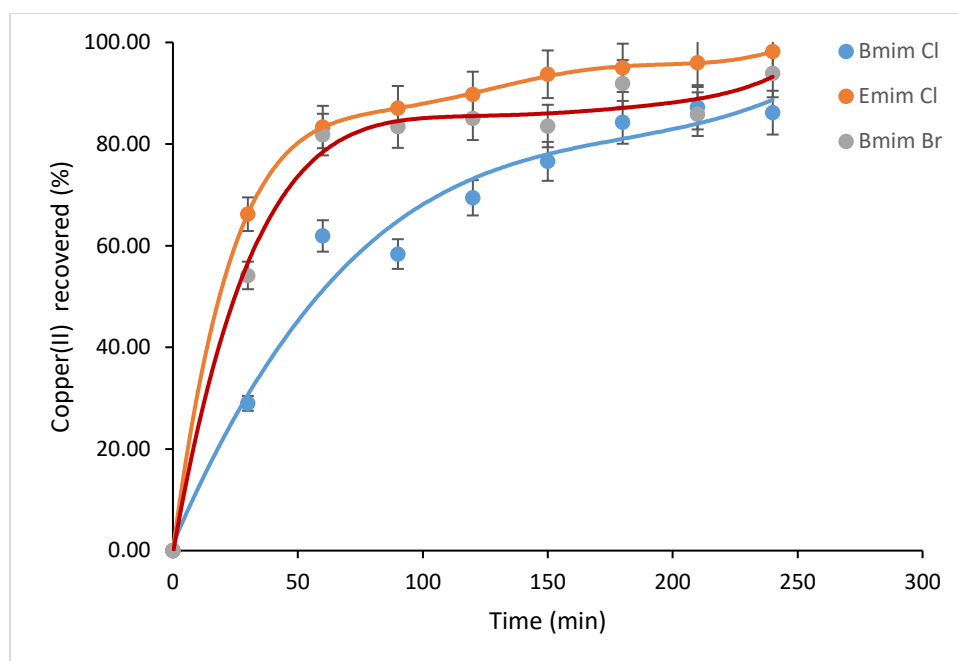


Figure 3. Graph of percentage of copper recovered versus time by using different supporting electrolytes of 3% Bmim[Cl], 3% Emim[Cl] and 3% Bmim[Br].

The other explanation is Emim[Cl] has a higher electrical conductivity compared to Bmim[Cl] and Bmim[Br] at room temperature [23]. Since Emim[Cl] possesses a high electrical conductivity, it facilitates the transfer of ions from the anode to the cathode with lower resistance. Thus, it contributes to total recovery of copper(II) ions.

Furthermore, Bmim[Cl] has the biggest molar mass among all three supporting electrolytes, while Emim[Cl] has the smallest molar mass. This confirms that the lower the molar mass of the supporting electrolyte, the higher the ion mobility in the electrolyte. To conclude, Emim[Cl] was chosen as the best-supporting electrolyte for this investigation.

Another essential parameter in this study is the supporting electrolyte's concentration. Supporting electrolyte increased the ion conductivity and maintained a constant and unchanged ionic strength throughout the reaction. Thus, the resistance of the solution was suppressed significantly [32, 33]. The analysis was conducted in a copper(II) solution with a variable in the concentration of Emim[Cl] (1, 3, 5 and 10%). Four different concentrations were studied in order to choose the optimum supporting electrolyte concentration. However, ionic liquids with the concentration of 5% and 10% were not completely dissolved in water. Thus, only ionic liquids with 1% and 3% were used as the supporting electrolytes. Bystron et al. (2009) stated that the ionic conductivity of an electrodeposition process increases as the

concentrations of supporting electrolyte used increase [16]. Figure 4 shows that the time for copper(II) recovery for 3% Emim[Cl] was shorter in comparison to 1% Emim[Cl]. The explanation to this result is concentration of 3% Emim[Cl] is considered optimum and did not cause any saturation on the cathode, which will contribute to high recovery of copper(II) [14]. Hence, 3% Emim[Cl] was chosen as the optimum supporting electrolyte concentration.

CONCLUSION

The present study has proven that copper(II) may be recovered from a CuSO₄ solution using an electro-generative process consisting of imidazole ionic liquids as the supporting electrolyte. According to the findings of the experiments, 3% Emim[Cl] appears to be the best performing supporting electrolyte, as 99.9% of copper(II) was effectively recovered in 90 minutes. In addition, ionic liquids were able to increase the current efficiencies of the electro-generative process. It shows ionic liquid has a massive potential to be used as a supporting electrolyte in the electro-generative process, replacing the conventional supporting electrolytes.

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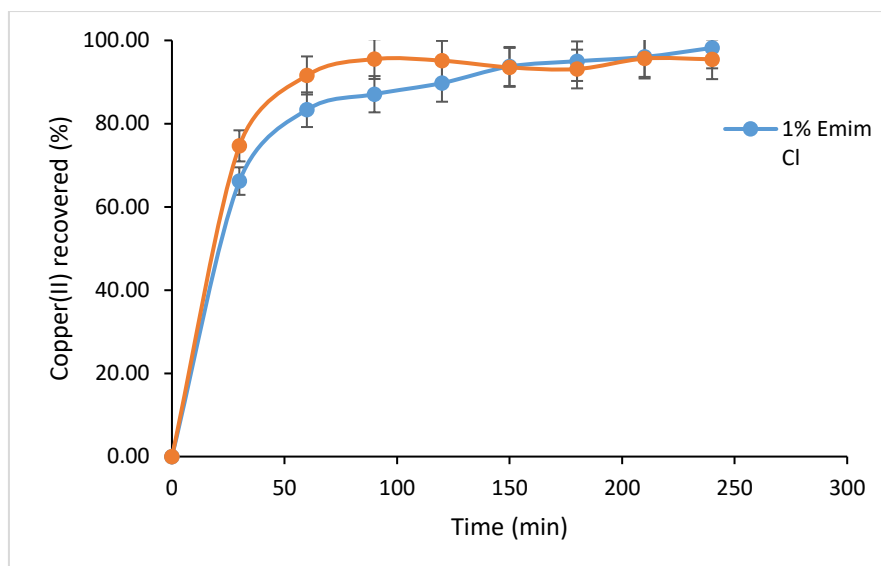


Figure 4. Graph of percentage of copper(II) recovered versus time using 1% and 3% Emim[Cl] for 5 mg L⁻¹ CuSO₄ solution.

REFERENCES

1. Fu, F. and Wang, Q. (2011) Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, **92**, 407–418.
2. Mustakeem, M. (2015) Electrode materials for microbial fuel cells. *Materials for Renewable and Sustainable Energy*, **4**, 1–11.
3. Yaqoob, A. A., Parveen, T., Umar, K. and Ibrahim, M. N. M. (2020) Role of nanomaterials in the treatment of wastewater: A review. *Water*, **12**, 495–524.
4. Liu, Y., Wang, P., Gojenko, B., Yu, J., Wei, L., Luo, D. and Xiao, T. (2021) A review of water pollution arising from agriculture and mining activities in Central Asia: Facts, causes and effects. *Environmental Pollution*, **291**, 118209–118219.
5. Paulino, A. T., Minasse, F. A. S., Guilherme, M. R. A., Reis, V., Muniz, E. C. and Nozaki, J. (2006) Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters. *Journal of Colloid and Interface Science*, **301**, 479–487.
6. Kanapathy, S. and Mohamed, N. (2013) Recovery of copper using an electro MP - Cell operated in an electrogenerative mode. *Separation and Purification Technology*, **118**, 279–284.
7. Kong, M., Wang, L., Chao, J., Ji, Z., Peng, F., Yang, F. and Zhang, Y. (2019) Removal of Cu²⁺ and Ni²⁺ from wastewater by using modified alkali-leaching residual wire sludge as low-cost adsorbent. *Water, Air, and Soil Pollution*, **230**, 1–13.
8. Russo, T., Fucile, P., Giacometti, R. and Sannino, F. (2021) Sustainable removal of contaminants by biopolymers: A novel approach for wastewater treatment. Current state and future perspectives. *Processes*, **9**, 719–738.
9. Yap, C. Y. and Mohamed, N. (2008) Electro-generative processes for environmental applications. *Clean–Soil, Air, Water*, **36**, 443–452.
10. Cheang, C. Y. and Mohamed, N. (2016) Removal of cobalt from ammonium chloride solutions using a batch cell through an electrogenerative process. *Separation and Purification Technology*, **162**, 154–161.
11. Basri, N. A. A. and Suah, F. B. M. (2019) Influence of different sulphate salts as anolytes towards the performance of copper(II) recovery by using an electrogenerative process. *Malaysian Journal of Chemistry*, **21**, 17–23.
12. Suah, F. B. M., Roslan, N. A., Dahlan, N. F. and Mohamed, N. (2018) A use of polymer inclusion membrane as anion exchange membrane for recovery of Cu(II) ions based on an electro-generative system. *Journal of the Electrochemical Society*, **165**, H310–H315.
13. Mansor, N., Mohamed, N. and Suah, F. B. M. (2021) Electrochemical recovery of low concentration of palladium from palladium(II) chloride of electroplating wastewater. *Journal of*

- Chemical Technology and Biotechnology*, **96**, 3216–3223.
14. Jajuli, M. N., Mohamed, N. and Suah, F. B. M. (2020) Electrochemical removal of cadmium from a sulphate solution using a three-dimensional electrode. *Alexandria Engineering Journal*, **59**, 4237–4245.
 15. Jayawardhana, D. A., Crank, J. A., Zhao, Q., Armstrong, D. W. and Guan, X. (2009) Nanopore stochastic detection of a liquid explosive component and sensitizers using boromycin and an ionic liquid supporting electrolyte. *Analytical chemistry*, **81**, 460–464.
 16. Bystroň, T., Hasník, Z. and Bouzek, K. (2009) The role of the supporting electrolyte in the electrochemical methoxylation of 4-methylanisole. *Journal of the Electrochemical Society*, **156**, E179–E186.
 17. Zein El Abedin, S., Ryder, K.S., Höfft, O. and Farag, H. K. (2012) Ionic liquids: Potential electrolytes for electrochemical applications. *International Journal of Electrochemistry*, **2012**, 978060.
 18. Zhang, L., Niu, D., Zhang, K., Zhang, G., Luo, Y. and Lu, J. (2008) Electrochemical activation of CO₂ in ionic liquid (BMIMBF₄): Synthesis of organic carbonates under mild conditions, *Green Chemistry*, **10**, 202–206.
 19. Jónsson, E. (2020) Ionic liquids as electrolytes for energy storage applications – A modelling perspective. *Energy Storage Materials*, **25**, 827–835.
 20. Tiago, G. A. O., Matias, I. A. S., Ribeiro, A. P. C. and Martins, L. M. D. R. S. (2020) Application of ionic liquids in electrochemistry—recent advances. *Molecules*, **25**, 5812.
 21. Zeng, X., Zheng, X., Guo, L., Xu, Q., Huang, H. and Tan, B. (2021) Three imidazole ionic liquids as green and eco-friendly corrosion inhibitors for mild steel in sulfuric acid medium. *Journal of Molecular Liquids*, **324**, 115063–115074.
 22. Liu, R., Zhang, P., Zhang, S., Yan, T., Xin, J. and Zhang, X. (2016) Ionic liquids and supercritical carbon dioxide: Green and alternative reaction media for chemical processes. *Reviews in Chemical Engineering*, **32**, 587–609.
 23. Singh, S. K., and Savoy, A. W. (2020) Ionic liquids synthesis and applications: An overview. *Journal of Molecular Liquids*, **297**, 112038.
 24. Niu, H., Wang, L., Guan, P., Zhang, N., Yan, C., Ding, M., Guo, X., Huang, T. and Hu, X. (2021) Recent advances in application of ionic liquids in electrolyte of lithium ion batteries. *Journal of Energy Storage*, **40**, 102659–102688.
 25. Roslan, N. A., Suah, F. B. M. and Mohamed, N. (2020) Influence of different 3-D electrodes towards the performance of gold recovery by using an electrogenerative process. *Arabian Journal of Chemistry*, **13**, 1440–1448.
 26. Cheng, H., Wei, L. and Cheng, F. (2020) Quasi-equilibrium and unsteady mass transfer of low-grade bloedite in the process of static water dissolution. *Applied Sciences*, **10**, 1–14.
 27. Kanagaratnam, J. and Suah, F. B. M. (2021) An innovative use of electrochemically modified three-dimensional carbon felt for a rapid recovery of gold from diluted chloride solution. *Journal of Chemical Technology and Biotechnology*, **96**, 2219–2227.
 28. Beltrop, K., Madrid, J. C., Meister, P., Heckmann, A., Winter, M., Akbay, T., Ishihara, T. and Placke, T. (2020) Experimental and computational studies of electrochemical anion intercalation into graphite from target-oriented designed borate-based ionic liquid electrolytes. *Journal of Power Sources*, **469**, 228397–228409.
 29. Zhang, D., Liu, Q., Shi, X. and Li, Y. (2012) Tetrabutylammonium hexafluorophosphate and 1-ethyl-3-methyl imidazolium hexafluorophosphate ionic liquids as supporting electrolytes for non-aqueous vanadium redox flow batteries. *Journal of Power Sources*, **203**, 201–205.
 30. Corrales-Luna, M., Le Manh, T., Romero-Romo, M., Palomar-Pardavé, M. and Arce-Estrada, E. M. (2019) 1-ethyl-3-methylimidazolium thiocyanate ionic liquid as corrosion inhibitor of API 5L X52 steel in H₂SO₄ and HCl media. *Corrosion Science*, **153**, 85–99.
 31. Verma, C., Obot, I. B., Bahadur, I., Sherif, E. S. and Ebenso, E. E. (2018) Choline based ionic liquids as sustainable corrosion inhibitors on mild steel surface in acidic medium: Gravimetric, electrochemical, surface morphology, DFT and Monte Carlo simulation studies. *Applied Surface Science*, **457**, 134–149.
 32. Germani, R., Mancini, M. V., Spreti, N., Di Profio, P. and Savelli, G. (2011) Cu(II) extraction in ionic liquids and chlorinated solvents: Temperature effect. *Green and Sustainable Chemistry*, **1**, 155–164.
 33. Martinez, J. G., Otero, T. F. and Jager, E. W. H. (2014) Effect of the electrolyte concentration and substrate on conducting polymer actuators. *Langmuir*, **30**, 3894–3904.