



Application of electro dialysis membrane process to recovery sulfuric acid and wastewater in the chalcopyrite mining industry

M.I. Aydin, B. Yuzer, B. Hasancebi, H. Selcuk*

Faculty of Engineering, Department of Environmental Engineering, Istanbul University-Cerrahpaşa, Avcilar, Istanbul, Turkey, email: hselcuk@istanbul.edu.tr (H. Selcuk)

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ABSTRACT

Pyrite (FeS_2) is the primary form of sulfur that occurs within colliery spoil. It is frequently present in base metal sulfide deposits. It is oxidized to ferrous sulfate (FeSO_4) and sulfuric acid (H_2SO_4) when exposed to atmospheric factors. In the desulphurization of coal/mine stone as well as in the extraction of copper from abundant copper pyrite called chalcopyrite, the aim is the dissolution of pyrite. Copper and sulfuric acid are the primary products in the chalcopyrite (CuFeS_2) mining industry. A large amount of acidic wastewater is generated during the flue gas pre-treatment system. Thus, this work aims to apply the electro dialysis (ED) membrane process to recovery sulfuric acid from waste acid liquor. Cationic ion exchange was used as a pre-treatment process to remove heavy metals before the ED system. The fate and transport of heavy metals (Zn, Cd, Cu, Pb, Ni, and As) and operational parameters (conductivity, current, pH, etc.) were monitored for the evaluation of the recovery system. The work performed in the relevant industrial environment confirms that the ED process may recover 90% acid from wastewaters of the chalcopyrite mining industry. Additionally, both obtained acid and recovered water have enough quality to be reused in the chalcopyrite industrial processing line. Thus, the ED-based recovery systems may provide environmentally and economically solutions in a circular economy concept.

Keywords: Acid recovery; Electro dialysis membrane; Membrane process; Pyrite; Wastewater reuse

1. Introduction

Pyrite, a mineral with a chemical formula of FeS_2 , is an iron disulfide, which is usually associated with other sulfides and oxides. Pure pyrite contains approximately 53% sulfur [1]. Pyrite wastes have a negative impact on the waters used in urban and agricultural areas because it increases the formation of acid drainage, thus pollutes the water sources with bio-accumulative metals with its sulfide-rich structure. Drainage acidification occurs in both atmospheric and aquatic medium as both air and water increase the oxidation process of wastes containing iron sulfides [2]. Pyrite can be used as a raw material in the production of commercial

products such as sulfuric acid, sulfur dioxide, ferrous sulfate, hematite, sulfur, and fertilizers [3,4].

Chalcopyrite (CuFeS_2) is a copper mineral and can be used in the production of copper and sulfuric acid. Industrial wastewaters of chalcopyrite processing may contain different heavy metals such as As, Zn, Cd, Cu, Pb, and Ni. Due to the severe effects of heavy metals on the environment; national and international legislation on heavy metal pollution have gradually become more rigid for the protection of the environment. The mining industry is one of the critical heavy metal pollution sources. Hence, the removal of heavy metals from the industrial mining processes has received much attention in recent years [5]. Acid mine drainage occurs

* Corresponding author.

when sulfide-containing polymetallic minerals react with water in oxidant conditions. This causes soluble metals and protons to form, causing a decrease of pH [6] in an aquatic medium. In the chalcopyrite industry, high SO_2 gas is used for sulfuric acid production. A high amount of water is used in the SO_2 purification process to remove heavy metals for a high quality commercial sulfuric acid. Thus, in the industry, a large amount of NaOH is used before a secondary/tertiary treatment system to neutralize acid wastewater to remove heavy metals. After the neutralization stage, salinity level increases two-fold, and thus the effluent of the secondary treatment plants of the industry is not suitable for any wastewater reuse proposes. Additionally, the operational cost of acid wastewater treatment plant may vary in the range of 7.7–16 \$/m³ depending on the acid level and heavy metals in the influent and sludge disposal method in the industry. Thus, in a circular economy concept, removal of heavy metals, wastewater reuse, and acid recovery should be considered together in the mining processes.

Electrodialysis (ED) is an industrial process of separating specific ions under an applied electrical potential difference through ion-exchange membranes [7]. Unlike most membrane applications, ED is an electrically driven process. Anion and cation exchange membranes are stacked between anode and cathode to establish an ED cell. Spaces between ion-exchange membranes utilize concentrate and dilute compartments and membranes function as a semi-barrier for ion transfer [8]. Most common applications of ED process is desalting brackish waters, brine production from seawater, demineralization of industrial wastewaters, however recent studies shown that ED can also be used in various biotechnological and chemical applications such as the production of organic acids, amino acids, sugar demineralization, blood treatment, etc. [9,10]. ED technology provides an alternative solution for the treatment of industrial waste acid, and salt solutions since advances in ion-exchange membrane technology enhance the efficiency of ED technology [11]. Recent studies show that it is possible to treat, separate or concentrate valuable acid solutions or metal liquors from various industries such as metallurgy industry, surface treatment processes, spent industrial solutions, industrial copper and zinc electrolytes, CuSO_4 and H_2SO_4 solutions with impurities, alumina alkaline solutions from alumina industries [9,12–15].

Because of high heavy metal concentrations in the acid wastewater of the chalcopyrite mining industry, the ion exchange (IEx) process may not be an effective pre-treatment method for the ED process. The main difficulties of the ED recovery system are finding a suitable pre-treatment technology for the removal of metals from the acidic wastewater. In recent years, the development of new cation and proton exchange membranes enhances the performance of ED technology for a selective acid recovery from heavy metal-containing acid solutions [9,16–18]. The main novelty of this study is the recovery of acid and wastewater from the acid wastewater generated from the SO_2 wet purification process in the chalcopyrite mining industry using a combination of best available technologies such as ion exchange and ED. As a case study of the circular economy concept, this work aims to contribute to the definition of IE and ED processes based on their combination for the integral

recovery of sulfuric acid and wastewater from acid wastewater in the chalcopyrite mining industry.

2. Methods

2.1. Chalcopyrite Mining Industry Wastewater

Wastewater from the flue-gas pretreatment system was obtained from a Chalcopyrite Mine in Turkey.

2.2. Electrodialysis

Experimental studies were carried out with a lab-scale batch ED set up (Fig. 1) manufactured by PCCell GmbH (PCCell 64 0 04). ED cell was operated with 110 mm × 110 mm ion exchange membranes with a 64 cm² active membrane area. The ED cell consists of a titanium anode coated with Pt/Ir and a stainless-steel cathode. Specifications of commercial anionic and cationic exchange membranes obtained from PCCell GmbH are given in Table 1.

ED cell has three compartments containing electrolyte solution, dilute, and concentrate. Five repeating dilute and concentrate compartments arranged to carry out studies. Stacking multiple compartments provide a larger active membrane area. 0.025 M H_2SO_4 solution was fed through the electrolyte and concentrate compartments to provide conductivity between electrodes and compartments. The wastewater was pumped through the dilute compartment, and an electrical potential is established between the electrodes using a DC power source.

After the conductivity of wastewater reached a desirable level, treated wastewater in the dilute compartment was discharged and re-fed with fresh wastewater while the solution in the concentrate compartment remains untouched. The duration between the start and re-feeding of wastewater is called a cycle.

2.3. Measurements

Continuous conductivity measurements were carried out with Hach SC1000 multi-parameter universal controller display module with Hach 3700 digital inductive conductivity sensors. Heavy metal analyses were performed with PerkinElmer atomic absorption spectrometer, according to

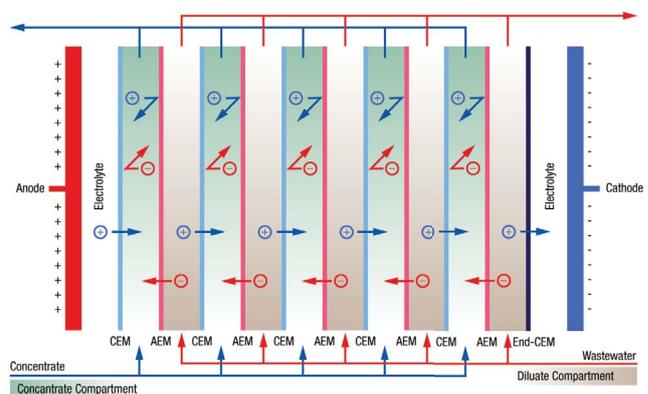


Fig. 1. Experimental setup of the ED process.

Table 1
Specifications of commercially available membranes (PCCell)

| Membrane type | PC SA | PC SK | PC SC |
|---------------------------------|-----------------|---------------|---------------|
| | Strong alkaline | Strong acidic | Strong acidic |
| Transference number | >0,95 | >0,95 | >0,94 |
| Resistance, Ωcm^2 | ~1.8 | ~2.5 | ~9 |
| Thickness, μm | 180–220 | 160–200 | 400 |
| Ionic form | Cl^- | Na^+ | Na^+ |

Standard Methods 3110 metals by atomic absorption spectrometry [19]. Acidity analysis was carried out according to Standard Methods 2310B acidity [19].

3. Results

3.1. Characterization of raw acidic wastewater of the copper-pyrite mining industry

In this study, acid wastewater effluent was taken influent of the chalcopyrite mining industry located at Samsun, Turkey. In the industry, copper-rich pyrite known as chalcopyrite (CuFeS_2) is used to produce copper and sulfuric acid. 3,200 m^3/d water is used for the purification of SO_2 gas. The acidic effluent of the SO_2 purification process containing sulfuric acid and metals of interest such as copper, zinc, cadmium, arsenic, manganese, aluminum, lead, nickel, silver, mercury, chromium, iron, in a concentration that can range from 10^{-6} to 10^2 g/L. The treatment plant containing neutralization and chemical coagulation processes is used for the treatment of acidic wastewater of the copper-pyrite mining industry. 35 ton/d NaOH and 2.5 ton/d $\text{Ca}(\text{OH})_2$ are used to neutralize acidic wastewater. Hazardous sludge is also produced in the neutralization process. Without wastewater reuse and acid recovery, the operational cost of the treatment plant was around 6.7 $\$/\text{m}^3$ except for sludge disposal. The operational cost of wastewater treatment plant may change in the range 6.7–16 $\$/\text{m}^3$ depending on the fluctuating acidity level (around 1%–2%) in the effluent of the flue gas treatment process.

In this study, the ED membrane separation system was run for the acid wastewater effluent of the gas purification process for acid and water recovery. In the effluent sulfuric acid, acidity was found to be 17 g/L. Heavy metal analysis has shown zinc, arsenic, iron, copper, cadmium, and lead were the primary heavy metals in the concentration of 94.2, 94, 62, 43.3, 16.8, and 3.9 mg/L, respectively. The conductivity of effluent is over 48 mS/cm. Thus, it is not possible to reuse the treated wastewater for any industrial and irrigational purposes.

3.2. Acid recovery from feeding wastewater

This study aims to apply the ED system for the effective separation and recovery of the sulfuric acid from the chalcopyrite mining industrial effluent with high heavy metals mixture of As, Zn, Cd, Cu, Pb, and Ni. With this purpose, experiments were carried out with 1 L raw acid drainage wastewater as a feeding solution to the ED membrane

process. In the first experiment, the feeding solution discharged when conductivity reached around 2 mS/cm in the feeding solution. After 70 min of experimental running, 98% of sulfuric acid was separated from the feeding solution, and an initial 17,275 mg/L acidity decreased around 275 mg/L. The decrease in the conductivity of the feeding solution exhibited the same trend, and 48 mS/cm of conductivity dropped to around 2.0 mS/cm while the conductivity in concentrate compartment increased around 50 mS/cm thus completing the first cycle (Fig. 2). 30 ED experiments (30 cycles) was run for the treatment of 30 L acid wastewater without discarding concentrate acid solution (Fig. 3). As can be seen in Fig. 3, process time to reach the desired conductivity shortens over cycles.

However, process time gets longer again after the 20th cycle and it gets harder to reach conductivity below 2 mS/cm. While the acidity of concentrate compartment reached around 103,000 mg CaCO_3/L (Fig. 4), the conductivity of the concentration compartment started decreasing after 40 min of the 30th cycle, conductivity reached 400 mS/cm then dropped around 390 mS/cm (Fig. 5). Concentration difference between concentrate cell and dilute cell formed concentration polarization and caused the ions to bleed back to the dilute compartment.

3.3. Fate and transport of heavy metals during ED treatment

After 75 min of experimental running, the concentrations of As, Zn, Cd, Cu, Pb, and Ni in the feed solution decreased in the dilute and increased in the concentrate. As can be seen from Fig. 6, the concentrations of heavy metals in the

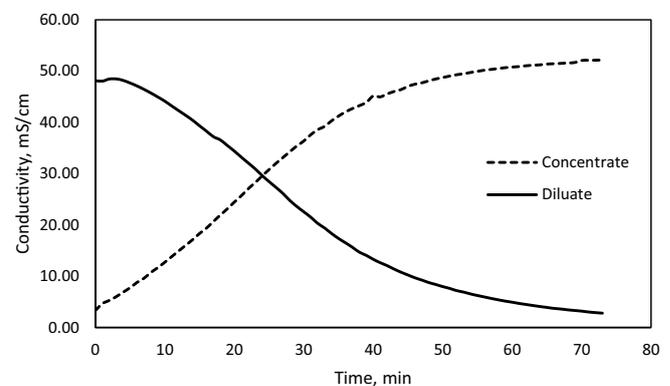


Fig. 2. Conductivity changes in the concentrate and dilutes compartments overtime at the first cycle.

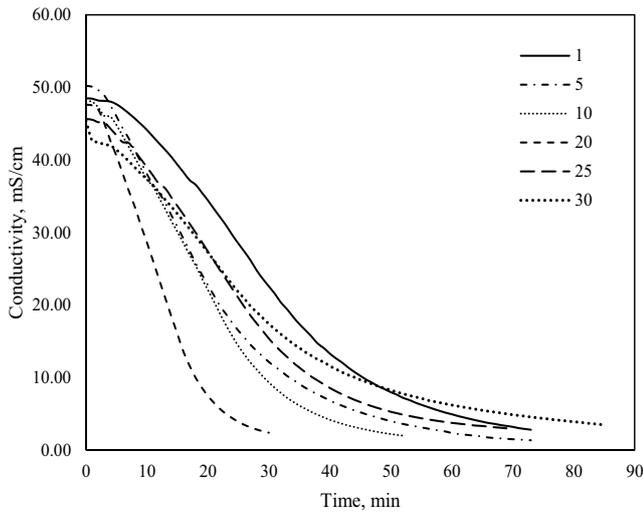


Fig. 3. Change of conductivity in various electro dialysis treatment cycles in the dilute compartment.

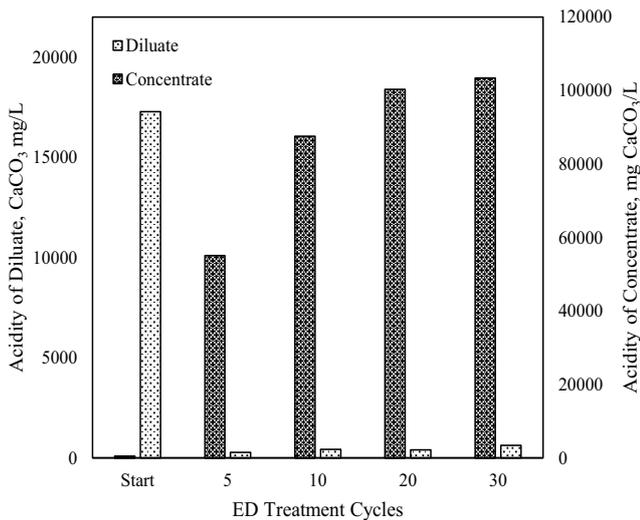


Fig. 4. Acidity in the ED treated dilute and concentrate compartments.

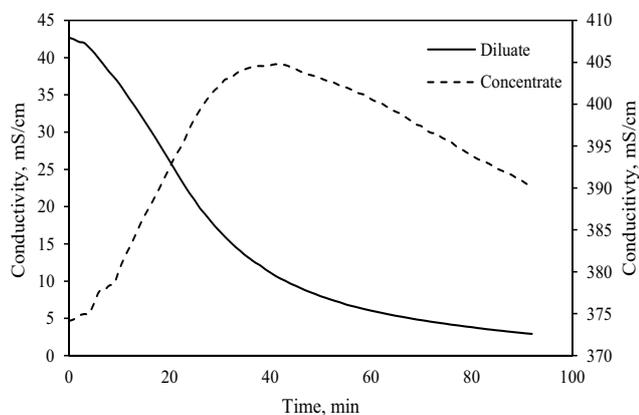


Fig. 5. Conductivity change in the concentrate and dilute compartments overtime at the 30th cycle.

recovered acid solution reached the initial concentrations after 20 cycles. However, concentrations started to increase after that point due to the concentration polarization. After the ED process, the treated wastewater solution was neutralized with NaOH, and 100 mg/L Ca(OH)₂ and precipitated for 1 h. The sample was taken from the supernatant part for the heavy metal measurements. It is observed that the concentrations of heavy metals in the coagulated sample decreased by over 98%.

Ion exchange was performed before the ED process to remove heavy metals from wastewater. 30 L wastewater (30 cycles) was treated with the ED process to investigate the effect of heavy metals on the acid recovery efficiency of the ED system. No differences were observed, and almost the same acid concentration (103,800 mg/L) was found in the concentrate compartment after 30 cycles.

4. Conclusions

In this study, ED membrane separation (with and without pretreatment) was applied for the recovery of sulfuric acid and wastewater in the chalcopyrite mining industry. The following conclusions were achieved from the results.

- The ED system was applied without any pre-treatment. During ED treatment, 17,475 mg/L initial acidity level in the raw wastewater decreased to around 275 mg/L, and almost 95%–98% sulfuric acid was accumulated in the concentrate compartment. 30 L acidic raw wastewater was treated by repeating 30 ED experiments without discharging acid solution in the concentrate compartment, and 450 mg/L of the initial acidity level increased to 103,000 mg/L after 30 cycles.
- All heavy metals were transferred in the recovered acid, and after 20 cycles, heavy metals in the recovered acid solution reached the initial concentrations.
- Cationic anion exchange process was used to remove heavy metals before the ED experiment. Application of the cationic exchange process as pre-treatment did not increase the performance of the ED system as almost the same acid (103,800 mg/L) was recovered under the same conditions. However, without heavy metals, the recovered acid solution was found suitable for the reuse in the production line of the industry.
- The post-treatment, including neutralization and coagulation process, was found efficient for the reuse of ED treated chalcopyrite mining wastewater in the industry.

As mentioned before, due to the high level of acidity level and high amount of neutralizing chemicals of (NaOH and Ca(OH)₂), the treatment cost of wastewater in the chalcopyrite mining industry is very high. The results reflect the fact that the ED integrated acid and wastewater recovery system maybe not only environmentally friendly but economical solution as well for the chalcopyrite mining industry. However, the ED system should be investigated in a pilot-scale in the appropriate environment for the identification of its challenges.

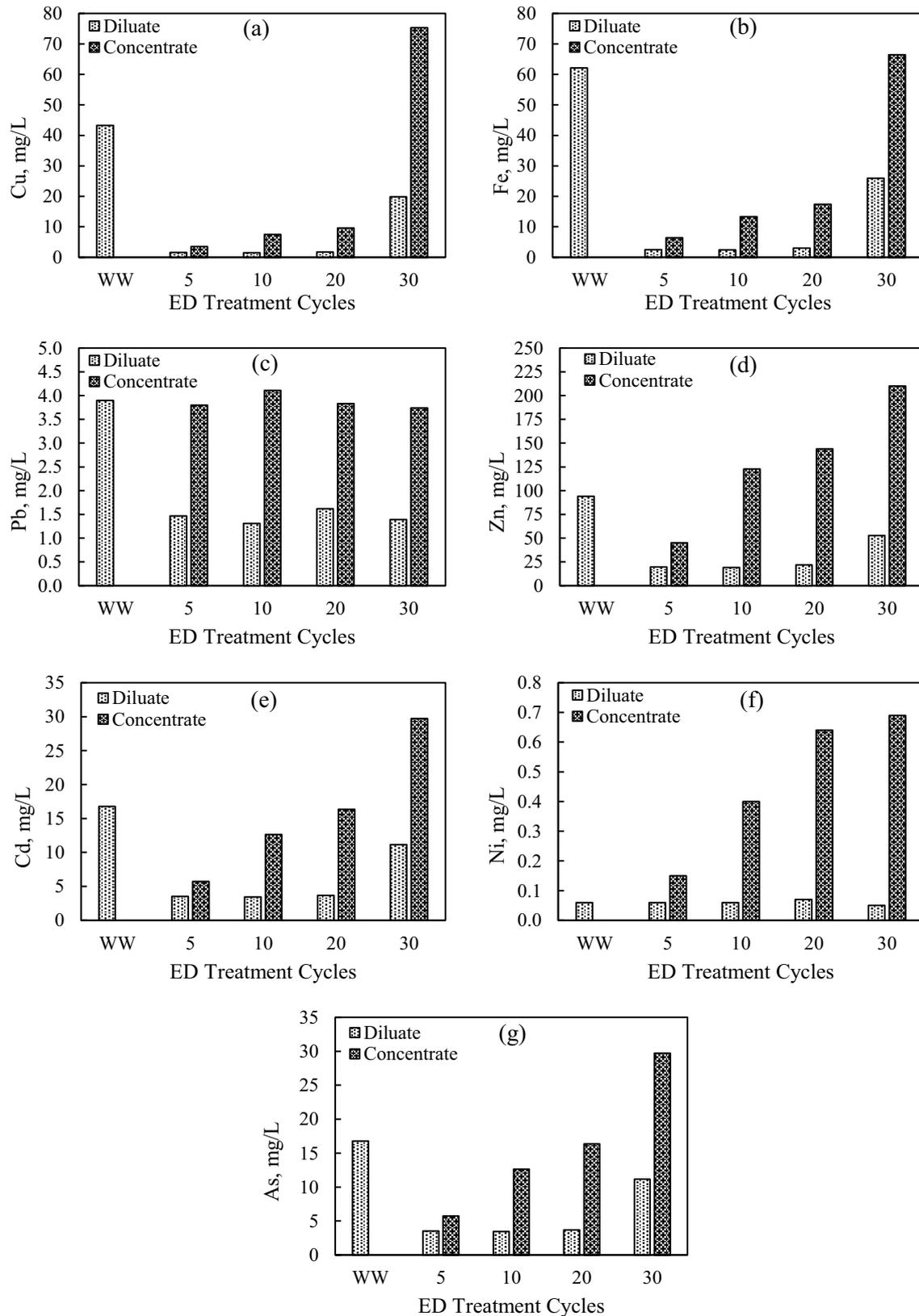


Fig. 6. Changes of heavy metal concentrations in dilute and concentrated solutions in various electro dialysis treatment cycles. (a) Cu, (b) Fe, (c) Pb, (d) Zn, (e) Cd, (f) Ni, and (g) As. WW: Wastewater.

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