Scientific Journal of University of Benghazi

SJUOB (2025) 38 (1) Applied Sciences: Matter, et la , 159 – 178
www.sjuob.uob.edu.ly

# Heavy metals in water associated with oil and soil were treated using chemical and electrophoretic precipitation methods.

Hamdy AB. Matter[1,2]*, Mohamed emgharbi[3]

*1 Associate Professor, Chemistry Department, Banghazi University, Elwahate, Jalow, Libya.*
*2 Associate Professor, High Institute of Engineering and Technology, El-Arish, Eygpt.*
*3 Libyan Academy postgraduate Studies/ Benghazi, Libya.*

Received: 28 / 02 / 2025 | Accepted: 05 / 10 / 2025 | Publishing: 29/06/2025

## ABSTRACT

Chemicals such as potassium hydroxide (KOH), potassium ferrocyanide ($K_4[Fe(CN)_6]$), and oxalic acid ($H_2C_2O_4$) have been used as agents capable of rapidly and efficiently forming precipitates with heavy metal ions under natural environmental conditions. The active components in these chemicals act as chelating agents, enabling them to form stable precipitates or complexes with heavy metals present in water associated with oil and in the surrounding soil.

This study compares the efficiency and characteristics of chemical precipitation products with those formed via cathodic deposition during electrochemical treatment. The ability of both methods to precipitate various heavy metals (HMs)—including Cr, Fe, Ni, Mg, Cu, Zn, Ag, Cd, Mn, and Pb—was investigated. Each method demonstrated varying effectiveness in removing specific metals, and it was measured deposition efficiency, standard deviation S and a coefficient of variation (CV).

Chemical and electrical methods have treated oil-related water and soil contaminated with common heavy metals, which could be removed and treated chemically and electrically. The results revealed very high concentrations of these harmful heavy metals, which have contaminated oil-related water, the soil, the groundwater beneath it, and the plants it irrigates. This poses risks to human and animal health and may even cause diseases and cancer.

***Keywords:*** heavy metals, water associated with oil soil water treatment, Electrophoretic Precipitation.

***Corresponding Author:*** Hamdy AB. Matter, hamdy.matter@uob.edu.ly

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

## 1- INTRODUCTION

Biochemical-electrochemical (BES) systems, as well as electrolytic reactors (ERs), have been evaluated for their effectiveness in removing heavy metals (HMs) and filtering fly ash. X-ray diffraction analysis revealed high concentrations of zinc, lead, and copper [1]. Various electrochemical treatment methods, such as electrocoagulation and electrolysis, have proven effective in removing residual impurities from contaminated water [2]. A new electrolysis technology, developed at laboratory scale, has been tested for deep extraction and separation of various metals, including heavy metals [3]. Microbial electrolysis cells (MECs) have been developed to treat acid mine drainage (AMD), simultaneously producing hydrogen gas ($H_2$). Dual-chamber microbial electrolysis cells have also been specifically designed for the removal of $Cu^+$, $Ni^+$, and $Fe^+$ under both single-metal and mixed-metal conditions [4]. Laboratory-scale microbial fuel cells (MECs) have successfully removed heavy elements such as lead and cadmium under various electrical conditions, operating times, and concentrations [5]. For the removal of heavy elements such as zinc, manganese, and nickel from process water, dual-electrode systems using steel as the cathode and coal- or platinum-coated titanium as the anode have shown promising results [6]. Further studies have investigated the role of bioreduction and electrochemical reduction in microbial fuel cells (MFCs) and microbial fuel cells (MECs) in the removal and recovery of harmful organic pollutants [7]. Platinum-coated coal and titanium electrodes showed good anode resistance at different current densities [8]. The performance of a continuous recirculation flow cell has also been evaluated at low current densities and different pH levels when treating wastewater and associated water in copper smelting plants, confirming the effectiveness of cathodic reduction in removing organic pollutants [9]. The removal efficiencies of Pb and Cd were found to be significantly influenced by factors such as applied voltage, current, purging solution type, soil pH, permeability, and zeta potential [10].

The electrochemical removal of CM cations from aqueous solutions was investigated using single-chamber (DKE) electrolyzers [11]. Although advanced oxidation techniques can produce high-purity water, their high operational costs limit large-scale

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

implementation. Chemical coagulation, while effective, is relatively slow and leads to significant sludge generation [12]. Solidification/stabilization (S/S) methods are being explored as potential treatments for electrolytic manganese residue (EMR) [13]. An improved electrokinetic (EK) process for heavy metal (HM) removal from electroplating sludge was developed by introducing electrolytes into the electrode chambers, significantly enhancing removal efficiency [14]. Moreover, an actively synthesized catholyte solution was employed for the electrochemical deposition of HMs such as Fe, Cu, and Zn, demonstrating its potential for electrocoagulation (electro-flocculation) applications [15]. A laboratory-scale process integrating electrolysis (EL) and electrodialysis (ED) was designed for the efficient treatment of Cu-containing wastewater [16]. A glow discharge plasma (GDP) system has been developed, combining redox mechanisms to decompose heavy metal and organic complexes, using Cu-EDTA as a model compound [17]. The simultaneous removal of $Fe^{2+}$ and $Pb^{2+}$ in microbial electrolysis cells (MECs), along with the targeting of ammonium ions in microbial desalination cells (MDCs), has also been demonstrated [18]. Electrochemical filtration pressure cells operating in batch recirculation mode for the removal of heavy metals from copper smelting waste have been tested and shown excellent results [19]. Adsorption and other various physical and chemical techniques have been explored, such as adsorption using new sorbents, ion exchange, membrane filtration, electrodialysis, reverse osmosis, ultrafiltration, and photocatalysis [20].Microbial electrolysis cells (MECs) have emerged as an efficient technology for the simultaneous removal and recovery of nickel (Ni) from electroplating effluents, effectively eliminating both organic matter and Ni ions [21]. The application of an electric field significantly enhances pollutant removal, as pollutant-containing particles behave as polarizable species, functioning similarly to pseudo-electrodes [22]. This method has achieved a total mercury removal efficiency of 60% [23].

A study investigating the electrodeposition of (Cu) and (Pb) onto palm shell–activated carbon electrodes evaluated current efficiency within a continuous packed-bed electrochemical cell [24]. The electrolysis process employed selective anodes and

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

cathodes to optimize Cu extraction, with maximum efficiency obtained by adjusting the current density [25]. Nanocrystalline Ni-Fe-C cathodes incorporating carbon have shown high electroactivity for the hydrogen evolution reaction (HER) in hot alkaline solutions, indicating their potential for improved electrochemical performance [26]. A novel cementitious composite material was also developed to stabilize electrolytic manganese residue (EMR), an industrial solid waste rich in sulfur and heavy metals (HMs) [27]. The performance of batch electrocoagulation (EC) using iron (Fe) electrodes in a monopolar configuration was evaluated for the simultaneous removal of Cu, Ni, Zn, and Mn from synthetic wastewater [28]. A combined internal micro-electrolysis (IME)–electrocoagulation process was also developed at the laboratory scale for treating real copper smelting wastewater [29]. Electrolysis using Fe electrodes resulted in the generation of $Fe^{3+}$ ions and $Fe(OH)_3$ precipitates, while Cu electrodes produced $Cu^{2+}$ ions and $Cu(OH)_2$ precipitates [30].

Electrolysis experiments were conducted using iron, steel, aluminum (Al), and zinc (Zn) electrodes under varying current densities and treatment durations to evaluate the removal of physico-chemical contaminants, heavy metals (HMs), and microbiological pollutants from different wastewater sources [31]. The results also indicated that a pretreatment process using quicklime effectively solidified and stabilized HMs [32]. Waste printed circuit boards (WPCBs) are among the most complex and valuable components of electronic waste, containing a variety of recoverable metals [33]. Electrolysis is used to remove mercury (Hg) from residual effluents generated during gold processing, using electrode-driven chemical reactions in an electrolyte solution [34]. Electrocoagulation is used to remove HMs such as Cu, Cr, Pb, and Zn from industrial wastewater [35]. Metal removal during electrocoagulation periods can be improved with longer time, increased sodium chloride (NaCl) concentrations, and increased electrical current [36].

To improve chromium (Cr) recovery, various combinations of electrodes have been tested to increase the extraction capacity [37]. Electrolytic membrane extraction (EME) is used to remove Cu from aqueous solutions, using a specialized electrochemical cell consisting of two glass chambers, a

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

supported liquid membrane (SLM), a graphite anode, and a stainless steel cathode [38]. Electrokinetic treatment of soils contaminated with copper, lead, and chromium has been piloted and has proven promising [39]. Stabilization of contaminants from electrolytic manganese residue (EMR) is critical to ensure its safe handling and potential reuse in environmental protection [40]. the active chemicals in Picovit, Clara, Drill, Endocer Givescon, Hydral, Laxofin, Maxlase, Motilium, Orapen, Scopinal, Maltvitamin, and Xilone drugs have been used as chelating agents for heavy metals remediation [41].

In this study, heavy metal ions were precipitated using oxalic acid, potassium ferricyanide, and potassium hydroxide. The efficiency of chemical precipitation was compared with that of electro-precipitation. Both methods were applied to remove heavy metals from water and soil associated with oil production in the Nafoora field, operated by the Arabian Gulf Oil Company in Jalu, Libya.

## 2- EXPERIMENTAL

### 2.1. Chemicals and Equipment's

Beakers of 250 ml capacity - Filter papers - Funnels - Cylinder tester - Cups - Conical flasks Sensitive balance – Standard measuring flasks 250 ml.

### 2.2. Preparation of solutions

100 ml of solution of 0.1 molar are prepared from the following materials: Cu $(NO_3)_2$ .$3H_2O$ (2.4g), $AgNO_3$ (1.7g), $MgSO_4$ (1.2g), $NiSO_4$ (1.54g), Fe $(NO_3)_3$ .$9H_2O$ (4.04g), Cr $(NO_3)_2$ .$9H_2O$ (4g), $CdSO_4.4H_2O$ (3.52), Pb $(NO_3)_2$ (3.3g), $ZnSO_4$. $7H_2O$ (1.61g) and $MnSO_4$. (1.69g). Add 50 ml of metal ion solution to 50 ml from 0.1M precipitating agents (Oxalic acid, $C_2H_2O_4$, Potassium ferricyanide $K_4[Fe(CN)_6]$ and Potassium hydroxide KOH, then, the solution was filtrated, dry, and weighted.

### 2.3. Method of precipitation

50 ml of heavy metal salts solution such as Cu $(NO_3)_2$ .$3H_2O$, $AgNO_3$, $MgSO_4$, $NiSO_4$, Fe $(NO_3)_3$ .$9H_2O$, Cr $(NO_3)_2$ .$9H_2O$, $CdSO_4.4H_2O$, Pb $(NO_3)_2$, $ZnSO_4$. $7H_2O$ and, $MnSO_4$, were added to 50 ml of 0.1 M solution of $H_2C_2O_4$ acid and the temperature was adjusted to 25 degrees and the pH value to 7-8 using a buffer solution of $H_2C_2O_4$ acid and $Na_2C_2O_4$ and the solution was left for 24 hours to ensure the complete precipitation process. Then the precipitate was filtered, washed with distilled water, dried and the precipitate was weighed and the precipita-

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

tion efficiency was calculated under those conditions. The work was repeated with three other precipitating agents; $H_2C_2O_4$ acid, ($K_4[Fe(CN)_6]$) and KOH) then the solution was filtrated, dry, and weighted.

**2.4. Digestion of the percipitation:**

The percipitation process took place for a period of one to three hours on a water bath or leaving it for a period of 12-24 hours at room temperature. During the digestion process, crystallization is continuously re-crystallized, which leads to elimination of pockets trapped inside the percipitation, Get rid of impurities, Creating bridges, which leads to the formation of larger granules, Dissolution of small granules and growth of large granules. It is the weight of the substance to be determined (the precipitate) contained in one gram of the precipitate. The gravimetric coefficient = the atomic weight of the element to be determined / the molecular weight of the precipitate.

$$\text{The gravimetric coefficient}(GC) = \frac{At.Wt}{M.Wt} \text{---} -(1)$$

**2.5. Electrolysis cell**

Electrochemical cell design, electrode setup, and principles of operation (maximum capacity of 100 mL of sample or electrolyte reservoir) and all the other apparatus are shown in Fig. 1. The device was composed of (a) a jacketed electro- chemical cell, a conventional three-electrode arrangement with a (b) Ag/AgCl (KClsat.) reference electrode, (c) a platinum wire auxiliary electrode, and graphite electrode.

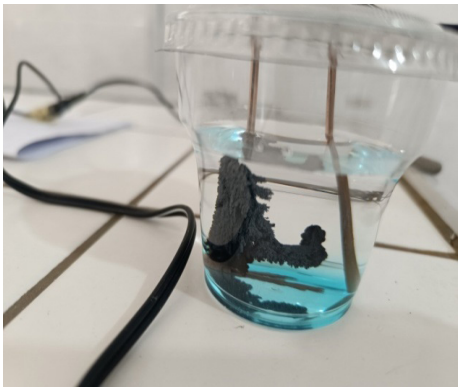


**Figure.(1).** Shows the electrolysis cell for $CdSO_4.8H_2O$.

**2.6. Electrophoretic Precipitation Method**

The feasibility of this process for the recovery of (HMs) from aqueous solutions was determined. The effects of three operational parameters, namely voltage, initial ion concentration, and water flow, on the recovery of metals and water were investigated and optimized. The feasibility of this process for the extraction of heavy metals from aqueous solutions was determined. The effects of three operational parameters were

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

investigated: voltage using a voltage range of 5 –12 V, initial ion concentration in all 0.1 M (HM) ion solutions, and the surface area of the electrodes used for electrodeposition. The process also included a 24-hour holding time, electrode drying, weighing, and calculating the amount of precipitate formed on the cathode as a result of the deposition process. The process also included calculating the deposition efficiency for solutions with a known concentration of 0.1 M. The same conditions were then applied to water associated with the oil and the precipitation of (HM) ions. The accompanying soil was also prepared by placing 100 grams of the accompanying soil in a liter of distilled water with continuous stirring for two hours, then filtering the solution and taking 100 ml of the filtered solution and precipitating the ions in it by electro-precipitation under the same previous conditions.

**2.7. statistical determination**

-Among these statistical indicators are the following:

-Variation coefficient CV and it get from the relationship:

$$CV = \frac{S}{X} \times 100 \quad ----- (2)$$

-where S is the standard deviation and it get from the relation:

$$S = \sqrt{\frac{\sum (X - x)^2 \ * f}{\sum f - 1}} \quad ------- (3)$$

-where X is the mean, which is the arithmetic average of the values, and it get from the relationship:

$$X = \frac{\sum f * x}{\sum f} \quad ------- (4)$$

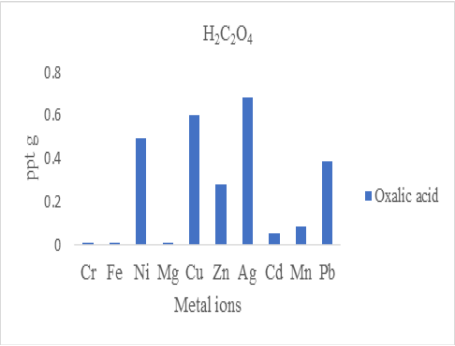
**3. RESULTS**

**3.1. Precipitate HMs by oxalic acid.**

**Table .(1)**. The GC, ppt, % eff. S, CV, and K sp., of heavy metal precipitate with oxalic acid.

| Ppt/g | Cr | Fe | Ni | Mg | Cu | Zn | Ag | Cd | Mn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| GC | 0.37 | 0.39 | 0.40 | 0.21 | 0.35 | 0.42 | 0.35 | 0.35 | 0.38 | 0.70 |
| ppt | 0.01 | 0.01 | 0.495 | 0.01 | 0.605 | 0.28 | 0.684 | 0.055 | 0.085 | 0.349 |
| .eff % | 1.5% | 1.4% | 70% | 1.8% | 80% | 37% | 46% | 8% | 12% | 25% |
| S | 0.001 | 0.001 | 0.05 | 0.001 | 0.05 | 0.02 | 0.05 | 0.001 | 0.001 | 0.02 |
| CV | 10% | 10% | 10% | 10% | 8% | 7% | 7% | 2% | 12% | 6% |
| .K sp | - | - | - | $10^{-5}\times8$ | - | $10^{-8}\times2.7$ | - | $10^{-8}\times1.5$ | - | - |

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018




From Figure.(2). The relationship between the metals oxalate which precipitated by adding 50 ml of 0.1M of oxalic acid to 50 ml 0.1M of metal ions.

**3.2. Precipitate HMs by ($K_4[Fe(CN)_6]$).**

**Figure.(2).** shows the weight ppt of metal oxalate in 100 ml of solution.

**Table .(2)**. The GC, ppt, % eff. S, CV, and K sp., of heavy metal precipitate with potassium ferricyanide.

| Ppt/g | Cr | Fe | Ni | Mg | Cu | Zn | Ag | Cd | Mn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| G C | 0.35 | 0.37 | 0.38 | 0.18 | 0.41 | 0.42 | 0.92 | 0.32 | 0.37 | 0.92 |
| ppt | 0.278 | 1.804 | 0.599 | 0.11 | 2.512 | 0.517 | 0.97 | 2.394 | 1.532 | 0.902 |
| .eff % | 23% | 99% | 40% | 8% | 99% | 33% | 42% | 99% | 99% | 40% |
| S | 0.03 | 0.06 | 0.05 | 0.01 | 0.05 | 0.02 | 0.05 | 0.08 | 0.05 | 0.05 |
| CV | 10% | 3% | 10% | 10% | 2% | 4% | 6% | 3% | 3% | 6% |
| .K sp | - | $10^{-11}\times1.21$ | - | - | $^{16-}10\times1.3$ | - | - | - | - | - |

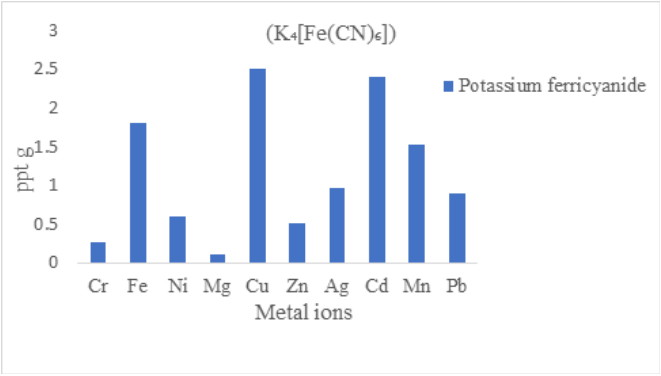



**Figure.(3).** Shows the weight ppt of metal ferricyanide in 100 ml of solution.

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

From Figure.(3). The relationship between the metals ferricyanide which was precipitated by adding 50 ml of 0.1M of ($K_4[Fe(CN)_6]$) to 50 ml 0.1M of metal ions.

### 3.3. Precipitate HMs by potassium hydroxide.

Table 3. The GC, ppt, % eff. S, CV, and K sp., of heavy metal precipitate with KOH

| Ppt/g | Cr | Fe | Ni | Mg | Cu | Zn | Ag | Cd | Mn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| G C | 0.6 | 0.63 | 0.63 | 0.41 | 0.65 | 0.65 | 0.86 | 0.58 | 0.61 | 0.86 |
| ppt | 2.276 | 0.092 | 0.349 | 0.473 | 1.004 | 0.329 | 0.765 | 1.452 | 1.313 | 0.225 |
| .eff % | 99% | 29% | 76% | 56% | 97% | 66% | 99% | 99% | 99% | 19% |
| S | 0.01 | 0.001 | 0.03 | 0.05 | 0.05 | 0.03 | 0.08 | 0.08 | 0.07 | 0.03 |
| CV | 1% | 1% | 10% | 10% | 5% | 9% | 10% | 6% | 6% | 13% |
| .K sp | $^{31-}$10× 6.3 | $^{38-}$10×4 | $^{15-}$10×2.0 | $^{11-}$10×1.8 | $^{20-}$10×2.2 | $^{17-}$10×1.2 | - | - | - | $^{15-}$10×1.2 |

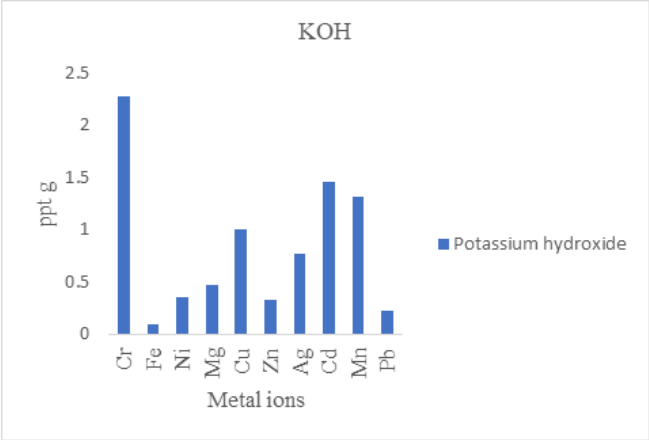



**Figure. (4).** Shows the weight ppt of metal hydroxide in 100 ml of solution.

From Fig.4. The relationship between the metals hydroxide which precipitated by adding 50 ml of 0.1M of potassium hydroxide to 50 ml 0.1M of metal ions.

### 3.4. Precipitate HMs by electrolysis.

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

**Table .(4)**. The ppt, % eff. S, CV, and V of heavy metal precipitate by electrolysis.

| Ppt/g | Cr | Fe | Ni | Mg | Cu | Zn | Ag | Cd | Mn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| ppt | 0.645 | 0.633 | 0.864 | 0.212 | 0.107g | 0.239 | 0.674 | 0.761 | 0.382 | 0.382 |
| % eff. | 62% | 57% | 75% | 44% | 9% | 18% | 62% | 90% | 35% | 19% |
| S | 0.06 | 0.06 | 0.06 | 0.02 | 0.01 | 0.03 | 0.05 | 0.06 | 0.03 | 0.03 |
| CV | 10% | 10% | 8% | 10% | 9% | 12% | 8% | 9% | 8% | 8% |
| V | - 0.91 | - 0.77 | - 0.23 | -2.3 | 0.34 | -0.76 | 0. 80 | 0.40 | -1.18 | − 0.13 |

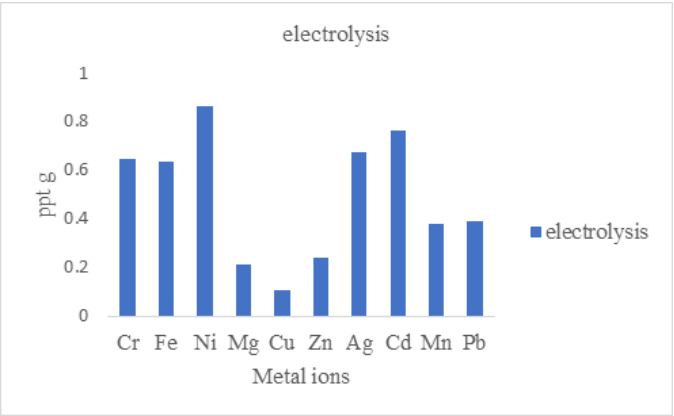



**Figure. (5).** Shows the weight ppt of metals at electrodes by electrolysis.

From Figure.(5). The relationship between the metals which was precipitated by electrolysis. Fig.5. displays the relationship between the metals which precipitated by electrolysis. The findings show that Cr, Fe, Ni, Ag, Cd, Mn, and Pb were the highest precipitated than other metal ions by electrolysis. The percentage of deposition on the negative electrode in the electrolytic cell is due to the value of the reduction potential of the ions on the cathode when all other factors are constant, which made the values of the percentage of deposition consistent with the values of the reduction potentials in order. Cr = − 0.91 V, Fe = - 0.77 V, Ni = − 0.23 V, Ag = + 0. 80 V, Cd = − 0.40 V, Mn = −1.18 V, Pb = − 0.13 V

**3.5. The differences between the precipitation of heavy metals by chemical precipitation and electrolysis**

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

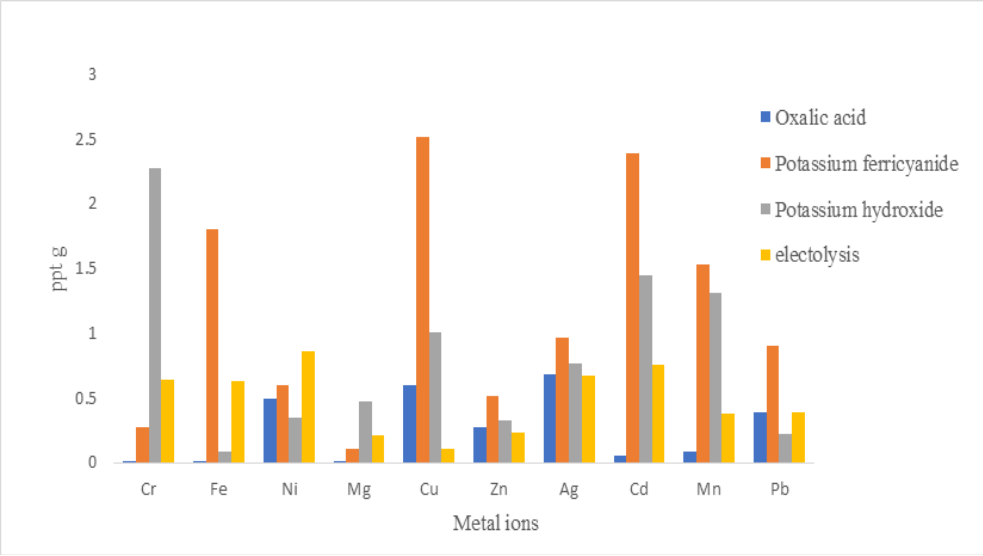



**Figure.(6).** Shows The differences between chemical precipitation and electrolysis

### 3.6. Application

#### 3.6.1. The differences between chemical precipitation of heavy metals at soil and water associated with oil.

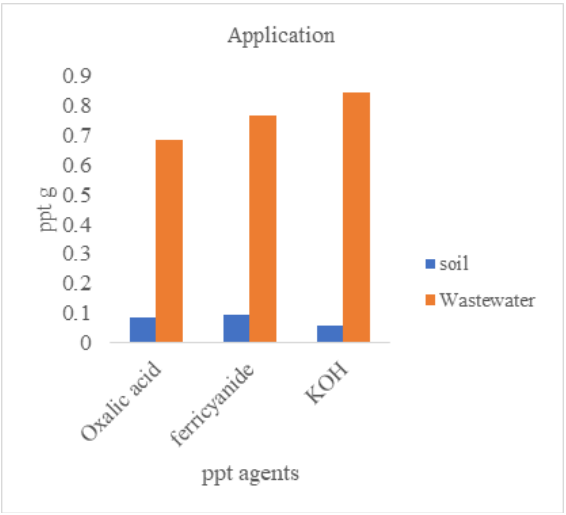



**Figure.(7).** Shows the weight ppt of metal oxalate, ($K_4[Fe(CN)_6]$)and KOH in 100 ml of solution at water associated with oil and soil.

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

**3.6. 2. The differences between the precipitation of heavy elements by electrodeposition of both soil and water associated with oil.**

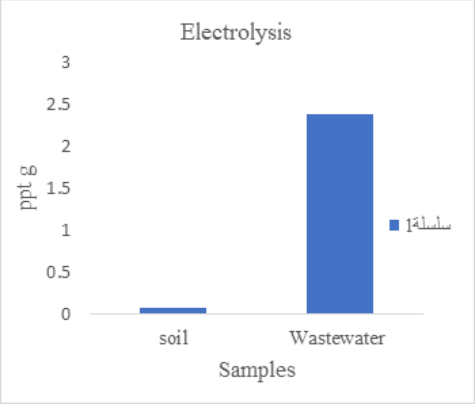



**Figure. (8).** Shows the weight ppt of metals at electrodes by electrolysis.

## 4. DISSECTIONS

**Table (1).** Shows that Cu, Ni and Ag have the highest deposition efficiency of 80%, 70% and 0.46 respectively, with oxalate, at standard deviation S= 0.05 and a coefficient of variation of C. V= 8%, 10% and 7% respectively.

**From figure. (2)**, shows that Ag, Cu, Ni, and Pb were the highest precipitated than other metal ions by oxalic acid. oxalic acid facilitated to the removal of $Pb^{2+}$ [42], $K_{sp}$. of $Ag_2C_2O_4$ white = $5.40 \times 10^{-12}$, $CuC_2O_4 = 2.9 \times 10^{-8}$, $NiC_2O_4 = 1\ 10^{-7}$, and $PbC_2O_4$ white = $4.8 \times 10^{-10}$, The results of the precipitation of heavy element ions using $H_2C_2O_4$ were consistent with the solubility product of each of the precipitates: $Ag_2C_2O_4$, then Cu, then Ni, then Pb.

**Table (2).** Shows that Cu, Fe, Cd and Mn have the highest deposition efficiency of 99%, 99%, 0.99 and 0.99 respectively, with standard deviations S= 0.05, 0.06 and 0.08 and a coefficient of variation of CV= 2%, 3%, 3% and 3% respectively, and the solubility product of K sp. of Cu is $1.3\times10^{-16}$ and K sp. of Fe $1.21 \times 10^{-11}$, respectively.

**From figure. (3),** shows that Fe, Cu, Cd, Pb, and Mn were the highest precipitated than other metal ions by Potassium ferricyanide. $K_{sp.}$ for Fe $=1.21 \times 10^{-11}$, [43].

**Table (3).** Shows that Cr, Ag, Cd and Mn have the highest deposition efficiency of

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

99%, 99%, 0.99 and 0.99 respectively, with standard deviations S= 0.01, 0.08, 0.08 and 0.5, and coefficients of variation CV = 1%, 10%, 6% and 6% respectively, and the solubility product Ksp. of Cr is $6.3\times10^{-31}$ and of Pb is $1.2\times10^{-15}$ respectively.

**In figure. (4),** shows that Cr, Cu, Cd, and Mn were the highest precipitated than other metal ions by potassium hydroxide KOH, $K_{sp.}$ Cr $(OH)_3$ gray-green = $6.3 \times 10^{-31}$, Cu $(OH)_2$ = pale blue = $2.2 \times 10^{-20}$, Cd $(OH)_2$ = $7.20 \times 10^{-15}$, Mn $(OH)_2$ light pink = $1.9 \times 10^{-13}$ [44]. The results of the precipitation of heavy element ions using KOH were consistent with the solubility product of each of the precipitates: Cr, Cu, Cd, Mn.

**Table (4)** Shows that through electrodeposition, cadmium, nickel, chromium and silver have the highest deposition efficiencies of 90%, 75%, 0.62 and 0.62 respectively, with standard deviations of 0.01, 0.08, 0.08 and 0.5 and coefficient of variation of 9%, 8%, 6% and 5% respectively, and reduction potentials as shown in Table 4.

**From figure. (5),** shows that Cr, Fe, Ni, Ag, Cd, Mn, and Pb were the highest precipitated than other metal ions by electrolysis. The percentage of deposition on the negative electrode in the electrolytic cell is due to the value of the reduction potential of the ions on the cathode when all other factors are constant, which made the values of the percentage of deposition consistent with the values of the reduction potentials in order. Cr = − 0.91 V , Fe = - 0.77 V, Ni = − 0.23 V, Ag = 80 .0+ V, Cd = − 0.40 V, Mn = −1.18 V, Pb = − 0.13 V

**From figure. (6)**, shows that Cr, Fe, Cu, Cd, and Mn were the highest precipitated than other metal at all, the order of the most precipitated elements was approximately consistent with both the solubility constant and the reduction potentials.

**From figure. (7),** shows that the highest metal ions were precipitated from wastewater than other metal the ions were precipitated from soil due to the concentration of metal ion in wastewater was greater the concentration of metal ions at soil.

**From figure.(8),** shows that the highest metal ions were precipitated from wastewater by electrodeposition than other metal the ions were precipitated from soil by electrodeposition due to the concentration of metal ion in wastewater was greater the concentration of metal ions at soil.

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

## 5. CONCLUSION

Chemical precipitation, offers a relatively simple and cost-effective approach for removing heavy metals (HMs) from contaminated water. The use of chelating agents such as (KOH), ($K_4[Fe(CN)_6]$), and ($H_2C_2O_4$) enables efficient removal of multiple metal ions simultaneously. While electrochemical methods can also remove heavy metals, they generally require more complex setups and higher energy input compared to chemical precipitation. Electrochemical precipitation may be particularly useful for the selective extraction of specific heavy metals.

Chemical precipitating agents such as KOH, $K_4[Fe(CN)_6]$, and $H_2C_2O_4$ act as chemical precipitating and chelating agents. These react with heavy metal ions in water and aqueous soil solutions, forming insoluble compounds that then precipitate. This process effectively removes various heavy metals from oil-related water, such as Cr, Fe, Ni, Mg, Cu, Zn, Ag, Cd, and Pb, with selective efficacy. The effectiveness of chemical precipitation and electrochemical precipitation (using a cathode) for the removal of heavy metals from oil-related water has been compared. Both methods have been shown to be capable of removing heavy metals, but they operate through different mechanisms. Chemical precipitation involves adding precipitating agents (such as KOH or $H_2C_2O_4$) that react with metal ions to form insoluble compounds, which then precipitate from solution. Electrochemical precipitation involves applying an electric current to reduce metal ions at a cathode, forming solid metal deposits. Different precipitating chemicals have been shown to exhibit varying efficiencies in precipitating heavy metals at varying rates. Oxalic acid ($H_2C_2O_4$) was particularly effective at precipitating cadmium or magnesium, while $K_4[Fe(CN)_6]$) may be more effective at precipitating metals such as copper or silver. Potassium hydroxide is known to raise the pH of water, facilitating the precipitation of metal hydroxides, and is particularly effective for metals such as copper and nickel. $K_4[Fe(CN)_6]$) is effective at forming stable complexes with metals such as copper and zinc, often resulting in highly efficient removal. $H_2C_2O_4$ is particularly effective at removing metals such as calcium, magnesium, and iron. These metals are harmful and carcinogenic and can accumulate in plants, animals, and humans, causing a range of ail-

University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629
National Library of Libya, Legal number: 154/2018

ments, including organ damage and cancer. Therefore, treating water contaminated with heavy metals from petroleum activities is critical to preventing environmental damage and protecting humans from disease.

**6.ACKNOWLEDGEMENT**

We thank of El-Khalij oil company in Elwahate Jalu, Libya for aid and cooperation to complete this paper. We also thank of an engineering and workers of El-Khalij oil company for the cooperation and aids.

**7. REFERENCES**

1.Tao, H. C., Lei, T., Shi, G., Sun, X. N., Wei, X. Y., Zhang, L. J., & Wu, W. M. (2014). Removal of heavy metals from fly ash leachate using combined bioelectrochemical systems and electrolysis. Journal of Hazardous materials, 264, 1-7. https://doi.org/10.1016/j.jhazmat.2013.10.057

2.Shim, H. Y., Lee, K. S., Lee, D. S., Jeon, D. S., Park, M. S., Shin, J. S., ... & Chung, D. Y. (2014). Application of electrocoagulation and electrolysis on the precipitation of heavy metals and particulate solids in washwater from the soil washing. Journal of Agricultural Chemistry and Environment, 3(04), 130. http://creativecommons.org/licenses/by/4.0/

3.Luo, H., Liu, G., Zhang, R., Bai, Y., Fu, S., & Hou, Y. (2014). Heavy metal recovery combined with $H_2$ production from artificial acid mine drainage using the microbial electrolysis cell. Journal of hazardous materials, 270, 153-159. DOI: 10.1016/j.jhazmat.2014.01.050

4.Colantonio, N. (2016). Heavy metal removal from wastewater using microbial electrolysis cells (Doctoral dissertation). https://doi.org/10.1016/j.jhazmat.2014.01.050

5.Fischer, R., Seidel, H., Rahner, D., Morgenstern, P., & Löser, C. (2004). Elimination of heavy metals from leachates by membrane electrolysis. Engineering in life sciences, 4(5), 438-444. https://doi.org/10.1002/elsc.200420049

6.Tsai, L., Fang, H., Lin, J., Chen, C., & Tsai, F. (2009). Recovery and stabilization of heavy metal sludge (Cu and Ni) from etching and electroplating plants by electrolysis and sintering. Science in China Series B: Chemistry, 52, 644-651. https://doi.org/10.1007/s11426-009-0047-6

7.Chakraborty, I., Sathe, S. M., Khuman, C. N., & Ghangrekar, M. M. (2020). Bioelectrochemically powered remediation of xenobiotic compounds and heavy metal toxicity using microbial fuel cell and microbial electrolysis

**University of Benghazi©2025 All rights reserved.** **ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

cell. Materials Science for Energy Technologies, 3, 104-115. https://doi.org/10.1016/j.mset.2019.09.011

8.Fischer, R., Seidel, H., Rahner, D., Morgenstern, P., & Löser, C. (2002). Elimination of heavy metals from process waters of the bioleaching process by electrolysis. Journal of Soils and Sediments, 2, 166-168. https://doi.org/10.1007/BF02991035

9.Basha, C. A., Bhadrinarayana, N. S., Anantharaman, N., & Begum, K. M. S. (2008). Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor. Journal of Hazardous Materials, 152(1), 71-78. https://doi.org/10.1016/j.jhazmat.2007.06.069

10.Kim, S. O., Moon, S. H., & Kim, K. W. (2001). Removal of heavy metals from soils using enhanced electrokinetic soil processing. Water, Air, and Soil Pollution, 125, 259-272. https://doi.org/10.1023/A:1005283001877

11.Gomelya, N., Melnychenko, Y., & Radovenchyk, I. (2018). Purification of wastewater from the ions of copper, zinc, and lead using an electrolysis method. Восточно-Европейский журнал передовых технологий, (6 (10)), 42-48. http://nbuv.gov.ua/UJRN/Vejpte_2018_6(10)7.

12.Bazrafshan, E., Mohammadi, L., Ansari-Moghaddam, A., & Mahvi, A. H. (2015). Heavy metals removal from aqueous environments by electrocoagulation process–a systematic review. Journal of environmental health science and engineering, 13, 1-16. https://doi.org/10.1186/s40201-015-0233-8

13.He, D., Luo, Z., Zeng, X., Chen, Q., Zhao, Z., Cao, W., ... & Chen, M. (2022). Electrolytic manganese residue disposal based on basic burning raw material: Heavy metals solidification/stabilization and long-term stability. Science of The Total Environment, 825, 153774. https://doi.org/10.1016/j.scitotenv.2022.153774

14.Peng, G., & Tian, G. (2010). Using electrode electrolytes to enhance electrokinetic removal of heavy metals from electroplating sludge. Chemical Engineering Journal, 165(2), 388-394. https://doi.org/10.1016/j.cej.2010.10.006

15.Gajda, I., Stinchcombe, A., Greenman, J., Melhuish, C., & Ieropoulos, I. (2017). Microbial fuel cell–A novel self-powered wastewater electrolyser for electrocoagulation of heavy metals. international journal of hydro-

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

gen energy, 42(3), 1813-1819. https://doi.org/10.1016/j.ijhydene.2016.06.161

16.Peng, C., Liu, Y., Bi, J., Xu, H., & Ahmed, A. S. (2011). Recovery of copper and water from copper-electroplating wastewater by the combination process of electrolysis and electrodialysis. Journal of hazardous materials, 189(3), 814-820. https://doi.org/10.1016/j.jhazmat.2011.03.034

17.Liu, Y., Lu, M., Yin, Y., Zhou, J., Qu, G., Zhang, Y., ... & Wang, T. (2022). Self-catalytic Fenton-like reactions stimulated synergistic Cu-EDTA decomplexation and Cu recovery by glow plasma electrolysis. Chemical Engineering Journal, 433, 134601. https://doi.org/10.1016/j.cej.2022.134601

18.Koomson, D. A., Huang, J., Li, G., Miwornunyuie, N., Ewusi-Mensah, D., Darkwah, W. K., & Opoku, P. A. (2021). Comparative studies of recirculatory microbial desalination cell–microbial electrolysis cell coupled systems. Membranes, 11(9), 661. https://doi.org/10.3390/membranes11090661

19.Basha, C. A., Somasundaram, M., Kannadasan, T., & Lee, C. W. (2011). Heavy metals removal from copper smelting effluent using electrochemical filter press cells. Chemical engineering journal, 171(2), 563-571. https://doi.org/10.1016/j.cej.2011.04.031

20.Gunatilake, S. K. (2015). Methods of removing heavy metals from industrial wastewater. Methods, 1(1), 14. www.jmess.org

21.Cai, W. F., Geng, D. L., & Wang, Y. H. (2016). Assessment of cathode materials for Ni (ii) reduction in microbial electrolysis cells. RSC advances, 6(38), 31732-31738. https://doi.org/10.1039/C6RA02082H

22.Rosestolato, D., Bagatin, R., & Ferro, S. (2015). Electrokinetic remediation of soils polluted by heavy metals (mercury in particular). Chemical Engineering Journal, 264, 16-23. https://doi.org/10.1016/j.cej.2014.11.074

23.Issabayeva, G., Aroua, M. K., & Sulaiman, N. M. (2006). Electrodeposition of copper and lead on palm shell activated carbon in a flow-through electrolytic cell. Desalination, 194(1-3), 192-201. https://doi.org/10.1016/j.desal.2005.09.029

24.Choubey, S., Goswami, P., & Gautam, S. (2021). Recovery of copper from waste PCB boards using electrolysis. Materials Today: Proceedings, 42, 2656-2659. https://doi.org/10.1016/j.matpr.2020.12.596

25.Flis-Kabulska, I., Flis, J., Sun, Y., & Zakroczymski, T. (2015). Hydrogen evolution on plasma carburised nickel and effect of iron

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

deposition from the electrolyte in alkaline water electrolysis. Electrochimica Acta, 167, 61-68. https://doi.org/10.1016/j.electacta.2015.03.132

26.Li, W., Gao, S., Wu, L., Qiu, S., Guo, Y., Geng, X., ... & Liu, L. (2013). High-density three-dimension graphene macroscopic objects for high-capacity removal of heavy metal ions. Scientific reports, 3(1), 2125. https://doi.org/10.1038/srep02125

27.Xue, F., Wang, T., Zhou, M., & Hou, H. (2020). Self-solidification/stabilisation of electrolytic manganese residue: Mechanistic insights. Construction and Building Materials, 255, 118971. https://doi.org/10.1016/j.conbuildmat.2020.118971

28.Al Aji, B., Yavuz, Y., & Koparal, A. S. (2012). Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes. Separation and Purification Technology, 86, 248-254. https://doi.org/10.1016/j.seppur.2011.11.011

29.Chen, F., Li, X., Luo, Z., Ma, J., Zhu, Q., & Zhang, S. (2018). Advanced treatment of copper smelting wastewater by the combination of internal micro-electrolysis and electrocoagulation. Separation Science and Technology, 53(16), 2639-2646. https://doi.org/10.1080/01496395.2018.1463265

30.Wahyono, Y., Irviandi, R., Lo, N. K., Rahman, M. I. A., Herdiansyah, F., Haliza, B. T., ... & Pratiwi, N. I. (2022, October). Producing Fe and Cu ions and oxides in water with electrolysis as artificial liquid waste. In IOP Conference Series: Earth and Environmental Science (Vol. 1098, No. 1, p. 012032). IOP Publishing. DOI 10.1088/1755-1315/1098/1/012032

31.Kumar, V. (2017). A review on the feasibility of electrolytic treatment of wastewater: Prospective and constraints. constraints, 2(1), 52-62. www.aesacademy.org

32.Du, B., Zhou, C. B., & Duan, N. (2014). Recycling of electrolytic manganese solid waste in autoclaved bricks preparation in China. Journal of Material Cycles and Waste Management, 16, 258-269. https://doi.org/10.1007/s10163-013-0181-2

33.Wang, J., Huang, Z., Yang, D., Zeng, X., Chen, M., Shu, J., ... & Xiao, Z. (2021). A semi-scaled experiment for metals separating and recovering from waste printed circuit boards by slurry electrolysis. Process Safety and Environmental Protection, 147, 37-44. https://doi.org/10.1016/j.psep.2020.09.030

34.Darmawan, D. U., & Sriwahyuni, S. U.

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

(2021). Removal of Heavy Metal Mercury (Hg) Liquid Waste through Electrolysis Method in Paya Ateuk Village, Pasie Raja District, South Aceh. The Indonesian Journal of Public Health, 8(2). DOI: https://doi.org/10.35308/j-kesmas.v8i2.4062

35.Petsriprasit, C., Namboonmee, J., & Hunsom, M. (2010). Application of the electrocoagulation technique for treating heavy metals containing wastewater from the pickling process of a billet plant. Korean Journal of Chemical Engineering, 27, 854-861. https://doi.org/10.1007/s11814-010-0145-3

36.Ayub, S., Siddique, A. A., Khursheed, M. S., Zarei, A., Alam, I., Asgari, E., & Changani, F. (2020). Removal of heavy metals (Cr, Cu, and Zn) from electroplating wastewater by electrocoagulation and adsorption processes. Desalin Water Treat, 179, 263-271. doi: 10.5004/dwt.2020.25010

37.Kakakhel, L., Lutfullah, G., Bhanger, M. I., Shah, A., & Niaz, A. (2007). Electrolytic recovery of chromium salts from tannery wastewater. Journal of Hazardous Materials, 148(3), 560-565 . https://doi.org/10.1016/j.jhazmat.2007.03.011

38.Kadhim, N. R., Abbar, A. H., & Flayeh, H. M. (2023). Removal of copper from a simulated wastewater by electromembrane extraction technique using a novel electrolytic cell provided with a flat polypropylene membrane infused with 1-octanol and DEHP as a carrier. Case Studies in Chemical and Environmental Engineering, 8, 100430. https://doi.org/10.1016/j.cscee.2023.100430

39.Kawachi, T., & Kubo, H. (1999). Model experimental study on the migration behavior of heavy metals in electrokinetic remediation process for contaminated soil. Soil science and plant nutrition, 45(2), 259-268. https://doi.org/10.1080/00380768.1999.10409341

40.Chen, H., Long, Q., Zhang, Y., & Qin, L. (2019). Simultaneous immobilization of $NH_4^+$ and $Mn^{2+}$ from electrolytic manganese residue using phosphate and magnesium sources. RSC advances, 9(8), 4583-4590. DOI: 10.1039/C8RA09615E

41.Matter, H. A., Ayad, T. M., & Alkatly, A. A. (2022). Treatment of Heavy Metals in Water Accompanied with Oil and A Soil Using some Expired Drugs at Al-Wahat/ Libya. Journal of Pure & Applied Sciences, 21(2), 114-119. DOI: 10.51984/JOPAS.V21I2.2046

42.Zeng, Q., Wang, S., Hu, L., Zhong, H.,

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018

He, Z., Sun, W., & Xiong, D. (2021). Oxalic acid modified copper tailings as an efficient adsorbent with super high capacities for the removal of $Pb^{2+}$. Chemosphere, 263, 127833. https://doi.org/10.1016/j.chemosphere.2020.127833

43.Bellomo, A., Casale, A., & De Marco, D. (1973). Formation of ferricyanides-I silver (I), copper (II) and cadmium (II). Talanta, 20(3), 335-338.https://doi.org/10.1016/0039-9140(73)80029-3

44.https://www.chm.uri.edu/weuler/chm112/refmater/KspTable.html

**University of Benghazi©2025 All rights reserved. ISSN: Online 2790-1637, Print 2790-1629**
National Library of Libya, Legal number: 154/2018