

Characterizations of Precipitated Zinc Powder Produced by Selective Leaching Method

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This work investigated the influence of concentration and applied potential on the characteristics of zinc powder (purity, apparent density, morphology, particle size distribution, and particle zeta potential) produced by the electrochemical process from waste brass. High-purity zinc powder is obtained using selective leaching of industrial brass waste in acidic, neutral, and alkaline solutions. The free immersion method with and without voltage using linear polarization technique is used. In the electrochemical process, hydrochloric acid HCl in three different concentrations (0.1, 0.2, and 0.3) M is used. The time and the distance between the electrodes are set to be 30 min and 3 cm, respectively. It has been found that the percentage purity is 98%, 96%, and 94% for the acidic, neutral, and alkaline solutions, respectively. In addition, the morphology of zinc powder analyzed by SEM was dendritic and mossy. It has been recorded that the purity of zinc increases with the increase of the concentration and applied potential. The highest value of purity for zinc powder was %98.58 in 1000 mV and 0.3M concentration for graphite cathode.

Keywords: Brass alloy, Selective leaching, Dezincification corrosion, Linear polarization and Purity

1. Introduction

Brass is an alloy consisting mainly of copper, zinc, and some elements in a few proportions. It is characterized by its attractive appearance, its ability to form and forge, while retaining its hardness, good thermal and electrical conductivity, and its resistance to corrosion, especially in moisture and other atmospheric media. Because of these characteristics and its relative ease of production, it has become one of the most widely used alloys, including: Nuts and bolts or bolts, Terminals, Jets, Taps and Injectors. Because of the many uses of these alloys, a lot of industrial waste harmful to the environment was generated. The present work aims to use of dezincification corrosion in the preparation of high-purity zinc powder from brass-industrial waste. dezincification is the removal of zinc from brass- alloys by de-alloying or selective leaching. In such cases, where the alloy is polarized, the less noble component of the alloy is selectively dissolved, leaving the remaining more noble component [1,2]. Dezincification can occur uniformly or in a localized fashion. In acid solutions, occurs uniformly, while locally occurs in

alkaline or neutral solutions. The actual mechanism of dezincification is still not completely agreed upon. Zinc and copper possess a different electrochemical behavior if each element is taken separately. Depending on the pourbaix diagrams, the electrochemical behavior of these two elements can be known. Fig. 1 shows the pourbaix diagram of zinc. It can be shown from the diagram that, the dissolution zone of zinc is located in the ranges of

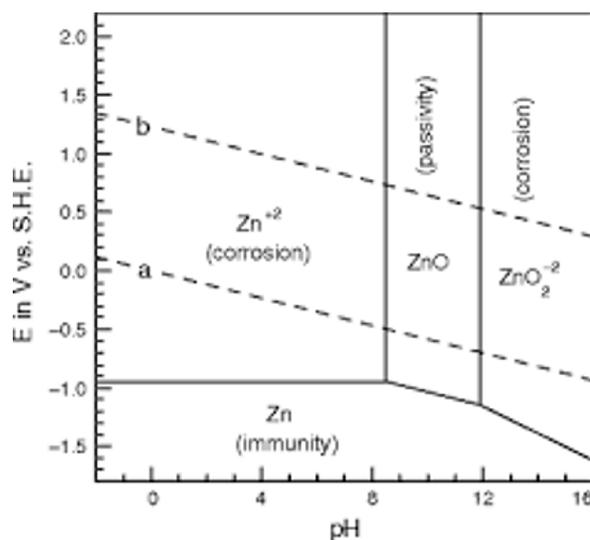


Fig. 1. Pourbaix diagram of zinc in aqueous solutions

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voltages between -0.8 to + 1.2 volts and in arrange of pH between 0 and 10, This explains why this range was chosen in the present [3,4].

In chloride solution, zinc dissolves by a vigorous reaction as shown equation (1) [1-6].



Actually, zinc reacts with the hydrogen ions of the solution and the chloride ion is not involved in the reaction, therefore the above equation can be written in the simplified form as equation (2).



Hence, zinc is oxidized to zinc ions and hydrogen ions are reduced to hydrogen. Therefore, the reaction can be conveniently divided into two partial reactions; the oxidation of zinc and the reduction of hydrogen ions, which takes place in the absence of oxygen or in small quantities, according to the equation's (3) and (4);



But if the medium is saturated with oxygen, the reduction reaction is occurred by the equation (5) in natural and alkaline solutions.



When copper is present with zinc, a potential difference is generated between them, because copper and zinc have a different oxidation potential to form ions in the solution. Zinc oxidizes more easily than copper, and this potential difference is what stimulates the reactions. Zinc oxidation process occurs in which zinc ions are liberated, which are reduced on the cathode electrode to form zinc atoms, which are transformed into pure zinc powder [7]. As previously discussed [6,7], special precautions must be taken to avoid the dezincification of brass. In one case, the zinc corrodes preferentially and is removed from the alloy, leaving the copper behind. Both copper and zinc corrode and are removed from the alloy in the other,

although copper ions in solution plate back onto the surface. In the first suggestion, the metal's surface should become porous after dezincification but otherwise remain the same. Although more complicated, the second proposal is required to explain cases where copper crystals develop on the surface following dezincification [8]. Recently, a third mechanism has gained traction [9], In this method, the zinc dissolves from the brass, leaving behind the copper, and the copper then rearranges on the metal's surface, resulting in the formation of copper crystals. Because the copper on the surface is attracted by negative ions in the solution, this rearrangement is allowed. The attraction is not strong enough to dissolve the copper, but it does reduce the copper's binding to the surface, allowing the copper to migrate more quickly [9]. Zinc is an important basic metal used in a variety of industries [1]. Some zinc was recovered from secondary processes such as galvanizing, electric arc furnace flue dust and brass smelting, smelting, zinc dross, zinc ash, scrap recycling, casting, and automotive shredder waste. Zinc is found in secondary resources in metallic, oxide, and alloy forms. And it is associated with varying degrees of impurities depending on its source [3]. The materials may be used to recover metallic values, or they could be discarded. Dust particles have a chemical character; hence they are classified as hazardous waste. Brass is widely used in various industries due to its stability in aggressive environments, The environment in which chloride ions are present is one of these [10,11]. Also, it was proved that the dissolution of copper in chloride solutions depended largely on the concentration of chloride ions [12,13] and corrosion processes in these environments are a major problem [14] But today, in our research, we will use this corrosion that occurs in brass to our advantage in extracting the most important minerals used in our daily lives.

2. Experimental Methods

The specimens of scrap material (brass waste) of dimensions of (4 cm × 8 cm) were employed for corrosion dezincification tests. Samples were smoothed with a polishing paper composed of silicon carbide with a granular size of 150, 200, 500, 800 microns. The specimens were rolled to a thickness of about 1 mm.

Table 1. The chemical analysis of brass waste

Elements	Cu	Zn	Other elements
Percentages % wt%	64	35.4	rest

Samples were cleaned using 96% ethanol by an ultrasound bath for 10 minutes then that were cleaned by distilled water. Table 1 shows the chemical composition of these specimens using the PMI-Master Pro OES spectrometer, which showed 35.4 % zinc content.

2.1 Dezincification process

Two stages were followed for this process in the first stage two electrodes were used one as cathode and the second as anode. The cathode and anode were made of stainless steel and brass, respectively. of applied potential that used also are different (1000, 1500, 2000, 2500, and 3000) mV, it was expected that at these potentials dezincification occurs in which zinc leaves the brass alloy and zinc element begins to release as zinc ions. The time of zinc release is beginning after 30 min of reaching steady state potential with different rate at room temperature the device of dezincification consists from Pyrex cell with dimensions (25, 12.5, and 6) cm. two parallel electrode one is working as anode electrode and the other made from stainless steel working as cathode electrode. The electrodes immersion in electrolyte solution with distance 3 cm where through a holder bridge made from Teflon as shown in Fig. 2 and used power supply with variable voltage and current was attached the negative side was connected stainless steel electrode, while specimen (anode electrode) to the positive side by wires, When the potential

was applied, the electrochemical reaction begins between the anode (specimen) and the cathode (stainless steel) in the cell, at room temperature. The cathode was washed by the washing system that consists of four stages, starting with washing the cathode in deionized water, then sodium tartrate, then sodium carbonate, and finally the deionized water in which contain the powder precipitated by dezincification from the anode to cathode. The deionized water containing the powder is filtered using a vacuum filter as shown in Fig. 2 And drying the powder filtered on filter paper at a temperature of 45 °C, After completion of the filtration and drying process, The powder was taken for XRF analysis to determine the percentage of copper and zinc deposited on the cathode surface. In the second stage, After completing the XRF analysis and knowing the percentage of zinc and copper deposited on the surface of the cathode. It was found that the percentage of zinc is very low compared to copper, which means that the zinc was not deposited on the surface, but rather dissolved in the solution, according to the dezincification mechanism [8], so we resort to the next step It is taking all the solutions in which the selective removal was done

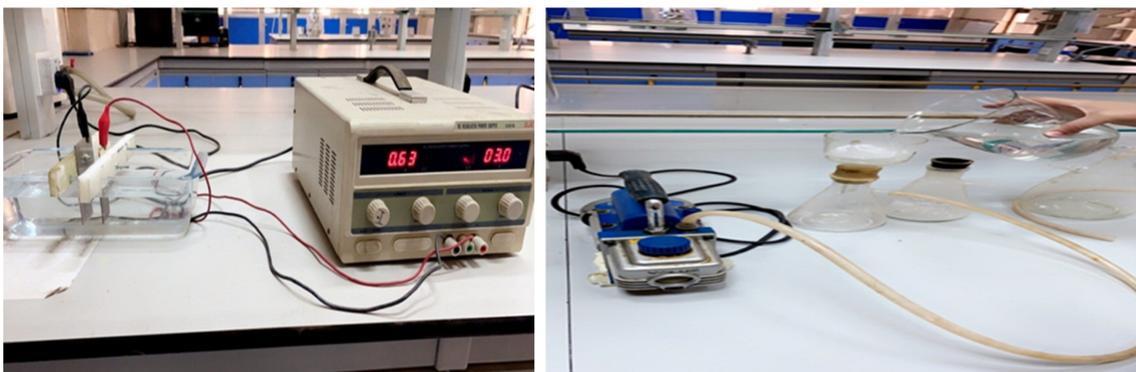
**Fig. 3. The deposition of zinc on the graphite electrode****Fig. 2. The device used in dezincification process and the filtration system**

Table 2. The values of zinc and copper ions for the electrolyte at various concentrations

Samples, of concentration 3.5%NaCl pH=10	Applied potential mV	Zn (ppm)	Cu (ppm)
1	1500	145	93
2	1550	181	156
3	1600	454	159
4	1650	409	125
5	1700	345	278
Samples, of concentration 3.5% NaCl pH=7	Applied potential	Zn (ppm)	Cu (ppm)
6	1500	421	363
7	1550	554	456
8	1600	463	353
9	1650	736	375
10	1700	609	265
Samples, of concentration 0.1M HCl pH=1	Applied potential	Zn (ppm)	Cu (ppm)
11	1500	1500	375
12	1550	681	346
13	1600	645	331
14	1650	772	406
15	1700	736	359

and repeating the process with a simple change in the circumstance such as using another cathode . the pH equation to obtain the dissolved zinc in the form of a powder and with high purity all the -electrolyte solutions are checked by atomic absorption AAS test. Table 2 indicated the best conditions for obtain pure zinc powder on the cathode. Fig. 3 shown repeat the dezincification process and using graphite electrodes, with scale the pH equation to a degree of 5 [15-17].

2.2 The analysis of X-ray fluorescence

The chemical composition of zinc powders produced was analyzed by XRF using model (XEPOS) – Germany types 76004814 with maximum power ~ 100 VA.

2.3 Scanning electron microscope and Energy Dispersive X-ray

To obtain images of high resolution (down to a few nm) for the morphology of the surface and very high focus depths, allowing imaging of very rough surfaces was observed by SEM model- INSPECT S-50- FEI, Model:

1450, Accelerating voltage range from (200 -30.000) V. This test was done in scanning electron microscopy (SEM) Lab in Department of Applied Sciences. The chemical composition of a sample, identifying and quantifying elemental compositions in a very small sample of material (even a few cubic micrometers), and the analyzing composition of the surface of a specimen determined by the EDX model –BRUKER

2.4 Atomic absorption spectrometer

The quantitative of chemical elements in solution and the concentration of a particular element (the analyte) in a sample to be analyzed can be determined by the atomic absorption spectrometer AAS model (Phenix 980) / UK. AAS can be used to determine over 70 different elements in solution using the absorption of optical radiation.

3. Results

The “Freely Corrosion Immersion Method” and the “Polarization Method” are two approaches used to obtain

precipitated pure zinc from brass waste alloys, both of which involve dezincification corrosion.

The first method relies on the corrosion potential of the brass alloy, precipitating pure zinc on the open circuit potentially without applying potential from external sources. This method is referred to as the “Freely Corrosion Immersion Method.” The second method is based on the determination of the linear polarization method to achieve a steady state. It involves using potentials (voltages) located in the region of steady-state on the anodic part of the linear polarization curve of potential–log current density relationships. This method is known as the “Polarization Method”. This method is accomplished at free voltage, i.e. at open circuit potential by immersion test. In this method three types of solutions were used. the first alkaline solution which is the 3.5% NaCl at pH =10, the second natural solution, which is 3.5% NaCl at pH =7. The third solution is acid solution of 0.1 M HCl at pH=1.

Fig. 2 compares the color of brass to the colors of pure copper and zinc. The significant difference in color between brass and copper is what leads to the dramatic changes in appearance when zinc is removed from the brass through dezincification. Samples were immersed for varying periods in different solutions. It was observed with the naked eye that after ten days in the acidic solution, the initial sign of dezincification in brass is a change in color, transitioning from the typical yellow to the salmon-pink hue of pure copper metal. The pink color may then shift to reddish and eventually brown as the surface copper corrodes to form cuprite. Severe dezincification produces a porous, weakened metal, predominantly composed of copper. In plumbing fixtures, severe dezincification can lead to perforation of the brass and cause leaks. The three solutions—neutral, acidic, and alkaline—can induce dezincification, but to varying degrees. In general, although at pH = 7, this type of corrosion occurs in lower proportions in neutral solutions, it is more pronounced in acidic solutions. However, it is observed that, despite the layer formed, a lower corrosion rate takes place. This is attributed to the formation of a multilayered dezincification structure, comprising a zinc-depleted layer and a corrosion product layer consisting of zinc and copper corrosion products. Dezincification may be visible to the naked eye, as the characteristically yellow brass transforms into red

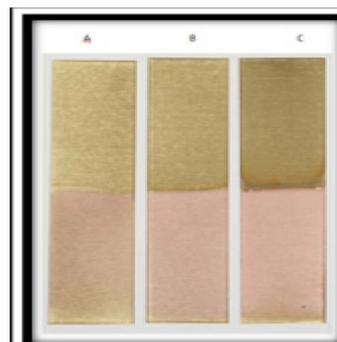


Fig. 4. Three strips of brass showing dezincification after, 24 hours of exposure in neutral solution of 3.5% NaCl, alkaline solution of 3.5 % NaCl And acid solution of 0.1M HCl

copper. The results in Fig. 4 demonstrate that dezincification progresses over time. It mainly occurs in the first few hours, with minimal change observed after 24 hours.

In all the solutions used, it was observed that after 24 hours of exposure, a brittle and weak adhesive layer formed on the surface of the samples. Subsequent polishing of the specimens with grit abrasive sheets, starting with 1800, then 3600, 4000, and finally, 6000, completely removed the dezincified layer from the surface of the brass specimens. The alloys suffered from spot dealloying that is preferential zinc dissolution already after 24 h immersion. Polarization curves tests showed that for all brasses corrosion rates slightly increased at increasing chloride concentrations and underwent a limited decrease with immersion time. The kinetics of the corrosion process was mainly under mass transport control.

3.1 Dezincification process in different solutions

Fig. 5 shows the anodic polarization curves for brass in different solutions. These solutions are as follows: (a) a neutral solution from NaCl with pH=7, (b) an alkaline solution from NaCl with pH=10, and (c) an acidic solution from HCl with pH=1. All three solutions contain chloride ions, with variations in their pH values. It is noted from Fig. 3 that there are minimal differences in the electrochemical behavior of the brass alloy when exposed to different basic, neutral, or acidic solutions. The three anodic curves exhibit three different regions based on the applied voltage. The first region is an active phase in which the current increases with the rise in the applied voltage. In this region, the removal of zinc may face challenges from

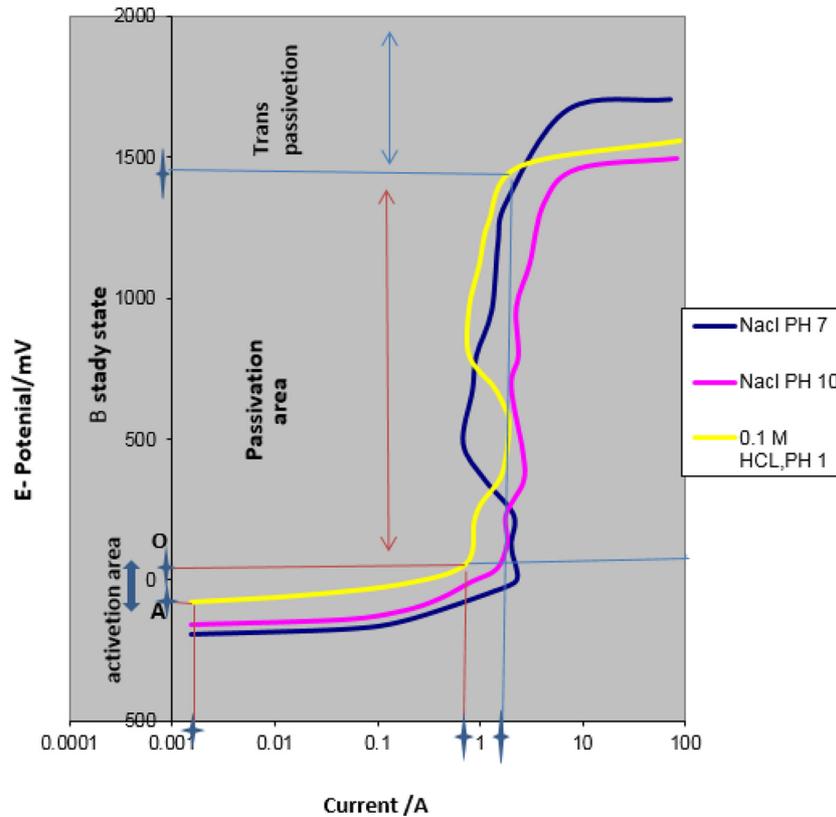


Fig. 5. Polarization curves for brass waste immersed in three solutions at different HCl concentrations with (A) neutral solution 3.5% NaCl pH7, (B) alkaline solution 3.5% NaCl, pH10 (C) acidic solution 0.1M HCl, pH 1

general corrosion caused by the simultaneous dissolution of both zinc and copper. This active region occurs at low voltages, confined to the range of -250 mV up to 0 mV, with a current between 500 and 1000 mA. The dissolution processes of zinc and copper in this region are more facile in neutral solutions compared to basic solutions, and then acidic solutions (Fig. 5). The second region is characterized as a passive (stationary) state. Thin layers of zinc and copper oxides form in this region, obstructing or impeding the dissolution processes of both zinc and copper. This passive zone extends from the end of the active zone up to 1500 millivolts, where the oxide layer begins to break and crack. The third region, known as the trans-passive region, initiates with local corrosion through selective leaching of zinc. This region requires voltages exceeding 1500 millivolts. Dezincification occurs in this region with the dissolution of zinc without the dissolution of copper. This can be inferred by the appearance of red spots, indicating the presence of copper and the absence of zinc depletion in these areas. Zinc decomposes, following the previous equations, transforming into zinc ions, which

then unite with each other to form zinc atoms. zinc atoms are collected in the form of a powder. The quantities of the precipitated powder and the degree of purity of the produced zinc are calculated according to the type of solution, alkaline, neutral, or acidic.

The third region is considered the optimal zone for the dissolution of zinc and subsequent precipitation to produce zinc powder. Table 2 presents the quantities of zinc ions and copper ions obtained from the dissolution processes within a fixed region, spanning five voltage values: 1500, 1550, 1600, 1650, and 1700 mV. In experiments involving Zn electrodeposition with HCl (Table 2 and 3), changes in the purity of zinc powder with varying voltages are illustrated. The experiments employed HCl solutions with concentrations of 3.5% NaCl (pH=10), 3.5% NaCl (pH=7), and 0.1 M HCl. Five different voltages (1500, 1550, 1600, 1650, and 1700 mV) were used in this study. Table 2 reveals that the quantities released depend on the applied voltage, varying with the solution used. In alkaline solutions (3.5% NaCl, pH=10), the highest amount of zinc ions was released at 1600 mV,

while the largest amount of copper ions was liberated at 1700 mV in the same alkaline solution. In neutral solutions (3.5% NaCl, pH=7), the largest amount of zinc ions was released at 1650 mV, while the largest amount of copper ions was released at 1550 mV. Conversely, acidic solutions (0.1 M HCl, pH=1) were characterized by releasing the highest quantity of zinc ions at the lowest applied voltage, which is 1500 mV. For copper ions in the same solution, the largest amount was released at an applied voltage estimated at 1650 mV.

At low voltages, the highest purity of zinc was obtained at the acidic and basic solutions, where the purity reached more than 98% at 1500 mV, while the basic solutions

gave a purity of 94.6% at the same applied voltage, while a purity of 96% was obtained in the neutral solutions when a voltage of 1600 mV was applied.

3.2 Morphology of zinc powder by SEM and EDX analysis

The SEM was employed to examine the details of zinc powders. Fig. 6 illustrates the impact of HCl concentration on the morphology of zinc powder on a graphite cathode at 2500 mV in 0.1 M. Fig. 7 depicts the effect of a 0.2 M concentration at 2000 mV, while Fig. 8 demonstrates the effect of a 0.3 M concentration at 1000 mV. In all experiments, the general shape of the particles is dendritic

Table 3. The values of purity in three different solutions with varying pH levels at different applied potentials

E (mV) MMMmV)	Purity in 3.5%NaCl (pH=10))	Purity in 3.5%NaCl (pH=7)	Purity in 0.1MHCl (pH=1)
1500	94.51	95.78	98.03
1550	90.3	88.06	86.89
1600	89.04	96.23	90.52
1650	91.63	82.04	81.64
1.700	82.28	78.01	75.92

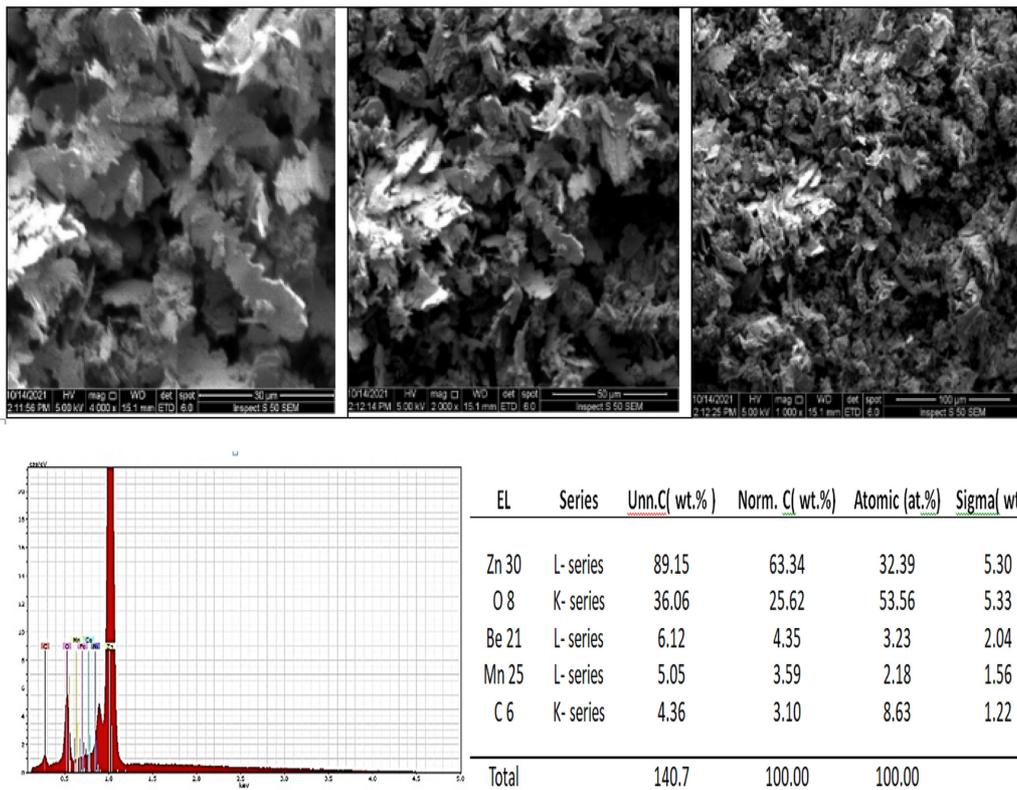


Fig. 6. SEM &EDX morphology of zinc powders deposited in graphite electrode at 2500 mV in 0.1 M HCl solution

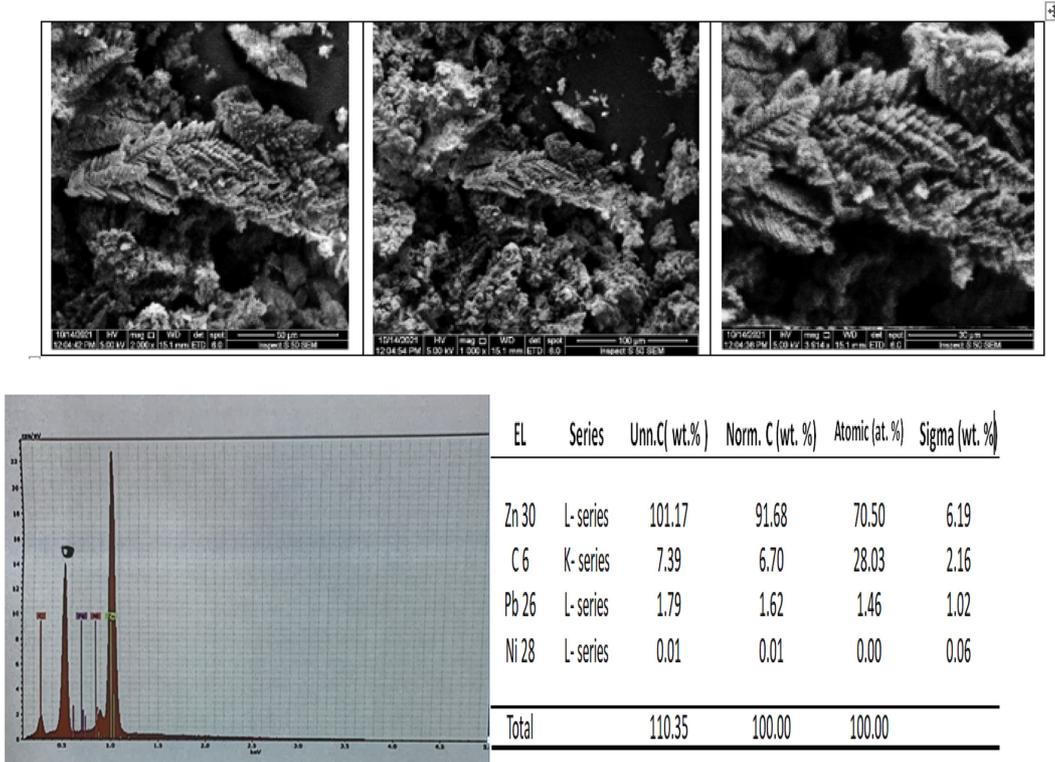


Fig. 7. SEM& EDX morphology of zinc powders deposited in graphite electrode at 2000 mV in 0.2 M HCl solution

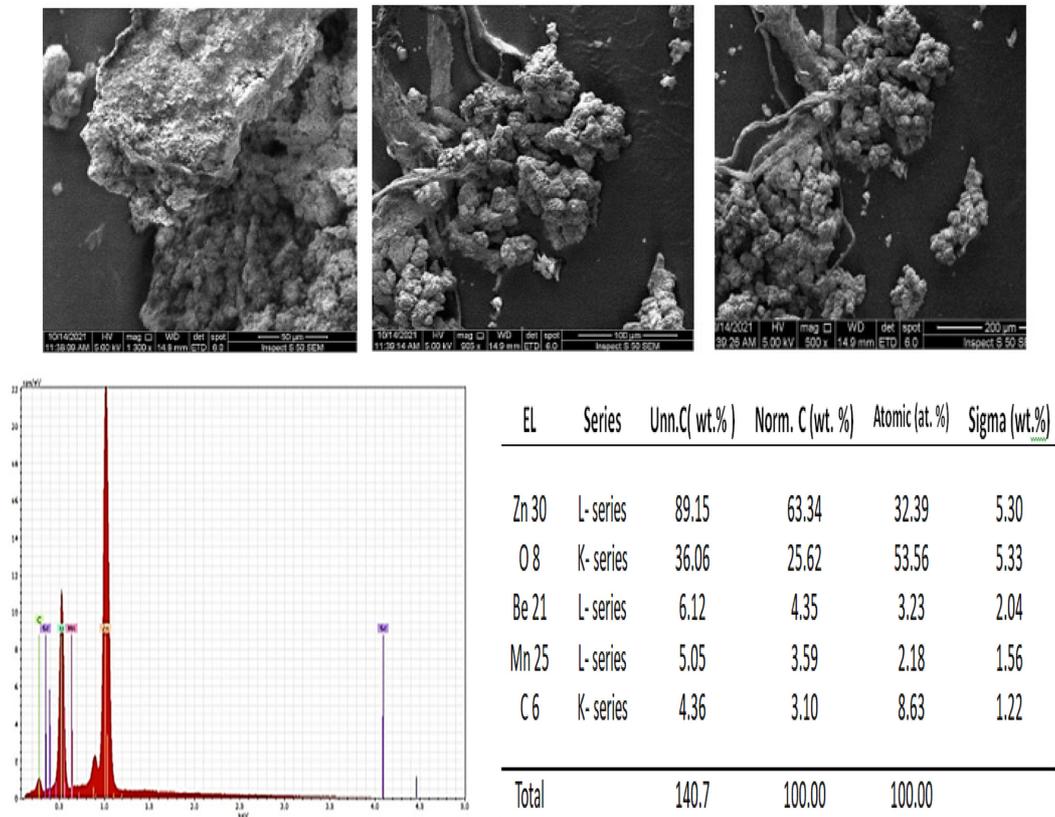


Fig. 8. SEM& EDX morphology of zinc powders deposited in graphite electrode at 1000 mV in 0.3 M HCl solution

and flaky. This morphology is attributed to the release of hydrogen gas at the surface of the cathode, with a small portion entering the structure of the powder layer, causing irregularities and promoting dendritic growth in the particles. Another contributing factor is the lack of Zn ions in the solution, leading to diffusion-limited Zn reduction.

4. Conclusions

The following conclusions can be obtained

1. The purity of zinc powder increased with increasing HCl concentration or lower applied potential of dezincification process.
2. The apparent density of electrodeposited zinc decrease with increasing applied potential or with decreasing HCl concentration of dezincification process.
3. The highest apparent density of electrodeposited zinc at 0.89 g/cm^3 was obtained by dezincification process at applied potential of 1 V and HCl concentration of 0.3 M while the lowest obtained at potential of 3 V and HCl concentration of 0.1 M.
4. Highest purity of zinc powder at 98.03% obtained by electrodeposited in dezincification solution at applied potential of 1 V and HCl concentration of 0.3 M.
5. The morphology of zinc deposited from dezincification solution at several conditions showed dendritic structure.

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