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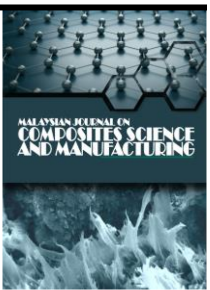

# Corrosion Resistance of Scraped Copper in Velocity Varied Inland Water of Bangladesh

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**ABSTRACT**

Copper (Cu) is widely used for electrical wires, equipment parts, and components in commercial, industrial, and marine fields due to its excellent electromechanical properties. With rapid scientific and technological advancement and economic development, the demand for copper is increasing continuously. As such, scraped items have become important to meet the rising demand considering the depletion level of copper ores in nature. But sometimes old copper contains tin (Sn), lead (Pb), etc., which may alter its properties. Thus, it is necessary to characterize different properties, including corrosion resistance, to explore the appropriate engineering applications of scraped copper waste items. In this context, the present research reports the study of the corrosion behavior of pure Cu and scraped Cu in the river water environment of Bangladesh for the submersed period of 36 days. The investigations have been carried out for three relative velocity conditions of fluid, i.e., 0, 2 and 4 m/s. A gravimetric analysis was done to find out the corrosion rate. The results of this study indicate that the presence of only 1%Sn and 1%Pb in copper has significantly increased the corrosion rate in all three velocity conditions. At the same time, scraped copper's average corrosion rate has been increased by about 10% while the relative velocity is changed from 0 to 4 m/s. Micrographs have confirmed the extent of corrosion severity resulting from chemical composition and fluid velocity alterations.

***Keywords:***
Scraped Copper, River Water, Gravimetric Investigation, Corrosion Rate, Relative velocity

## 1. Introduction

Bangladesh is a riverine country whose economic strength is directly related to water-borne activities. As a result, the use of ships, boats and structures in water is widespread for livelihood and

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transportation [1]. Since the river water is being affected by the inclusion of many ingredients being carried from upper streams and pollutants from industries, the aggressive behavior of the river water as corrosive media is well accepted [2,3]. So, shipbuilders and marine engineers prefer corrosion-resistant materials such as copper (Cu) and its alloys for the components in contact with river water. However, copper is costlier than ferrous materials, which can be balanced by the durability of copper-based products and the utility of scraped copper as a cheaper source than copper ingots. The investigation of the scraped copper collected from diverse sources has revealed that it contains a tiny portion of lead (Pb), tin (Sn), etc. [4]. Although the presence of these elements is not significant, the effect on the alteration of copper properties due to their mere presence cannot be avoided. It has been observed that the electromechanical and tribological properties support many useful applications in different chemical, mechanical and shipbuilding industries [4-6]. Questions come from various corners about whether the scraped copper can be useful in corrosive environments. As such, the corrosion resistance level of scraped copper, especially in river waters in Bangladesh, remains a question that needs to be resolved.

Fundamentally, Cu is corrosion-resistant due to its relationship with the noble metals family based on the theory of survival of pure copper in the earth's shell. A very thin layer of brown-greenish color is formed on the copper surface as a reaction of copper with the environment and stays long. This layer is known as patina, which protects the core copper from corrosion [7]. The behavior of copper for corrosion immunity is also demonstrated by intact items acquired in the ground after several hundred years and the roofs made of copper existing in rural areas with negligible corrosion rates for years together. However, copper corrodes once it comes into contact with water because of numerous factors. For instance, chemical or electrochemical corrosion reactions can vary due to variations in pH value, relative flow condition, thermal condition, and presence of certain elements/compounds in the vicinity of the reaction region. A good number of research works are guiding the search for further investigation on the corrosion of copper, especially scraped copper [8-14]. Copper also shows specific behavior of inter-granular stress corrosion cracking [15], and alloying elements affect copper corrosion [16]. Overall, the corrosion severity and copper-made component durability can remain a concern to the users, especially in contact with river water, which has aggressiveness suspended and dissolved ingredients and pollutants being added continuously. At the same time, there is an issue of relative velocity between the material and media for material degradation due to corrosion severity.

At this outset, the corrosion of scraped copper in Bangladesh's inland (river) water is pertinent to investigate to explore wider applications. Consequently, the current investigation attempts to characterize the corrosion resistance level of scraped copper in corrosive river water at stagnant as well dynamic conditions; thereby, the effect of relative velocity on the corrosion of scraped copper can be assessed.

## 2. Sample Preparation and Experiments

### *2.1 Material preparation*

Two sample materials were taken to investigate the corrosion behavior, i.e., old/scraped copper (wires and machine parts of copper collected locally) and pure copper (copper ingot imported from China). Here, the scraped copper served as the primary material for the current experimental investigation, and approximately 80 kg of old wires and electrical waste were collected from diverse locations, including shipbreaking yards, buildings, factories, etc. Then, the collected scraped copper wires melted in the furnace, and their chemical compositions were measured using an Olympus DPO-2000-CC XRF analyzer. Composition tests revealed that scraped copper items contain Cu of 97.1132%, Sn of 1.2572%, Pb of 1.1949% and few negligible elements. For a comparative assessment, 80 kg of pure copper was used alongside the scraped copper in the investigations. The chemical composition analysis results of pure and scraped copper are presented in Table 1.

From both the sample materials, several coupons of dimensions 60mm× 15mm×3mm were prepared as per the guidelines of ASTM G4 to carry out corrosion tests. The sample materials were kept in an electric furnace at 500°C for eight hours to solidify their chemical integration. Then, annealing was done for two hours at a temperature of 700°C to improve workability. After that, coupons were ground mechanically using 300, 600, 900, 1200, 1500 and 1800 grits of SiC emery cloths sequentially. On completion of dry polishing, coupons were wet polished using Al2O3 in the presence of water. After polishing, the coupons were dried up using the air blow at the atmospheric temperature, preparing the samples for an onward series of experiments.

**Table 1**
Chemical composition of sample materials used in the study (mass fraction %)

| Materials /Elements | Pure copper (%) | Scraped copper (%) |
|---|---|---|
| Cu | 99.9862 | 97.1132 |
| Sn | - | 1.2572 |
| Pb | - | 1.1949 |
| Si | 0.0026 | 0.1726 |
| P | 0.0112 | 0.2621 |

### *2.2 Experimental details*

To observe the corrosion resistance behavior of scraped copper and copper ingot in the river water environment, 2000 liter of water was collected from the Meghna River across Munshiganj in Bangladesh. The geographical location from where the river water was collected is indicated in Figure 1. The laboratory test results have revealed that the pH value of collected river water is different from pure water, and a number of corrosive ingredients are present, such as dissolved solids, suspended solids, sulphate, chloride, etc., as presented in Table 2.

In the present study, scraped copper's corrosion resistance behaviour was investigated using a gravimetric method, i.e., change in coupon mass over time due to immersion in the collected river water at static and dynamic conditions at different velocities. The relative velocity of the sample concerning water in the dynamic condition is maintained using a motor speed where the samples were placed at a particular radius in a tank, as shown in Figure 2.

Before water immersion, the coupons were weighed using a digital balance machine of model ASB-60-220-C2 with high precision (0.00001 g). The micrographs were observed and recorded using a computer-plugged optical electronic microscope (OEM). Then, coupons were kept submerged in river water with a relative velocity of zero, 2 m/s and 4 m/s, and the readings were taken for every predetermined period after being taken off the water, washed in distilled water and dehydrated in the atmosphere. The first reading was taken for the mass change once 24 hours submerged duration of sample materials was completed in river water. Subsequently, mass degradation of the coupons was measured after 3, 6, 12, 18, 24, 30 and 36 days of submersion in both stagnant and running water.

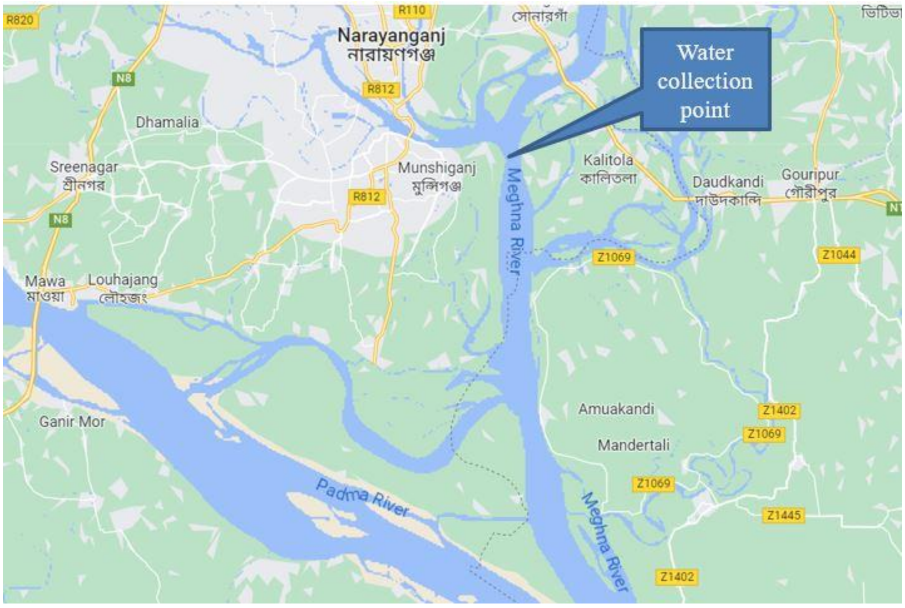

**Fig. 1.** Geographical location of water collected from Meghna River. (https://www.google.com/maps/@23.6127834,90.599186,11.74z?hl=bn&entry=ttu)

**Table 2**
Ingredients and properties of collected water and pure water

| Parameter | Values (pure water) | Values (collected water) | Unit |
|---|---|---|---|
| pH | 7.0 | 7.09 | - |
| Dissolved Solids | 0 | 850 | mg/liter |
| Suspended Solids | 0 | 45 | mg/liter |
| Chloride | ~1 | 2900 | mg/liter |
| Sulphate | ~2 | 20 | mg/liter |
| Dissolved $O_2$ | ~8 | 7.29 | mg/liter |
| Electric Conductivity | ~5-50 | 1800 | µS/cm |

Mass degradations of sample coupon per exposed surface area and the resultant corrosion rates against each examination phase were calculated using the following two equations [17].
Mass degradation of sample coupon:

$$\Delta W = \frac{(W_o - W_f)}{A} \tag{1}$$

The rate of corrosion:

$$R_{corr} = \frac{(K \times \Delta W)}{(\rho \times T)} \tag{2}$$

$\Delta W$ = Mass degradation against exposed surface area (gm/ cm$^2$)
W= Initial mass (gm)
W = Mass at the investigation phase after particular submersion (gm)
A = Exposed surface area in the media (cm$^2$)
R = Rate of corrosion (mmpy)
K = Unit conversion factor = 87.6 x 10 for corrosion rate in mmpy
ρ = Coupon material density (gm/ cm$^3$)
T = Submerged phase duration (hour)

**Fig. 2.** Experimental setup for corrosion tests

Once the submerged period of coupon is completed for 36 days, the material degradation is not noticeable. It is taken as the last reading, and the microstructure images of surfaces of corroded scraped copper were viewed using an optical electron microscope (OEM) and field emission scanning electronic microscope (FE-SEM) to observe the corrosion severity and mechanism.

## 3. Results and Discussion

### *3.1 Material degradation in static condition*

The river water is a corrosive media because of its complex electrolytic behavior as several ingredients like salts, biological agents, suspended solids, dissolved solids or gases, etc., are present. Consequently, copper, associated with noble metal family, could not endure immunity from the chemical/electrochemical corrosion attack. The obtained readings in the gravimetric experiments have been used in equation (1) to calculate the material degradation per exposed surface area (ΔW) in the river water for both copper ingot and scraped copper. The corrosion results for static conditions depict a noticeable difference in the amount of mass loss per exposed surface area between the sampling materials, as seen in Figure 3.

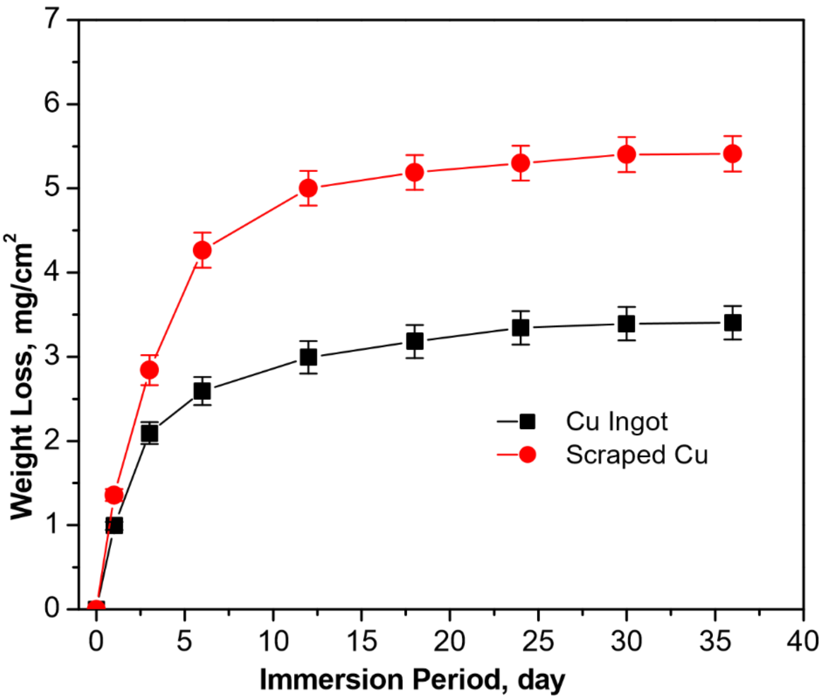

**Fig. 3.** Degradation of mass against immersion period for pure copper and scraped copper at static condition in Meghna River water

However, the graphs are of a similar pattern with respect to the immersion period. The graphs are sharper at the initial immersion period, indicating higher mass loss during the primary attack. Once the immersion period is increased for the number of days, the curves in Figure 3 become very steady, and in the last leg, it is almost horizontal. The central reason for such a mass loss curve shape might be a delay period, which is required to develop the patina on the surface of copper materials. Once the patina is formed, the copper materials are shielded, causing a reduction in corrosion attack. This result matches with the results obtained from previous works of ongoing projects, i.e., the corrosion of copper-made heat exchanger tubes in the river and coastal water [8], Solder Affected Copper in the Bay of Bengal Water Environment [9], solder-affected copper in pH varied environments [10] and commercial copper alloys in seawater [18].

### *3.2 Corrosion Rate in Static Condition*

The rates of corrosion of copper ingot and scraped copper were calculated using the mass loss data of their coupons obtained from the experimental readings employed in Eq. (2) after every submersion phase period up to 36 days. The attained corrosion rates are presented in Figure 4, where the corrosion rate has been observed to be reduced gradually in a hyperbolic pattern for both copper ingot and scraped copper. Figure 5 depicts that the peak value of corrosion rates is 0.384 mmpy, and their average value is 0.127 mmpy for copper ingot and the same for scraped copper are 0.623 mmpy and 0.215 mmpy, respectively. Therefore, regarding the maximum value of corrosion rate, the corrosion observed in scraped copper is approximately 62% higher than that in pure copper. Similarly, when considering the average value of corrosion rate, the corrosion rate in scraped copper is approximately 69% higher than that of pure copper. This indicates a significant difference in the corrosion rates between the two forms of copper, with scraped copper experiencing a higher degree of corrosion in terms of maximum and average corrosion rate values.

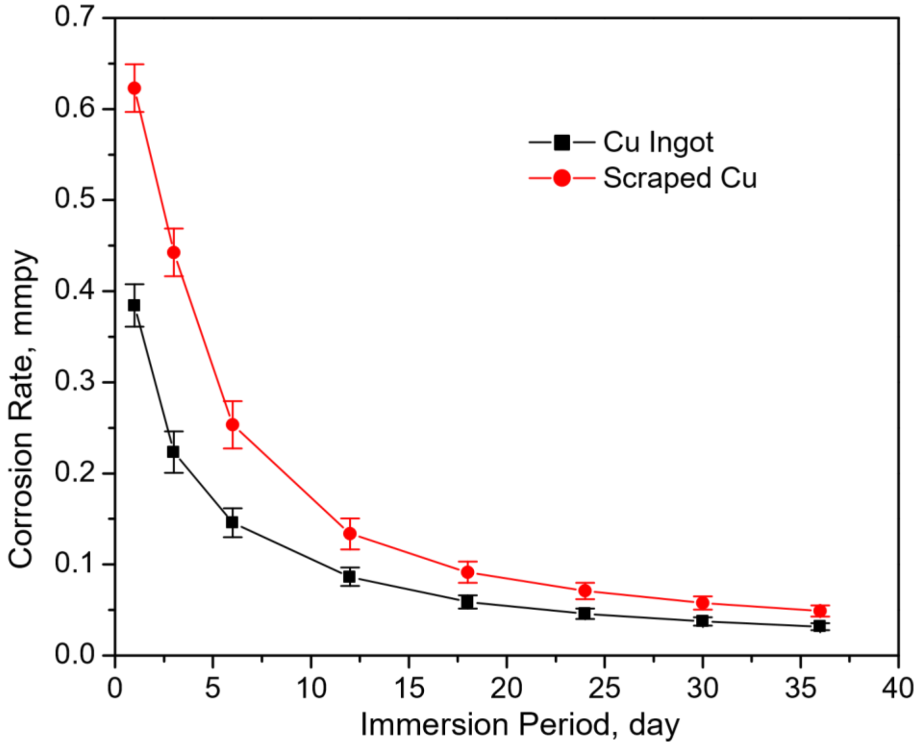

**Fig. 4.** Corrosion rates against immersion period for pure copper and scraped copper in Meghna River water at static condition

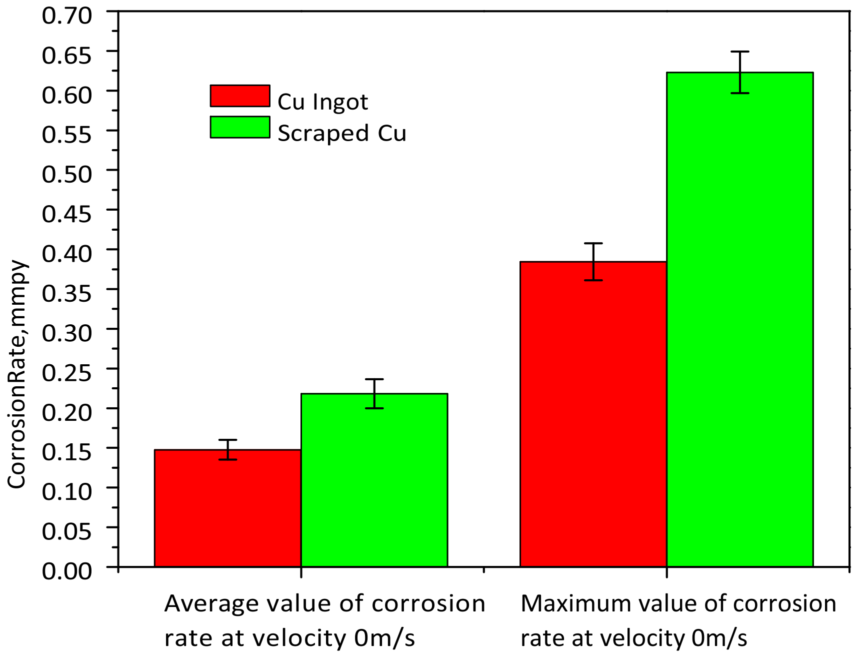

**Fig. 5.** Corrosion rates for pure copper and scraped copper at 0m/s in Meghna River water (Max and average values)

### *3.3 Effect of Relative Velocity on Corrosion Rate*

The degradation and corrosion rates obtained in dynamic conditions of copper ingot and scraped copper are similar to those of static conditions. However, the corrosion magnitudes are higher for dynamic conditions than those of static for both the sample materials. The peak values of corrosion rates at static and dynamic conditions at a relative velocity of 2 and 4 m/s are presented in Figure 6. It is evident that the peak value of the rate of corrosion is amplified with the rise in relative velocity. For 2 m/s, the corrosion rate has been amplified by 2%, but for 4 m/s, it is enlarged by 10% from its stagnant condition result. The present results also agree with the previous findings for the river and coastal water corrosion of copper tube heat exchangers [8].

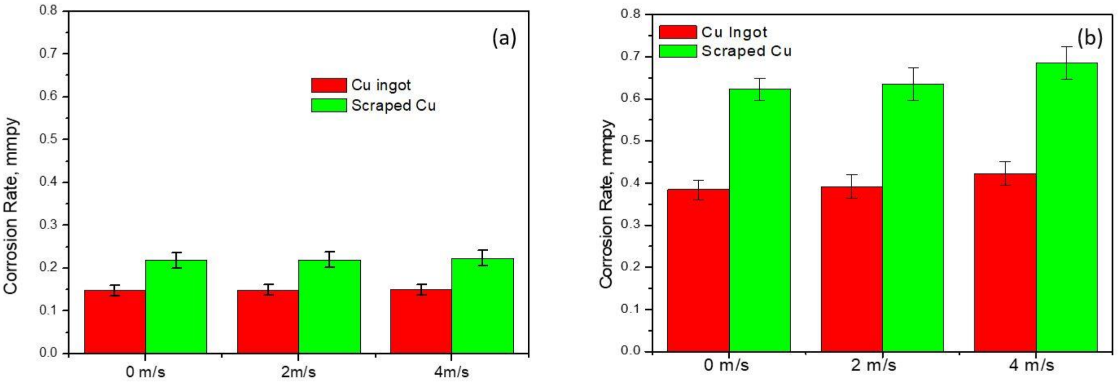

**Fig. 6.** Corrosion rates (peak value) for pure copper and scraped copper at static (zero velocity) and dynamic conditions (2 and 4m/s) in Meghna River water: (a)average value of corrosion rate at velocity 0, 2 and 4 m/s (b) maximum value of corrosion rate at velocity 0, 2 and 4 m/s

### *3.4 Micrographs of Corroded Samples*

Figure 7 displays the metallographic images of scraped copper observed in the optical electron microscope (OEM) before and after 36 days of immersion in river water at static and dynamic conditions. Figures 7 (b) and (c) are different due to the velocity effect on the corrosion of copper materials. The corroded surface shown in Figure 7(c) indicates that the patina (results from the natural oxidation process, creating a greenish or brownish layer that enhances the metal's appearance and protects it from further corrosion) formed after the initial attack is getting streaked off with the erosion type of corrosion occurred by the momentary impingement of suspended solid particles moving in the river water. As it does not happen in static conditions, the patina layer is sustained, and the microstructure of the corroded surface is not affected severely, as seen in Figure 7(b).

Scanning electron microscope (SEM) images of corroded sample materials after 36 days' immersion in stagnant water and with a relative velocity of 4 m/s are presented in Figure 8. Figure 8(a) indicates a similar phenomenon of the patina layer observed in the OEM micrograph in static corrosion. Figure 8(b) demonstrates the breakage of the patina as a dynamic effect due to the relative velocity of the coupon against water. It establishes that the relative velocity of material with respect to corrosive media increases the rate of corrosion, reducing the useful life of the component.

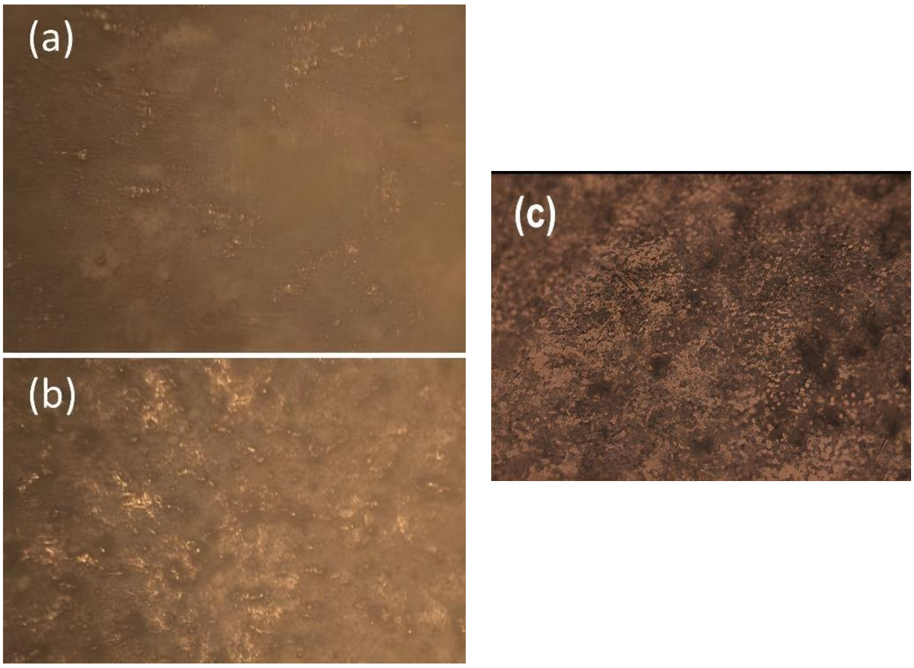

**Fig 7.** OEM micrographs of 320x: (a) before immersion, (b) after immersion for 36 days in static water (zero velocity), and (c) after immersion for 36 days at a relative velocity of 4 m/s

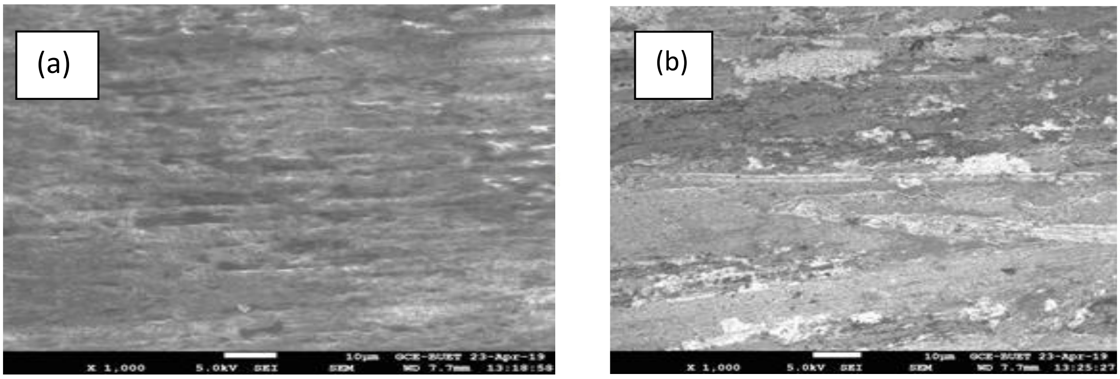

**Fig 8.** SEM images of scraped copper after exposure for 36 days: (a) in static river water, and (b) in moving river water at the velocity of 4 m/s

## 4. Conclusions

The summarized findings of the investigations carried out on the corrosion resistance behavior of copper ingot and solder-affected scraped copper in river water of Bangladesh are appended below:

a) The water of Meghna with pH 7.09 has demonstrated that copper ingot and scraped copper are not fully corrosion-resistant. Material degradation observed through mass loss at the initial corrosion attack is the highest, then decreases, reaching a flat pattern.

b) In line with mass loss, the corrosion rates are maximum at the first attack. The rate decreases in a hyperbolic pattern due to patina formation over the corroded surface of copper ingot and scraped copper.

c) The addition of alloying elements like Sn and Pb has significantly increased the corrosion rates of copper. On average, the corrosion rate of scraped copper is about 69% higher than copper ingot's.

d) The material degradation and corrosion rate are affected significantly by the relative motion of material with respect to media. With the increase of relative velocity by 4m/s, the corrosion rate is amplified by 10%.
e) Micrographs of corroded surfaces have acknowledged the corrosion severity of copper in river water at both static and dynamic conditions. FESEM shows that the corroded surface indicates the highest corrosion occurrence at scraped copper's dynamic condition.
f) Therefore, corrosion allowance needs to be considered during the design calculations when using solder-scraped copper in marine applications.

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