

One-Step Electrodeposition of Superhydrophobic Coatings on Steel: Influence of Process Parameters

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Abstract. Steel is inherently susceptible to corrosion due to its hydrophilic nature (water contact angle $< 90^\circ$). This study developed superhydrophobic coatings (water contact angle $> 150^\circ$) using a one-step electrodeposition method, a simple and cost-effective approach that simultaneously enhances surface roughness and lowers surface energy using non-polar chemicals. The fabrication process was optimized using the Taguchi method experimental design and statistically validated with ANOVA, assessing the impact of current density, salt concentration ratio, electrodeposition time, and reagent concentration on surface wettability. Results confirmed that current density and salt concentration ratio significantly influenced the water contact angle on the surface of the deposited coatings. After 13 days of exposure to atmospheric conditions, the coating layer produced with optimum conditions experienced a minor reduction in its superhydrophobic performance while still retaining its classification as superhydrophobic.

1 Introduction

Steel possesses an excellent balance of strength and toughness, making it suitable for a wide range of engineering applications. However, in aqueous environments, it remains susceptible to corrosion. The steel surface is inherently hydrophilic, which means it attracts water [1]. The wettability of the surface can be measured by water contact angle. When water droplets hit the surface of steel, they spread out instead of beading up, resulting in the water contact angle that less than 90° , which indicates strong wettability.

One effective strategy to reduce the wettability of steel surfaces involves surface modification to achieve hydrophobic (water contact angle $90^\circ - 150^\circ$) or superhydrophobic (water contact angle $> 150^\circ$) characteristics. Application of protective coating with superhydrophobic properties can isolate the steel surface from corrosive environment and preventing the formation of an electrolyte film on the surface. In the absence of this electrolyte film, the electrochemical pathway required for corrosion is disrupted, as no electrical current can be established across the surface.

Superhydrophobic properties can be achieved through the formation of hierarchical micro/nanostructures combined with surface energy modification. Common fabrication techniques for superhydrophobic coatings include template-assisted methods, sol-gel processing, chemical etching, dip coating, spray coating, hydrothermal synthesis, and electrodeposition [2]. Among these, the electrodeposition method offers several advantages, such as low cost, ease of control, rapid processing, and broad applicability to various substrates [3].

Recent research on the fabrication of superhydrophobic coatings via electrodeposition has predominantly employed a two-step process, wherein electrodeposition is followed by surface energy modification. In contrast, one-step electrodeposition presents a more streamlined approach, as both the formation of hierarchical micro/nanostructures and the reduction of surface energy occur simultaneously. This method is not only simpler but also more time-efficient, making it an attractive alternative for practical applications.

Hu et al. reported that a Ni-Co superhydrophobic coating fabricated on steel via one-step electrodeposition exhibited strong adhesion and film durability [4]. Similarly, Tang et al. successfully developed a Cu-Mn coating on steel using the same technique, demonstrating high corrosion resistance [5]. In both studies, myristic acid was employed to facilitate the formation of hierarchical micro/nanostructures with low surface energy, thereby enhancing water contact angle. However, the effect of process parameter has not been evaluated systematically. On the other hand, Abiyu used a Taguchi experimental design to fabricate a Cu-Zn superhydrophobic coating by one-step Electrodeposition [6]. His study reported that constant voltage and the salt concentration ratio were the dominant contributors to the superhydrophobic properties of the coating layer. In this study, a Cu-Mn superhydrophobic coating was fabricated on a carbon steel surface using the Taguchi method to design the experimental matrix. An L9 orthogonal array was employed, incorporating four factors: the molar ratio of $\text{Cu}^{2+}/\text{Mn}^{2+}$, current density, electrodeposition time, and myristic acid concentration, each varied across three levels (34). The contribution of each factor to the surface

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wettability of the Cu-Mn coating layer coating was assessed through Analysis of Variance (ANOVA).

2 Materials and Methods

2.1 Sample preparation

Carbon steel substrates (50×20×13 mm) were prepared through a multi-step process. First, the substrates were mechanically polished with a series of silicon carbide (SiC) papers, progressing from 60 to 2000 grit. The polished steels were subsequently cleaned in an ultrasonic cleaner using acetone and ethanol, each for five minutes at 40 °C. Degreasing step was performed by immersing the substrates in an alkaline solution composed of 30 g/L NaOH, 20 g/L Na₂CO₃, 20 g/L Na₃PO₄, and 10 g/L Na₂SiO₃.

Subsequently, the degreased substrates underwent electrolytic polishing for two minutes in an electrolyte solution containing 8 g/L KOH, 8 g/L sodium dodecyl sulphate (SDS), and 60 g/L Na₂CO₃ at a current density of 0.02 A/cm². The final step involved surface activation in a 10% HCl solution to remove naturally formed oxide film. After each preparation steps, the substrates were thoroughly rinsed with distilled water and dried.

2.2 One-step electrodeposition

The electrodeposition of a Cu-Mn coating was conducted using a DC power supply at 60 °C with a constant anode-to-cathode distance of 20 mm. The prepared steel substrates act as cathodes and graphite rods were used as anodes. The electrolyte solution was prepared by dissolving CuCl₂·2H₂O, MnCl₂·2H₂O, myristic acid, and SDS in 96% ethanol. Boric acid (H₃BO₃) was also added to the solution at a concentration of 30 g/L. The concentration of SDS was kept equal to that of myristic acid. After the electrodeposition was complete, the samples were dried for 24 hours prior to water contact angle measurements.

2.3 Experimental design

The electrodeposition process parameters were systematically varied to investigate their effects on the wettability of the resulting coating surface. The experimental setup was developed using Minitab software, incorporating three levels across four distinct factors, using the Taguchi L₉ orthogonal array. The specific parameters and their levels are detailed in Table 1, and the exact setup for each of the nine experimental runs can be found in Table 2. To ensure reliable results, each of the nine experimental runs was replicated twice, bringing the total number of runs to 18.

2.4 Water contact angle measurement

A 5 µL droplet of distilled water was dispensed onto the surface of the coating using a micropipette. The droplet image was captured using a digital microscope equipped with a backlighting setup to enhance the droplet's

silhouette against the background, ensuring a clear and well-defined image. The water contact angle was subsequently measured from the captured images using ImageJ software. The experimental setup for this water contact angle measurement is depicted in Fig. 1.

Table 1. Electrodeposition factors and their levels

Electrodeposition factors	Level			Performance parameter
	1	2	3	
Current density (A/dm ²)	1	3	5	
[Cu ²⁺]:[Mn ²⁺] ratio	0.1:1	0.4:1	1:1	Water contact angle
Time (min)	5	10	15	
Myristic acid concentration (g/L)	2	4	6	

Table 2. Taguchi L₉ orthogonal array experimental design

Test Run	Current density (A/dm ²)	$\frac{[Cu^{2+}]}{[Mn^{2+}]}$ ratio	Time (minutes)	Myristic acid concentration (g/L)
1	1	0.1:1	5	2
2	1	0.4:1	10	4
3	1	1:1	15	6
4	3	0.1:1	10	6
5	3	0.4:1	15	2
6	3	1:1	5	4
7	5	0.1:1	15	4
8	5	0.4:1	5	6
9	5	1:1	10	2

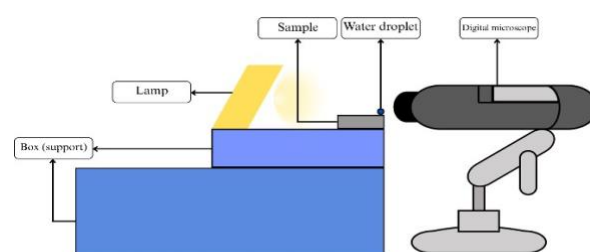


Fig. 1. Apparatus for water contact angle measurement.

3 Results and discussion

3.1 Surface wettability of Cu-Mn coating layer

The water contact angle (WCA) measured for each experimental run is listed in Table 3. Not all factor and level combinations successfully produced superhydrophobic coating layer, as some runs resulted in a WCA of less than 150°. This outcome suggests that the resulting coating layers were lack of homogeneity, where the first run yielded the lowest WCA. In contrast, Experiment number 5 consistently showed superior results, with average WCAs of 156.7° and 158.2°. The image of water droplet during water contact angle

measurement for Experiment 5, which represents the empirical optimum parameter, is shown in Fig. 2

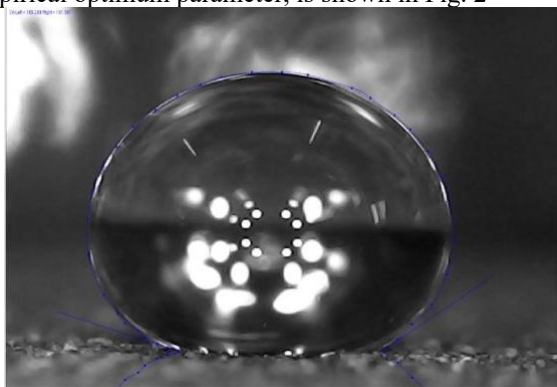


Fig. 2. Water contact angel measurement for coating layer produced from experiment number 5

3.2 Analysis of factor significance by ANOVA

To analyse the significance of each factor, first we need to calculate the sum of response by summation of the WCA for each level of factors. For example, for duration level of 5 minutes, the resulted WCA are 102.9°; 105.4°; 147.8°; 123.6°; 153.0°; 158,0°, so that the sum of response for duration of 5 minutes is 790.8°. The same calculation was conducted for each level. The complete results of the ANOVA calculation are presented in Table 4.

From the calculated sum of response and total sum of response, a comprehensive analysis was performed using the ANOVA method. This analysis included calculating the degree of freedom (DOF), sum of squares (SS), mean square (MS), and variance ratio (F). The significance of each variable's effect can be determined from its calculated F-value. If the F-value is greater than the standard F-value, the variable is considered to have a significant effect on the results. We used the standard F-table for a significance level of 0.05, which corresponds to a 95% confidence level. The standard F-value was determined by combining the DOF of the variable (numerator) with the DOF of the error (denominator), as shown in Table 4. Based on these DOF values, the standard F-value was found to be 4.26 for $F_{0.05;2;9}$. Therefore, the experimental variables are considered significant if their calculated F-value is greater than 4.26.

Table 4 shows that not all variables used in this study were significant. While the significance analysis provides a qualitative assessment, a quantitative analysis can be performed by determining the percent contribution of each variable. The percent contribution is calculated as the ratio of each variable's SS to the total SS. The results of this calculation are displayed as a graph in Fig. 3. From the percent contribution analysis, we can conclude that the $[Cu^{2+}]:[Mn^{2+}]$ ratio (34.82%) and the current density (34.49%) are the two factors with the most significant influence on the response. In contrast, electrodeposition time (10.49%) and myristic acid concentration (5.90%) showed a much lower contribution.

The dominant influence of current density and $[Cu^{2+}]:[Mn^{2+}]$ ratio can be attributed to the fundamental

mechanisms of electrocrystallization. Current density governs the competition between the nucleation rate and the crystal growth rate. At intermediate levels (3 A/dm²), the current density provides sufficient overpotential to promote a high nucleation rate, which is essential for forming the necessary micro-nano hierarchical structures, without causing excessive hydrogen evolution that typically occurs at higher current densities (5 A/dm²) and leads to coating porosity. Similarly, the $[Cu^{2+}]:[Mn^{2+}]$ ratio is critical for phase composition. Since copper is more noble than manganese, a specific stoichiometric ratio (0.4:1) is required to co-deposit the manganese and form the targeted superhydrophobic Cu-Mn-myristate complex. Deviations from this ratio result in either pure copper deposition (hydrophilic) or unstable film formation. In this context, current density and salt ratio act as the fundamental prerequisites that determine the existence of the superhydrophobic phase.

3.3 Signal-to-Noise Ratio

The signal-to-Noise (S/N) ratio analysis was used to identify the optimal levels for each factor that would produce the best results. Since our goal was to achieve a superhydrophobic coating, which requires a higher water contact angle, we chose the "Larger the Better" S/N ratio. The S/N ratio for each parameter combination was calculated using the following formula:

$$\frac{s}{N} \text{ larger the better} = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (1)$$

where y represents the responses for the given factor level combination, and n represents the number of replications in the given factor level combination. The mean Signal-to-Noise (S/N) ratio for each factor level is presented in Table 5 and shown graphically in Fig. 4. This analysis helps identify the specific factor levels that are most likely to produce optimum and robust results.

Based on Fig. 4, the optimum point for each variable is determined by the highest point or the largest S/N ratio value. A higher S/N ratio indicates a higher water contact angle for the coating. The S/N ratio analysis suggests the following optimum parameters for this study are 3 A/dm² of current density, 0.4:1 of $[Cu^{2+}]:[Mn^{2+}]$ ratio, 10 minutes of electrodeposition time, and 6 g/L of myristic acid concentration.

To confirm the optimization results based on the S/N ratio, we fabricated a Cu-Mn coating using the predicted optimum parameters and performed a water contact angle test. However, the confirmation runs revealed that the combination of parameters predicted as optimum by the S/N ratio analysis did not produce a superhydrophobic coating. The two replications of the optimum experiment only achieved an average WCA of 149.09° and 149.00°, which is quantitatively below the 150° superhydrophobic threshold. A comparison of the coatings from the S/N ratio optimum parameters and experiment number 5 is provided in Fig. 5.

The discrepancy between the predicted optimum (S/N ratio) and empirical results highlights a limitation of the standard Taguchi L₉ orthogonal array, which assumes that process variables act independently (linear

main effects). Although ANOVA indicated that electrodeposition time and myristic acid concentration were not statistically significant as independent factors, empirical observations suggest a strong synergistic interaction between them. The predicted optimum combined a high acid concentration (6 g/L) with a short deposition time (10 minutes). Physically, a high concentration of large myristic acid molecules likely led to rapid, chaotic adsorption and steric hindrance, preventing the orderly formation of the cauliflower-like structure within the short timeframe, resulting in the non-uniform/ inhomogeneous surface morphology clearly evidenced in Fig. 5. In contrast, experiment number 5 (2 g/L acid, 15 minutes) succeeded because the lower concentration reduced molecular crowding, while the extended time allowed sufficient kinetics for the self-assembly of metal-myristate complexes into a uniform hierarchical structure.

3.4 Stability test of superhydrophobic properties

To evaluate the stability of the superhydrophobic coating under atmospheric conditions, the sample with the highest WCA was observed for 13 days at room temperature. Fig. 6 shows a gradual decrease in the WCA over time, from an initial value of 156.73° to 151.73° by the eighth day, followed by significant drop on the eleventh day down to 147.64°. This indicates a performance degradation from a superhydrophobic state (WCA > 150°) to a hydrophobic one. This degradation can be attributed to the adsorption of volatile organic contaminants and moisture from the air onto the coating surface, which gradually increases its surface energy. Nevertheless, a slight recovery to 150.9° was observed on the thirteenth day, demonstrating that the coating retains some ability to maintain its superhydrophobic properties over this period.

Table 3. WCA measured for each experimental run

Test Run	Mean WCA (°)	Test Run	Mean WCA (°)
1	102.9	6	147.8
	105.4		123.6
2	152.4	7	138.2
	139.1		132.2
3	113.9	8	153.0
	135.0		158.0
4	154.0	9	131.9
	148.5		146.2
5	156.7		
	158.2		

Table 4. ANOVA results for the WCA response

Source of Variation	DOF	SS	MS	F	Significance
Current density	2	1820	910	10.9	Significant
[Cu ²⁺]/[Mn ²⁺]	2	1837	919	11	Significant
Time	2	553	277	3.3	Not significant
Myristic acid concentration	2	311	156	1.86	Not significant
Error	9	755	84	-	-
Total	17	5276.1			

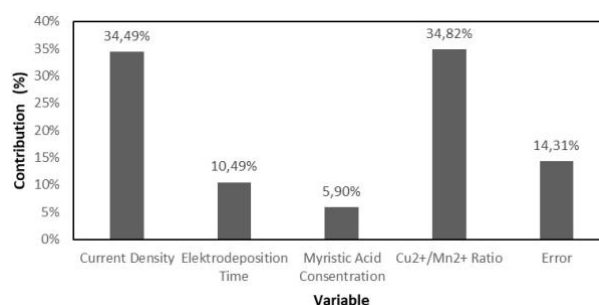


Fig. 3. Percent of contribution of each factor to the WCA value

Table 5. Mean of S/N ratio larger the better for each level of factors

Electrodeposition factors	Level	Mean of S/N
Current density (A/dm ²)	1	41.8
	3	43.36
	5	43.09
[Cu ²⁺]:[Mn ²⁺] ratio	0.1:1	42.18
	0.4:1	43.67
	1:1	42.39

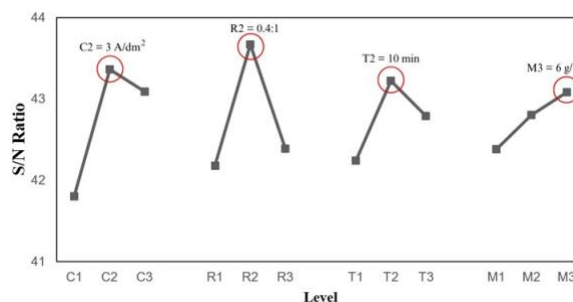


Fig. 4. Mean S/N ratio for each level of electrodeposition factors (C refers to current density; R refers to concentration ratio of Cu²⁺/Mn²⁺; T refers to electrodeposition time; M refers to myristic acid concentration)

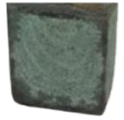

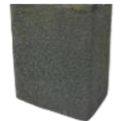

Factor and level combinations	Coating surface appearance	
Current density: 3 A/dm ² [Cu ²⁺]/[Mn ²⁺] ratio: 0.4:1 Electrodeposition time: 10 minutes Myristic acid concentration: 6 g/L		
Current density: 3 A/dm ² [Cu ²⁺]/[Mn ²⁺] ratio: 0.4:1 Electrodeposition time: 15 minutes Myristic acid concentration: 2 g/L		

Fig. 5. Coating appearance produced by optimum parameter based on S/N ratio and experiment number 5

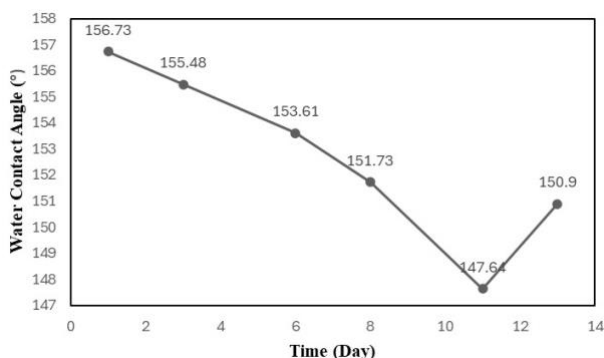


Fig. 6. WCA stability over 13 days in atmospheric conditions

4 Conclusion

Based on the research conducted, the following conclusions can be drawn:

1. Based on ANOVA analysis, only two of the four variables, the [Cu²⁺]/[Mn²⁺] ratio and current density, had a significant effect ($\alpha=0.05$) on the water contact angle. The highest percent of contribution was from the [Cu²⁺]/[Mn²⁺] ratio at 34.82%, followed by the current density at 34.49%.
2. Although the main effect S/N ratio analysis predicted an optimum combination, empirical confirmation tests showed that the true optimum conditions were achieved with the parameters of experiment number 5: a current density of 3 A/dm², a [Cu²⁺]/[Mn²⁺] ratio of 0.4:1, an electrodeposition time of 15 minutes, and a myristic acid concentration of 2 g/L. These conditions consistently produced a Cu-Mn coating layer with an average water contact angle of 157.5°.

3. The Cu-Mn coating layer fabricated with the empirically determined optimum parameters demonstrated good stability. Its superhydrophobic properties were maintained throughout the 13-day testing period under atmospheric conditions, despite a gradual degradation trend caused by the adsorption of environmental contaminants.

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