

Analysis of effective parameters on cadmium cementation reaction from the perspective of diffusion

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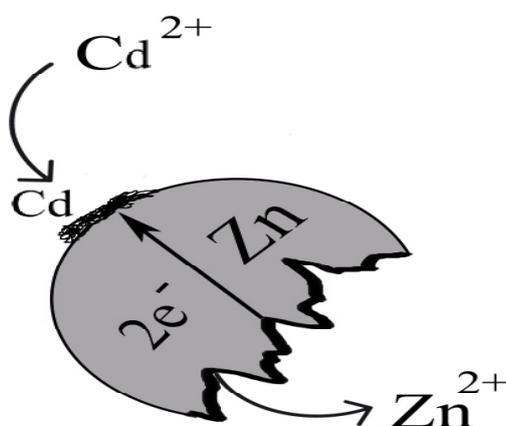
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HIGHLIGHTS

- Analysis of parameters affecting the cadmium cementation process from the point of view of diffusion coefficient.
- Investigation of the interaction of effective parameters on the removal of cadmium by zinc powder from zinc electrolyte solution.
- Removal of high concentrations of cadmium from zinc electrolyte solution by zinc powder cementation method.
- Use of response surface method for data analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

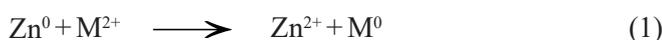
Cadmium is one of the impurities to be removed from the electrolyte solution before zinc electrowinning. Removal of cadmium by cementation with zinc powder is diffusion-controlled. This study analyzed the parameters that effective the removal of cadmium by zinc powder from the point of view of molecular diffusion. Studies have shown that parameter changes can be easily justified by this mechanism, and a logical connection is raised between the theoretical issues and what is happening in reality.

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1. Introduction

In the hydrometallurgical production of zinc, the purity of the solutions of the electrolysis is of great importance. The purity of the electrolyte solution reduces energy consumption and results in high purity zinc production, which ultimately significantly reduces production costs [1-3]. The main impurities that must be removed before electrolysis are cobalt, nickel, and cadmium. The destruction of the oxide layer of the aluminum cathode results in cobalt and nickel (which cause zinc re-dissolution into the electrolysis cells) and zinc (which forms on its surface). As a result, black spots, vents, and conical holes are formed on the inner side of the sediment that is in contact with the electrode [4-6]. Cadmium also precipitates either before or simultaneously with zinc. This leads to zinc re-dissolving in the acidic electrolyte and also acts as a catalyst for the reduction of hydrogen gas, which may result in a large drop in efficiency. Ultimately, the presence of these impurities in the electrolyte solution can also greatly reduce the purity of the product [7,8]. In addition, cadmium is considered to be a very toxic heavy metal that is hazardous to the environment, and in particular, to human health. Therefore, preventing natural water pollution by cadmium ions is a very serious issue in zinc production units. Accordingly, the optimal removal of these impurities, which is carried out in the purification stage, is essential and very important [9-13]. In most zinc production units worldwide, the removal of these impurities is carried out in two stages of cold and hot purification processes using cementation with zinc powder [14-16]. In the hot purification stage, cobalt and nickel are removed by adding arsenic or antimony compounds, copper sulfate, and zinc powder at temperatures above 85°C. In the cold purification process, cadmium is removed from the zinc sulfate solution using zinc powder at 75°C. Cementation is the removal or reduction of those elements whose chemical potential exceeds the chemical potential of zinc; the elimination mechanism is shown in Eq. (1)[17-21].



From other perspectives, the cementation reaction is a heterogeneous electrochemical reaction, in which the cation reaches the solid surface and takes the electron from the anode, which makes the zinc cation releases

in the solution. In this electron interaction, the intruder cation sedimentation forms on the anode. Fig. 1 shows the cementation mechanism of a metallic impurity by zinc powder [22-24].

In many cases, the kinetics of such a reaction is controlled by the diffusion of ions into the solution through the boundary layer at the metal-solution joint. Eq. (2) is a simple velocity equation, which is true in many cases [25].

$$\frac{dc}{dt} = \frac{CAcD}{V\delta} \quad (2)$$

In which C is the concentration, Ac is the surface area of the cathode, D is the diffusion coefficient, V is the volume, and δ is the thickness of the diffusion layer.

Most researchers have stated that the reaction of cementation with zinc powder follows the first-order kinetics, and diffusion is the controlling stage of the reaction [6,26-30]. In this regard, Younesi *et al.* [31] have studied possible kinetic models for controlling the different cementation reactions of cadmium ions by zinc powder and temperature, the concentration of zinc powder, and the stoichiometric ratio with regards to cadmium concentration. The results of their experiments showed that an initial concentration of cadmium greater than 1000 ppm, the ash diffusion model

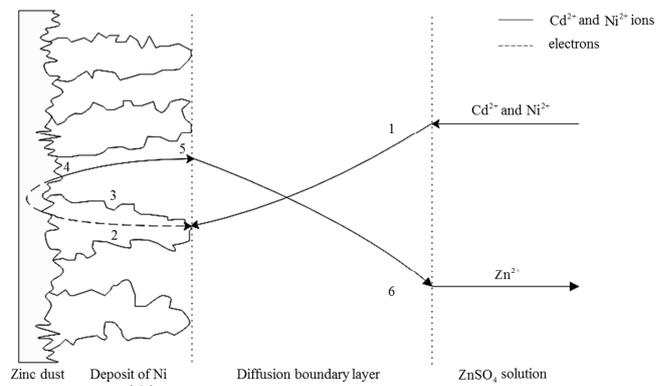


Fig. 1. Stages of reactions of metallic impurities to zinc dust cementation [22,24].

1. Transport of the deposition metal ions, M^{2+} , from the bulk of the solution to the metal-solution interface through the liquid boundary layer.
2. Conductance of electrons from the anodic dissolving zinc to the cathodic sites through cemented deposit and electron transfer.
3. Dehydration of the depositing metal, M , and incorporation of the atoms of the deposited metal, M , into the crystal lattice.
4. Release and hydration of Zn^{2+} ions from their anodic sites.
5. Transfer of Zn^{2+} ions into the solution through the deposited layer.
6. Transfer of Zn^{2+} ions into the bulk of the solution through the liquid boundary layer.

has good control, while in concentrations less than 500 ppm, the data showed a good agreement with the film diffusion model. For concentrations between 500-1000 ppm, the speed of the reaction was best controlled by a combination of the ash diffusion and film diffusion models. Based on the numerical analysis, the activation energy was calculated at 7.2 - 9.6 kJ.mol⁻¹ in high and low concentrations [31].

According to previous research and considering that the concentration of cadmium in the purification stage is less than 500 ppm in most of the world's zinc manufacturing plants, it can be concluded that the controlling mechanism is the diffusion reaction from the diffusion layer. Several researchers have examined the parameters that influence the rate of cadmium cementation, such as temperature, mixing speed, the concentration of zinc particles, additive content, and initial concentration of cadmium in the solution. Considering the importance of diffusion, the controller phase of the reaction, it is surprising that no one has analyzed any of the effective parameters of the reaction from a diffusion point of view [32-35].

In the present study, with regard to the importance of the transfer of cadmium ions from the mass solution to the surface of the zinc powder, the parameters affecting the cadmium cementation reaction from a diffusion viewpoint was analyzed using response surface experiments, and the ability of the proposed mechanism was then investigated by analyzing the parameters affecting the response.

2. Design of experiments

One of the goals of experiment design is to optimize the process and achieve the desired conditions. To this end, the response surface methodology was used in the statistical design of the experiments. In the response surface method, response maps were either contour lines or three-dimensional views. These maps are just like geological topography diagrams, except that in the response surface method, parallel lines indicate the test response instead of height.

Designs executed in a two-level factorial method are not able to fit the response surface. To identify the curvature and its form, there is a need to add some central points to the surface of factors, which constitutes a basis for the design of response surface techniques. Of course, based on how these central points are added

to the surface of factors, response surface methods are subdivided into the generally used subcategories, the Box-Behnken and the central composite, in designing the response of surface.

When the curvature between the levels of parameters is important, adding more points to the surfaces of the factors can lead to a precise determination of the behavior of the response function. The central composite method is obtained by adding new points along the axis of space between the surfaces of the factors. Fig. 2 illustrates a two-factor and three-factor design of this method.

To increase the impact of the axial points (marked with the star in the figure), these points must be placed at a specific distance from the main points (factorial points). The ideal distance can be obtained by research, but this distance is very close to the square root of the number of factors. For example, for two-factor testing, the position of the added axial points is 1.4 ($\sqrt{2}$) units away from the central points. Table 1 illustrates the variables and their levels by the central composite design method and specifies the type of points. Increasing the number of points increases the estimation power and defines the curvature properties better. In the central composite design method, each factor is varied in five levels: lower axial, lower factorial, central, upper factorial, and upper axial. It is noteworthy that this method is different from the five-level factorial method because 25 (5^2) tests are required for two factors in the five-level method. However, the central composite design method is a two-level factorial method in which the central and axial points are added so that the curvature behavior in the model can be well-defined. Similarly, if the factorial approach is to be used in this experiment to find the optimal point, the number of levels, 5, to the 5th power (5 factors), is equal to 3125 tests. This number drops to 50 tests based on the response surface model, which is very important in terms of economic cost and reduced time of experiments.

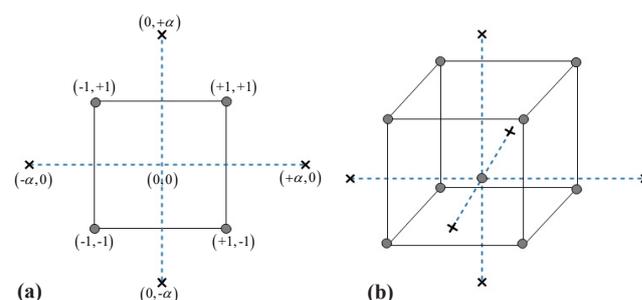


Fig. 2. Central composite method: (a) two-factor and (b) three-factor.

Table 1. Independent variables and their levels for central composite design.

| Code | Variable | Units | Type | Low actual | High actual | Low coded | High coded |
|------|-------------------------|-------------------|---------|------------|-------------|-----------|------------|
| A | Temperature | °C | Numeric | 65 | 85 | -1 | 1 |
| B | pH | | Numeric | 3 | 5 | -1 | 1 |
| C | Time | min | Numeric | 15 | 75 | -1 | 1 |
| D | Mixing speed | rpm | Numeric | 300 | 700 | -1 | 1 |
| E | Zinc dust Concentration | g.L ⁻¹ | Numeric | 1 | 3 | -1 | 1 |

3. Materials and process

The solution used in this work was a post-filtered solution from an Iranian zinc smelting plant. The chemical analysis of this solution is given in Table 2.

Distilled water was used for solubilization and dilution. Industrial-grade zinc dust was provided by the Zanjan dust production plant. Pure sulfuric acid and soda (Merck, Germany) were used to adjust the pH. Copper sulfate, zinc sulfate, nickel sulfate, and cadmium sulfate were supplied by Merck.

All experiments were carried out in a two-liter glass reactor. Optimal temperature conditions were achieved using a hot-plate-mixer (Heidolph MR 3001 K). The pH of the leached solution and its temperature were adjusted by a pH meter (WTW mul 9310). The amount of metal was measured by atomic absorption equipment (AA 240 Varian, Australia).

According to Table 3, 50 experiments were carried out to reach optimal response regions using Design-Expert software. In the cold purification stage of the zinc plant, one liter of the incoming solution with an initial pH of 4.5 was poured into the glass reactor and heated by a heater to reach the desired temperature. Then, predetermined amounts of zinc dust were added to the solution and mixed in the mixer, and the mixture was then filtered. Finally, the sub-filter solution was sampled, and the impurities were measured by atomic absorption equipment. It should be noted that the parameters considered in this study were temperature, time, amount of zinc dust, pH of the solution, and mixing speed. Each test point in this article was the result of an average of 3 repetitions of the experiment. According to Eq. (3), the results are given in the form of removal percentage.

Table 2. Chemical analysis of the post-filtered solution.

| Ion | Zn ²⁺ | Co ²⁺ | Ni ²⁺ | Cd ²⁺ | Fe ²⁺ | Mn ²⁺ | As ³⁺ | Sb ³⁺ |
|-------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Concentration (mg.L ⁻¹) | 85000 | 1.1 | 167 | 600 | 1 | 8 | < 1 | < 1 |

Removal percent of cadmium =

$$\frac{\text{Initial concentration of cadmium} - \text{Secondary concentration of cadmium}}{\text{Initial concentration of cadmium}} \times 100 \quad (3)$$

4. Results and Discussion

The best statistical model was fitted by the software with the information obtained from the removal of cadmium. Eq. (4) is the fitted polynomial model for cadmium with a regression coefficient (R^2) of 0.9921. This value represents a good fit for the response data. Based on this model, the most effective parameters are concentration of zinc dust, residence time, and temperature.

$$\begin{aligned} \text{Removal percentages of Cd} = & -114.50 + 3.74A + 9.92B + 0.35C \\ & + 0.06D + 15.88E - 0.03AB + 1.87 \times 10^{-3}AC - 1.06 \times 10^{-4}AD - \\ & 0.01AE + 3.37 \times 10^{-3}BC - 2.31 \times 10^{-4}BD - 0.15BE - 3.95 \times 10^{-6}CD \\ & - 0.03CE - 2.68 \times 10^{-4}DE - 0.02A^2 - 0.77B^2 - 4.14 \times 10^{-3}C^2 \\ & - 5.05 \times 10^{-5}D^2 - 2.38E^2 \end{aligned} \quad (4)$$

As shown in Fig. 3, there is a close correlation between the values predicted by the software and the actual values, and these models were able to adequately cover these values.

Fig. 4 shows the effect of temperature on the reaction of cadmium cementation. Temperature is one of the most important parameters on the reaction of cadmium cementation by zinc powder, and the reaction speed is very slow at low temperatures. As shown in Fig. 4, the reaction speed increases as the temperature increases up to 80°C, but it reduces at temperatures above that. Since the cadmium cementation reaction is low in activation energy and is controlled by mass transfer, the diffusion effect of cadmium to the surface of zinc powder plays a significant role in determining the reaction speed [31].

Table 3. Design of experiments by the central composite method.

| Test number | Residence time (min) | Amount of zinc dust (g.L ⁻¹) | pH | Mixing speed (rpm) | Temperature (°C) | Removal percentage of Cd (%) |
|-------------|----------------------|--|-----|--------------------|------------------|------------------------------|
| 1 | 60 | 2.5 | 4.5 | 400 | 80 | 99.87 |
| 2 | 15 | 2 | 4 | 500 | 75 | 92.57 |
| 3 | 30 | 1.5 | 4.5 | 400 | 70 | 92.54 |
| 4 | 45 | 2 | 5 | 500 | 75 | 98.67 |
| 5 | 30 | 2.5 | 3.5 | 400 | 70 | 95.83 |
| 6 | 30 | 1.5 | 3.5 | 400 | 80 | 93.75 |
| 7 | 60 | 2.5 | 3.5 | 600 | 70 | 97.03 |
| 8 | 30 | 2.5 | 3.5 | 400 | 80 | 97.46 |
| 9 | 45 | 2 | 4 | 500 | 75 | 98.96 |
| 10 | 45 | 2 | 4 | 700 | 75 | 96.94 |
| 11 | 60 | 1.5 | 4.5 | 600 | 80 | 97.2 |
| 12 | 60 | 2.5 | 4.5 | 600 | 80 | 99.95 |
| 13 | 30 | 2.5 | 3.5 | 600 | 70 | 96.26 |
| 14 | 45 | 2 | 4 | 500 | 75 | 98.97 |
| 15 | 30 | 1.5 | 3.5 | 600 | 80 | 93.93 |
| 16 | 45 | 1 | 4 | 500 | 75 | 93.42 |
| 17 | 45 | 2 | 4 | 500 | 75 | 99.05 |
| 18 | 60 | 2.5 | 3.5 | 400 | 70 | 96.76 |
| 19 | 75 | 2 | 4 | 500 | 75 | 98.15 |
| 20 | 60 | 2.5 | 4.5 | 600 | 70 | 98.25 |
| 21 | 30 | 1.5 | 4.5 | 600 | 70 | 92.97 |
| 22 | 30 | 1.5 | 3.5 | 400 | 70 | 91.75 |
| 23 | 60 | 2.5 | 4.5 | 400 | 70 | 97.82 |
| 24 | 30 | 2.5 | 4.5 | 600 | 80 | 98.28 |
| 25 | 30 | 2.5 | 4.5 | 400 | 80 | 98.05 |
| 26 | 45 | 2 | 4 | 500 | 75 | 98.96 |
| 27 | 60 | 1.5 | 4.5 | 600 | 70 | 95.38 |
| 28 | 45 | 2 | 4 | 500 | 75 | 98.97 |
| 29 | 60 | 1.5 | 3.5 | 400 | 80 | 96.3 |
| 30 | 30 | 2.5 | 4.5 | 600 | 70 | 96.87 |
| 31 | 30 | 1.5 | 4.5 | 400 | 80 | 94.47 |
| 32 | 30 | 1.5 | 4.5 | 600 | 80 | 94.63 |
| 33 | 45 | 2 | 4 | 500 | 75 | 98.96 |
| 34 | 45 | 2 | 4 | 500 | 75 | 99.03 |
| 35 | 60 | 1.5 | 4.5 | 400 | 80 | 97.1 |
| 36 | 45 | 2 | 4 | 500 | 75 | 98.96 |
| 37 | 45 | 2 | 4 | 500 | 85 | 99 |
| 38 | 60 | 1.5 | 3.5 | 600 | 70 | 94.37 |
| 39 | 60 | 1.5 | 4.5 | 400 | 70 | 94.91 |
| 40 | 60 | 1.5 | 3.5 | 600 | 80 | 96.7 |
| 41 | 60 | 2.5 | 3.5 | 600 | 80 | 99.67 |
| 42 | 30 | 2.5 | 4.5 | 400 | 80 | 96.52 |
| 43 | 60 | 2.5 | 3.5 | 400 | 80 | 99.61 |
| 44 | 45 | 3 | 4 | 500 | 75 | 99.99 |
| 45 | 30 | 1.5 | 3.5 | 600 | 70 | 92.13 |
| 46 | 45 | 2 | 4 | 300 | 75 | 97.19 |
| 47 | 45 | 2 | 3 | 500 | 75 | 97.95 |
| 48 | 30 | 2.5 | 3.5 | 600 | 80 | 97.83 |
| 49 | 45 | 2 | 4 | 500 | 65 | 94.64 |
| 50 | 60 | 1.5 | 3.5 | 400 | 70 | 93.84 |

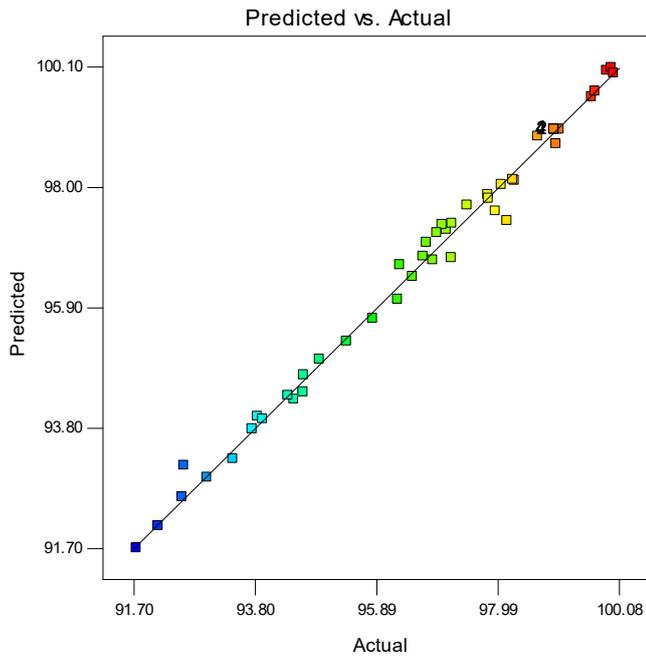


Fig. 3. Comparison of actual values and predicted values for cadmium.

The phenomenon of diffusion results from the thermal motion of the charged and neutral species in the solution, without the effects of the electric field. Therefore, increasing the temperature up to 80 °C enhances the kinetic energy and the mobility of cadmium ions; thus, they more easily diffuse to the surface of zinc powder for the reaction. But at temperatures above 80 °C, the hydrogen reduction, as a competitive reaction with cadmium to gain electrons from the zinc surface, is the dominant reaction, which reduces the yield of the cadmium reduction [36,37].

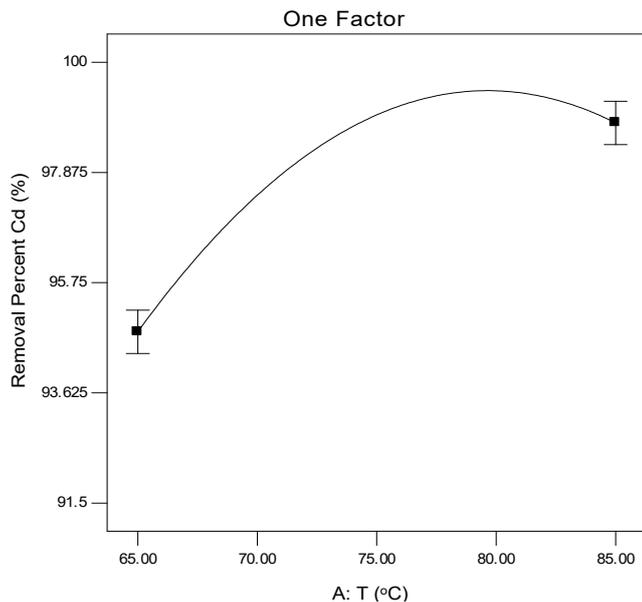


Fig. 4. Effect of temperature on removal of cadmium.

The interaction of temperature and residence time on the reaction of cadmium cementation is presented in Fig. 5. As can be seen, the weakest performance is observed in the first 30 minutes of the reaction and in the temperature range of 65-70°C. However, the reaction efficiency increases with a simultaneous increase in temperature and residence time; and at almost all temperatures, the best performance is obtained in the 45 to 60 minutes intervals and at temperatures of 75 to 80°C. This figure shows that an excessive increase in temperature and time can have an adverse effect on the removal of cadmium by zinc powder and ultimately increases the production cost of zinc ingot.

Fig. 6 demonstrates the interaction of temperature and mixing speed on the reaction of cadmium cementation, the speed of which increases significantly with increasing temperature in a constant mixing speed. Mixing in the solution increases the flux of species to the point where the diffusion layer begins, but after that, the diffusion of cadmium ions from the diffusion layer to the surface of zinc powder mainly determines the reaction speed. In constant mixing, increasing the temperature would increase the diffusion of cadmium ions from the diffusion layer to the surface of zinc powder, which ultimately increases the overall reaction speed [32].

The effect of pH on the cadmium cementation reaction is observed in Fig. 7. According to the figure, the rate of cadmium cementation reaction increases when increasing the pH to 4.5 due to the reduction of the number of hydrogen ions in the solution. Hydrogen ions

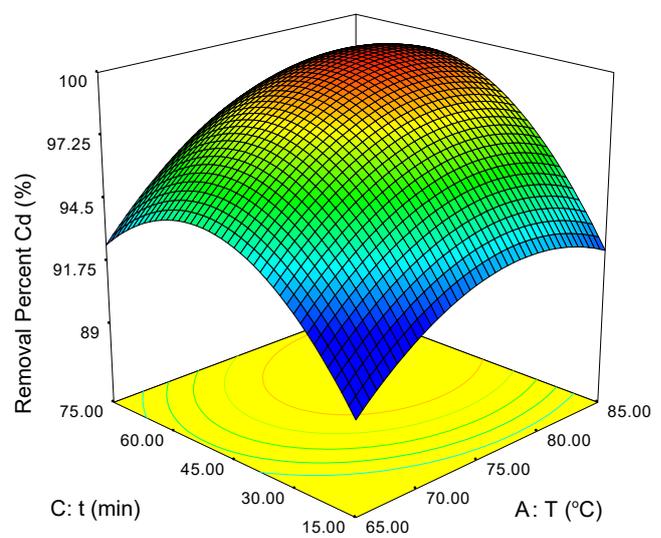


Fig. 5. Interaction between temperature and time on the reaction of cadmium cementation.

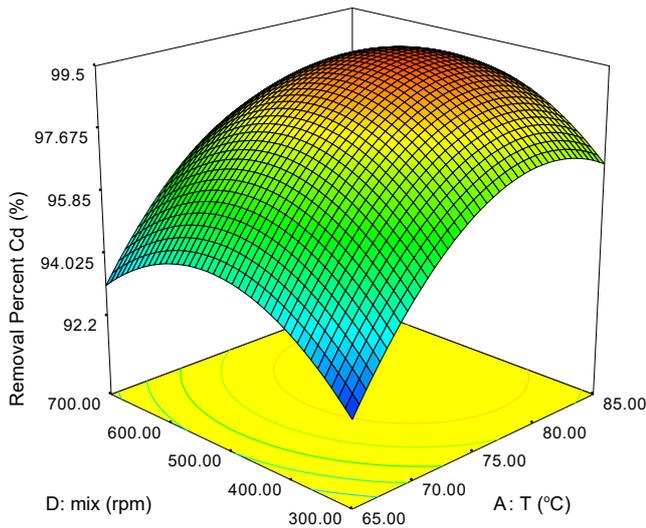


Fig. 6. Interaction between temperature and mixing speed on the reaction of cadmium cementation.

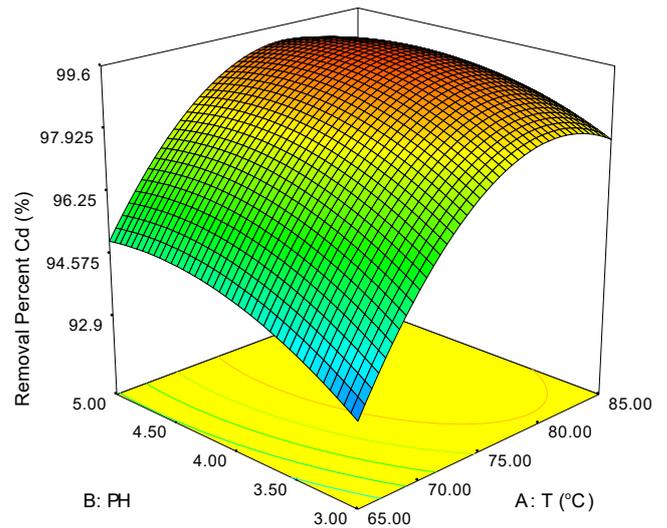


Fig. 8. Interaction between temperature and pH on the reaction of cadmium cementation.

with a higher diffusion factor than the cadmium ions can more easily reach the surface of the zinc powder, so increasing the pH makes the competition easier for cadmium ions and can increase the reaction speed. At pH values above 4.5, the concentration of hydroxide ions in the solution increases, which, due to their high diffusion rate, can then easily reach the surface of the zinc powder where they react with zinc ions in the diffusion layer to produce zinc hydroxide and zinc oxide [23,24,38]. These compounds are deposited on the surface of the zinc powder and affect the reaction of cadmium reduction by creating resistance to electron transfer, which slows down the cementation reaction of

cadmium [39]. As a result, a pH of 4.5 creates a balance between the hydrogen ions and hydroxide ions in the solution providing the best conditions for the reduction of cadmium on the surface of the zinc powder.

Fig. 8 evaluates the interactions between pH and temperature. Based on Fig. 8, the lowest removal percentage is obtained at the lowest temperature and pH. In this situation, cadmium ions have the least kinetic energy making it is difficult for cadmium ions to reach the surface of zinc powder, whereas hydrogen ions have the highest concentration and can easily reach the surface of zinc powder due to their high diffusion rate. As a result, the conditions become much more difficult for the reduction of cadmium regarding either the diffusion into the surface of zinc or in terms of electron capture. By increasing the temperature and pH at the same time, conditions are more favorable for the reduction of cadmium, with the best performance occurring at a temperature of 80°C and a pH of 4.5.

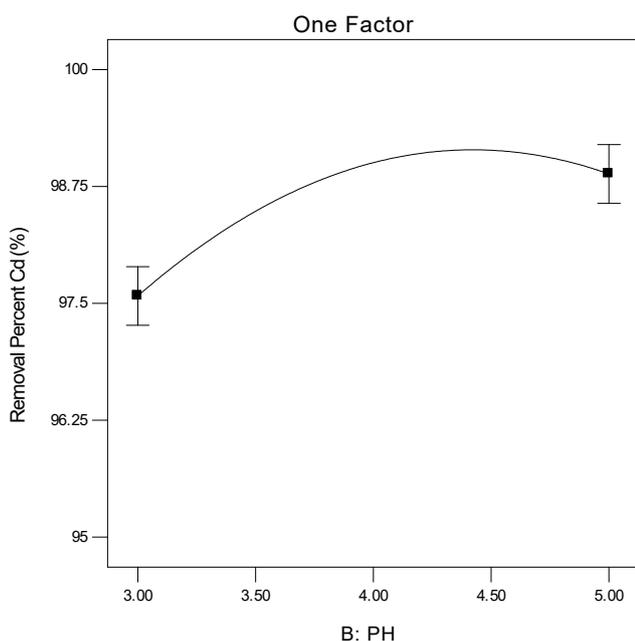


Fig. 7. Effect of pH on the removal of cadmium

Fig. 9 examines the interactions between pH and residence time on the reaction of cadmium cementation. The best performance for cadmium reduction is achieved after 60 minutes and at pH values higher than 3.5, with the best pH of 4.5, as shown in Fig. 7. As the figure shows, increasing amounts of hydrogen ions are consumed and the pH of the solution increases by increasing the reaction time. For this reason, favorable results can be achieved within 60 minutes at pH values fewer than 4. In fact, at the residence time of 60 minutes, pH changes have a lower effect on the cadmium cementation reaction.

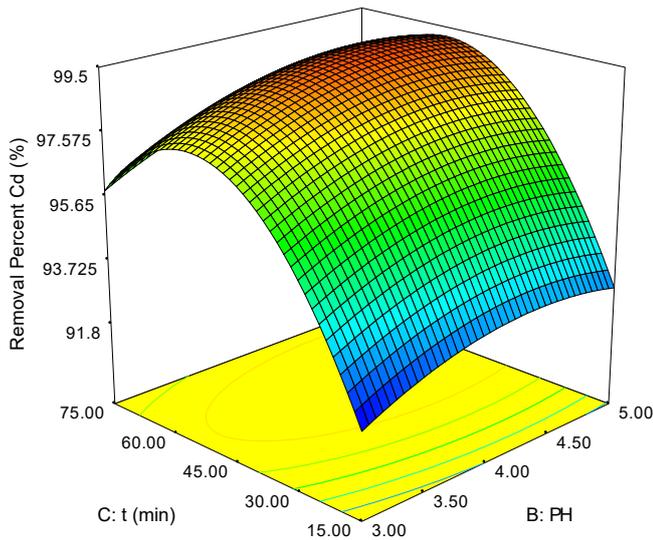


Fig. 9. Interaction between time and pH on the reaction of cadmium cementation.

The effect of residence time on the reaction of cadmium cementation is demonstrated in Fig. 10. While the cadmium cementation is faster when increasing the residence time up to 60 minutes, the cadmium removal efficiency decreases the time higher than 60 minutes. By increasing the residence time, cadmium ions will have more chance of diffusion to the surface of the zinc powder, but as the time increases, more hydrogen ions must be reduced, and the hydrogen reduction (which competes with the cadmium reduction) is weakened and becomes less of a barrier for the cadmium reduction. On the other hand, this serious decrease in hydrogen, to the

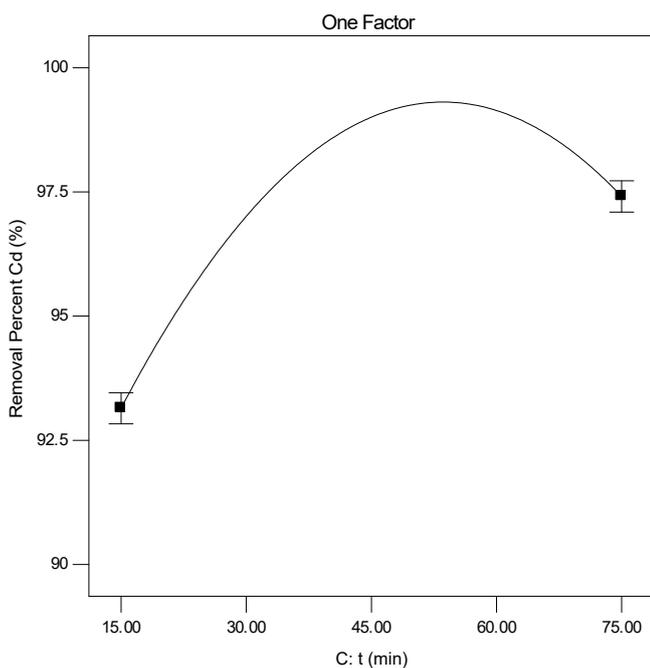


Fig. 10. Effect of residence time on removal of cadmium.

extent that the hydroxide ions would not be predominant in solution, can ideally be useful. Hydroxide ions can diffuse to the surface of zinc, where it reacts with zinc ions to produce compounds such as zinc hydroxides. Zinc hydroxide is a white precipitate that is very difficult to diffuse into the solution stream, which is why it remains in the film layer and causes difficulty for the reaction of cadmium reduction [38].

Fig. 11 represents the interaction of residence time and mixing speed. As can be seen, the yield of reaction will increase with a simultaneous increase of the residence time and the mixing speed, attaining the highest removal percentage at mixing speeds of 400 to 600 rpm and residence times of 45 to 60 minutes. In this condition, the diffusion layer reaches its minimum thickness, which facilitates the diffusion of cadmium to the surface of the zinc powder as well as the diffusion of zinc ions into the solution. Moreover, a time period of 45 to 60 minutes creates an equilibrium between hydrogen ions and hydroxide ions that is the most desirable condition for the reduction of cadmium.

Fig. 12 shows the interaction between the residence time and the concentration of zinc powder, where increasing the concentration of zinc powder and the residence time increases the percentage of cadmium removal. At high concentrations of zinc powder, a high percentage of cadmium removal can be achieved even at lower residence times.

Fig. 13 examines the effect of mixing speed on the reaction of cadmium cementation with zinc powder. As can be seen, the speed of cadmium cementation reaction

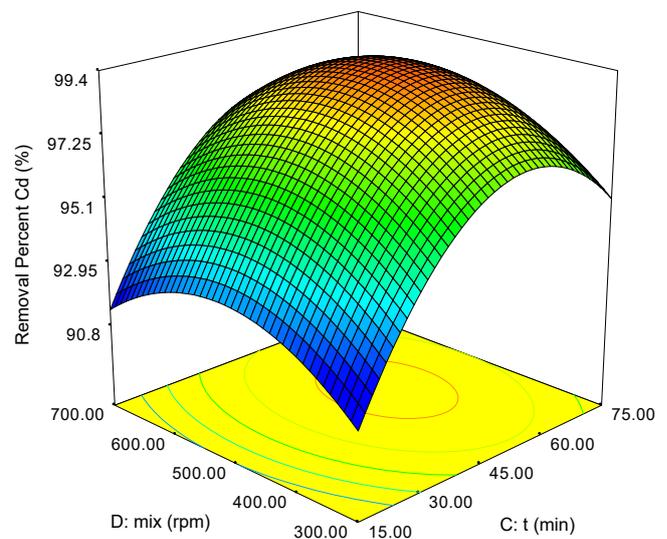


Fig. 11. Interaction between residence time and mixing speed on the reaction of cadmium cementation.

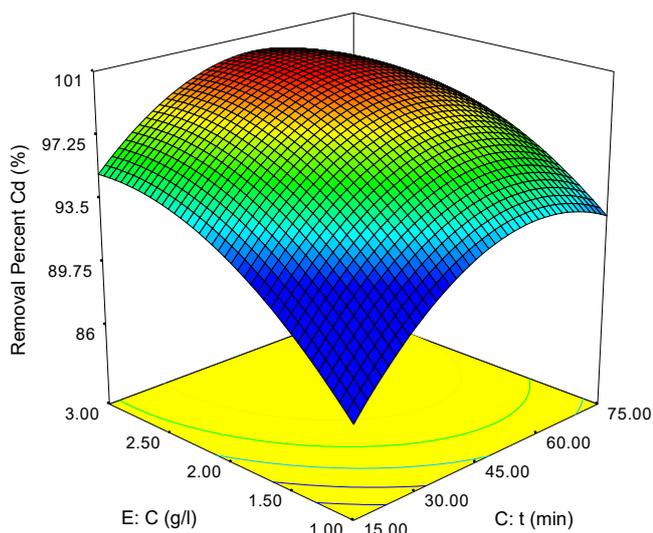


Fig. 12. Interaction between residence time and concentration of zinc dust on the reaction of cadmium cementation.

increases as the mixing speed increases up to 500 rpm, but then the cadmium reduction efficiency decreases at higher mixing speeds. The diffusion layer that forms on the zinc powder is about 0.05 cm in static conditions and can be reduced to 0.001 cm with proper mixing [25,37]. In fact, better mixing makes a smaller diffusion layer, and due to the independence of the diffusion process from time, it creates a greater concentration gradient on the surface of the zinc powder. Cadmium ions should diffuse from the electrolyte solution into the diffusion layer and then pass through the layer width to the surface of the zinc powder. Zinc ions that are

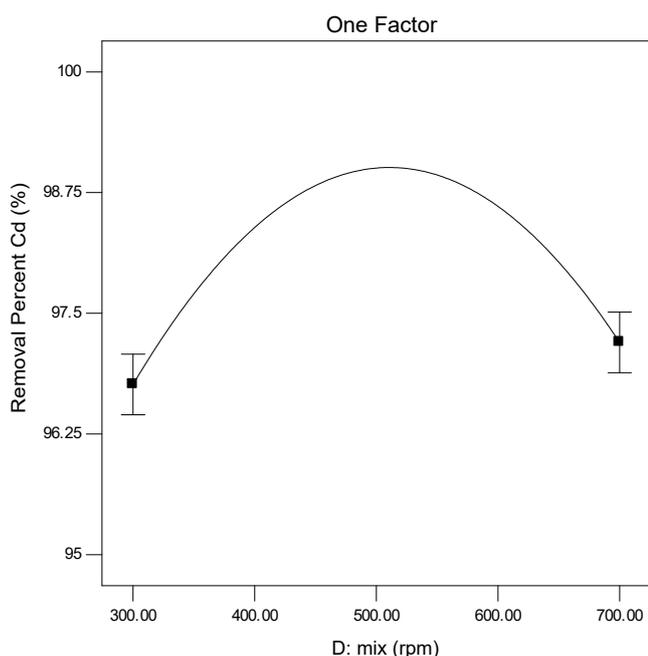


Fig. 13. Effect of mixing speed on removal of cadmium.

separated from the surface of the zinc powder should pass through the diffusion layer to enter the electrolyte solution. According to Fick’s law, if the thickness of the diffusion layer is decreased as much as possible, the transfer flux of cadmium to the surface of the zinc powder and the diffusion of zinc ions into the mass solution will be decreased according to Eq. (5), resulting in a faster reaction. Also, the accumulation of hydrogen gas produced by the reduction of hydrogen on the surface of zinc powder decreases, which reduces the resistance of the gas layer created on the surface of the zinc powder [40,41].

Increase the mixing speed to the extent that the diffusion layer reaches its minimum can increase the reaction speed, but further increases in mixing speed create a tangential velocity component around the vortex shaft. Based on the centrifugal force, the fluid tends to be thrown towards the reactor wall [42]. Accordingly, layers of fluid adhere to the wall of the reactor, making a gap between the mixing shaft and the fluid. Therefore, more molecules of the air enter the solution, which reduces the efficiency of the mixer and causes damage to the shaft due to the many stresses that enter the parts of the mixer [43]. Hence, the zinc powder will not be well distributed and will be deposited due to not using the entire reactor space, the accumulation of fluid on the wall, and the presence of a centrifugal force that is more effective on the solid. The greater diffusion of oxygen molecules into solutions can also reduce the rate of cadmium cementation reaction by forming zinc oxide and zinc hydroxide in the diffusion layer.

Fig. 14 illustrates the interaction of mixing speed and the concentration of zinc powder on the reaction of cadmium cementation by zinc powder. With regards to the figure, the reaction speed first increases then decreases after 500 rpm at all concentrations of the zinc powder. The optimum range for removing cadmium is between 400 to 600 rpm and a concentration of 2 to 3 g.L⁻¹. Fig. 15 also presents the interaction of mixing speed and pH, with the best mixing at 500 rpm at various pH values.

Fig. 16 evaluates the effect of the concentration of zinc powder on the rate of cadmium cementation. The cadmium cementation reaction speed increases significantly with the increase of zinc powder up to 2.5 g.L⁻¹, but then there is almost a uniform trend at higher concentrations. In fact, the percentage of cadmium removal is approximately 100 at a concentration of

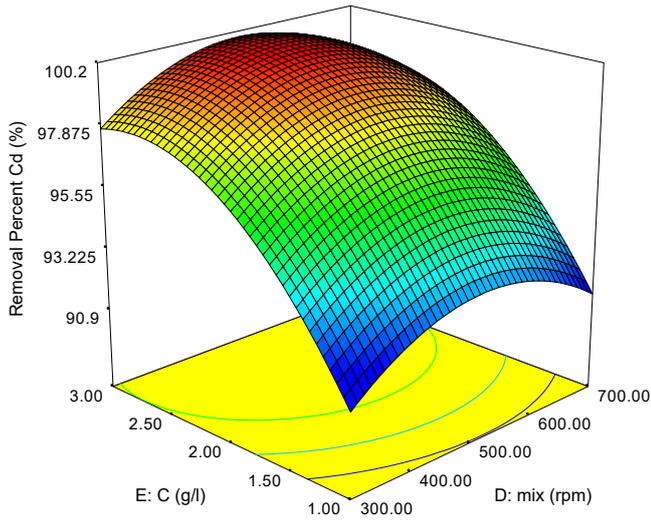


Fig. 14. Interaction between mixing speed and concentration of zinc dust on the reaction of cadmium cementation.

2.5 g.L⁻¹ after 45 minutes, which means that adding more than 2.5 g.L⁻¹ of zinc powder into a solution does not seem to be rational for the complete removal of cadmium. However, increasing the zinc powder can further reduce other parameters. As shown in Fig. 12, a higher removal percentage is obtained at a concentration of 3 g.L⁻¹ at a lower residence time.

Also, there is a high removal rate at concentrations higher than 2.5 g.L⁻¹, even at 70°C (in accordance with Fig. 17, which shows the interaction of temperature and the concentration of zinc powder on the removal of cadmium with zinc powder). At 80°C, cadmium ions diffuse faster to the surface of the zinc powder due to higher kinetic energy, resulting in a decrease in the

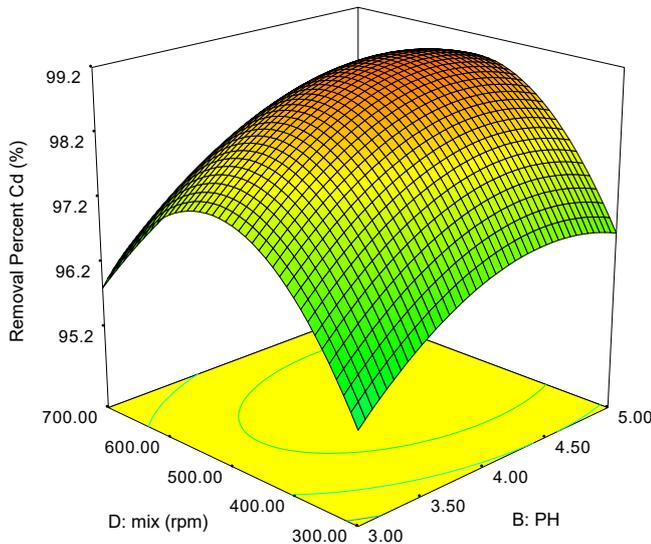


Fig. 15. Interaction between mixing and pH on the reaction of cadmium cementation.

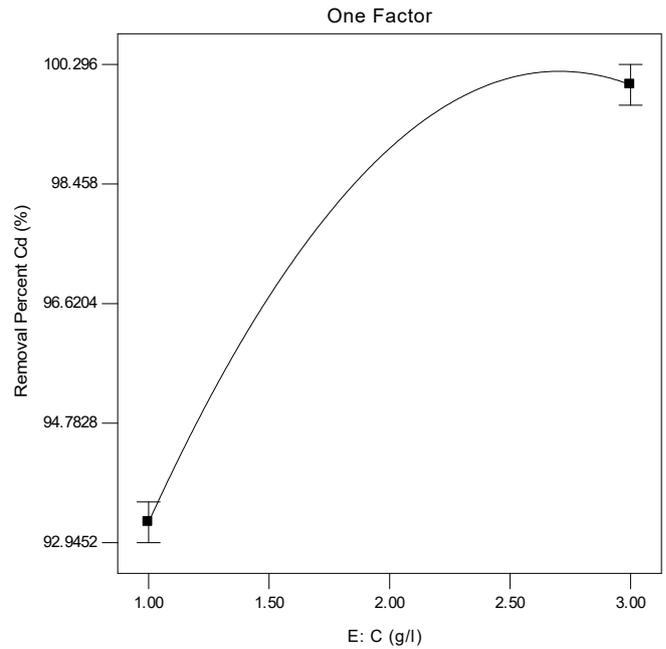


Fig. 16. Effect of concentration of zinc dust on cadmium.

consumption of zinc powder to 2 g.L⁻¹ to achieve a 1% optimal removal.

Fig. 18 shows the interaction of pH and the concentration of zinc powder on the reaction of cadmium cementation; it is clear that the highest removal rates occur at concentrations higher than 2.5 g.L⁻¹ at almost all pH values. So, the pH changes are relatively ineffective on reaction efficiency. An increase in the concentration of zinc powder increases the surface available for the cadmium cementation reaction and makes it easier for cadmium ions to transfer to the surface of the diffusion layer resulting in increased reaction speed.

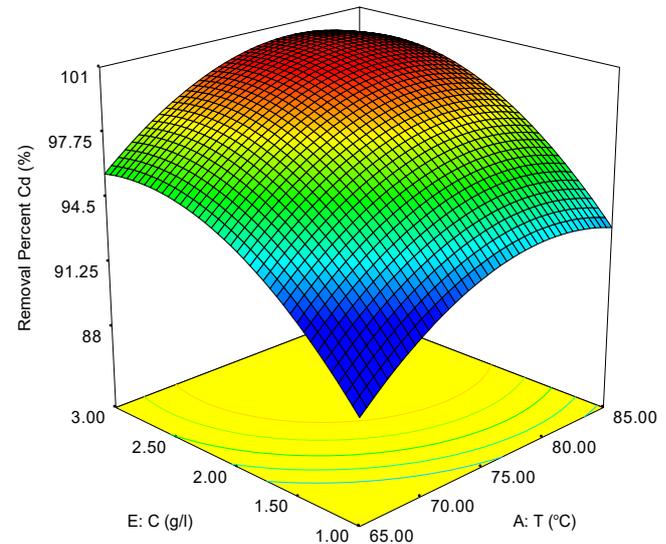


Fig. 17. Interaction between temperature and concentration of zinc dust on the reaction of cadmium cementation.

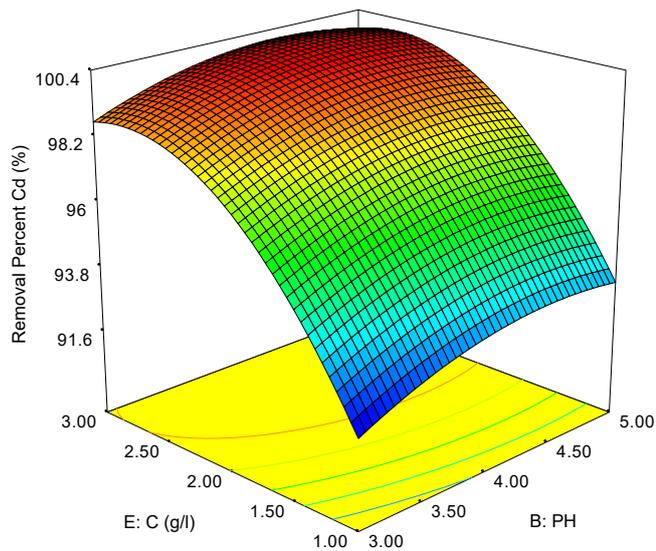


Fig. 18. Interaction between pH and concentration of zinc dust on the reaction of cadmium cementation.

As shown in Fig. 14, there is a high percentage of removal at a concentration of 3 g.L^{-1} at all mixing speeds, indicating that an increase in the surface could also compensate for inappropriate mixing. Also, when the surface is high, the effect of the hydrogen reduction, which competes with the reduction of cadmium, is reduced, resulting in faster and better cadmium reduction.

4. Conclusion

The current study has investigated the influence of diffusion on the speed of the cadmium cementation reaction. The results of the studies showed that the temperature, with the increase in kinetic energy of cadmium ions, caused them to be more mobile, resulting in easier diffusion to the surface of zinc powder. Cadmium ions are usually less successful than hydrogen ions in reaching the surface of the zinc powder due to their high diffusion coefficient that causes them to accumulate more in the film layer and the surface of the powder. For this reason, a pH increase is an effective way to increase the efficiency of the reaction by preventing zinc oxide and zinc hydroxide from forming on the surface of the zinc powder. Although these compounds are more likely to be formed at residence times of more than 60 minutes, the hydrogen ion concentration decreases, allowing the cadmium ions to more readily diffuse within the first 60 minutes. Increasing the concentration of zinc powder also increases the surface of the diffusion layer as well as the transfer of cadmium ions from the solution to

the diffusion layer. An increase in the mixing speed can also increase the reaction speed by decreasing the diffusion layer.

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