Journal of Engineering Research and Applied Science
Available at www.journaleras.com
Volume 13 (1), June 2024, pp 2483-2489
ISSN 2147-3471 © 2024

Increasing the Anticorrosive Property of Zinc Plating Process with Modified Zeolite

Ece Zeybek, Banu Irmak, Sinem Ulusoy, Canan Uraz*

Ege University, Faculty of Engineering, Chemical Engineering, 35100, Izmir, Turkey

Accepted 5 March 2024

Abstract

The plating is done to protect the material and to increase the material's corrosion resistance. This study is aimed to increase the corrosion resistance, to reduce the cost of the alkaline zinc plating process and to make it eco-friendlier by adding modified zeolite. In addition, it is aimed to increase the red rust formation time on iron plates by using modified zeolites. Zeolite modifications were carried out in laboratory conditions and they were prepared by using different chemicals, zeolite sizes, and zeolite amounts. Zinc acetate, magnesium chloride, calcium chloride, molybdic acid, and lanthanum (III) nitrate solutions were used for the modification of natural zeolites. Modified zeolites were added to the alkaline zinc plating bath and were subjected to corrosion tests. Corrosion tests are the most important part of this study. Characterization of the modified zeolite samples was performed by FT-IR and SEM analysis. With the SEM analysis results, high resolution images are provided that clearly show the surface morphology of the modified samples. The functional groups in the structure of the zeolites and the bond states in their structures were determined by FT-IR analysis. According to the results obtained, the most effective and applicable modification method with the best anticorrosive effect was determined. The best anticorrosive effect was observed on the plate that was plated with 7 grams, 10 µm zeolite with molybdic acid in experiment 6.

Keywords: *Zeolite, corrosion, zinc, metal plating, modification, anticorrosive*

1. Introduction

Corrosion is one of the biggest problems of the metal industry. The rust formed on the metal not only creates a bad appearance on the surface, but also makes it difficult to process the material. Corrosion is the deterioration of a metal by the action of corrosive substances (Schofield, M. J. 2002). Iron, steel, aluminum, and alloys are prone to corrosion by reacting with atmospheric oxygen (Kaesche, H. 2003). Corrosion causes problems such as equipment downtime, material failure, and wastage of valuable resources. Corrosion can be prevented by cathodic protection, anodic protection, use of inhibitors, selection of durable metals and alloys, paint and plating methods.

Metal plating has a very important place in the world. It is used to form an effective barrier against corrosion, inhibit anode-cathode reactions by forming a path with high electrical resistance, and passivate the metal surface with soluble pigments (Ahmed, N. M., et al. 2011). Plating provides long-term protection to metals. Although there are many types of plating baths, zinc and its alloys are the most widely used plating baths to protect metal components, due to their antitoxic effect, low cost, and success in preventing corrosion (Holland, R., and Larick, 2003). The zinc plating process is alkaline with excellent metal dispersion and plating power.

The study of zinc in the literature is very limited and largely focused on the acid bath and the effects of organic additives. Although there are studies aimed at reducing the toxic effect in plating baths and preventing corrosion that occurs after plating, there has not been a study conducted to prevent corrosion that occurs on metal surfaces by adding modified zeolite to an electric current metal plating bath.

Zeolites are used in many applications due to their versatile properties and they are crystalline microporous aluminosilicates with well-defined structures consisting of AlO_4 tetrahedra (Pokhmurskii, V. I. et al. 2013; Nezamzadeh-Ejhieh A., Raja G. 2012). Zeolites are naturally negatively charged and have a high ion exchange capacity. Thanks to the capacity to accommodate extra ions and molecules in the regular porous structure of the zeolite, they can

---

*Corresponding author: canan.uraz@ege.edu.tr form a protective layer on the metal substrate and they can reduce the corrosion rate by passivating its surface (Calabrese, L. 2018).

One of the most important zeolite found in nature is clinoptilolite. Clinoptilolite has a large amount of pore spaces, high resistance to extreme temperatures, and a chemically neutral base structure. It has features such as high absorption level, ion exchange capacity, catalysis, dehydration activity and easy formability (Demir H., and Polat E.2003).

Molybdic acid, lanthanum (III) nitrate, zinc acetate, magnesium chloride, and calcium chloride have been used for the modification of natural zeolites (Ahmed, N. M., et al. 2011; Deyá, C. et al.2007, Roselli, S. et al. 2014). Molybdenyl cations perform ion exchange with the Na cation of the natural zeolite. Molybdates are compounds used as inhibitors on steel alloys (Calabrese, L. 2018). Lanthanum cations are used in another modification of natural zeolite and they are effective for corrosion inhibition. Free cations form a lanthanum hydroxide complex, forming a protective layer for corrosion. In addition, lanthanide salts have lower toxicity compared to sodium chloride (Roselli, S. et al. 2014). It is safer and more efficient to use cation exchange zeolites to replace hazardous pigments. Na ions are cationically exchanged with Zn, Ca, and Mg ions (Ahmed, N. M., et al. 2011).

2. Experimental part

The experimental study was carried out in three stages: modification of the zeolite with different parameters, adding the modified zeolites to the alkaline zinc plating bath, performing corrosion tests (salt spray test) to check the corrosion resistance of the plating, and performing FTIR and SEM analyses for the characterization of the modified zeolites.

Scanning electron microscopy (SEM) provided high-resolution images that clearly showed the surface properties of the modified zeolites. SEM is an effective method used in the microimaging of many surfaces. This method could be applied to investigate the surface structure and determine the texture and particle size of the surface (Pokhmurskii, V. I. et al. 2013; Nezamzadeh-Ejhieh A., Raja G. 2012). The experimental parameters are the amount of zeolite (7 g and 14 g), the zeolite particle size (10 µm, 50 µm, and 100 µm), and the types of chemicals (zinc acetate, magnesium chloride, calcium chloride, molybdic acid, and lanthanum (III) nitrate). The plating process was applied to the iron plates. Iron plates were made suitable for the plating process by being drilled from the middle points of their upper sides with a drill. The plates are 1 cm thick and have an area of 1 dm^2. The weight of plates is 16.8 grams before plating. The alkaline zinc plating process was established on a laboratory scale and experiments were carried out at this scale. Natural zeolite (clinoptilolite) taken from the Manisa Gordes region was used in the experiments. Clinoptilolite is a natural zeolite that is advantageous in terms of cost and used in many fields such as scientific studies. The corrosion resistance of the plates was measured with the help of the salt spray tests. DCTC 600P was used as a salt spray test device. The plates were put in the salt spray test at the same time and they were examined under the same test conditions. The salt spray test cabinet was opened at the same time every day, and a periodic visual inspection was carried out on the plates.

2.1. Modifications of zeolite

Different modifications were made in line with literature surveys. These are molybdic acid modification, lanthanum (III) nitrate modification and zinc acetate, magnesium chloride, and calcium chloride modification.

2.1.1. Molybdic acid modification

Molybdenyl cation solution was prepared with a mixture of 10 g of molybdic acid, 90 mL of 1M sulfuric acid, and 10 ml of concentrated sulfuric acid. Molybdenyl cation solution and zeolite were mixed with an ultrasonic homogenizer and then it was filtered. After filtration, it was washed with distilled water and 1% sodium hydrogen carbonate solution until it reached a neutral solution. Lastly, the modified zeolite was dried at room temperature.

2.1.2. Lanthanum (III) nitrate modification

Zeolite and 0.2 mol/L nitric acids are mixed and it is heated to a boiling point of 83 ˚C to remove ferric compounds. Then it is filtrated and washed several times with distilled water. It is mixed with 2 mol/L sodium acetate for 3 hours under continuous stirring to put it back in the Na^+ form. The zeolite is separated by filtration and washed with distilled water. The zeolite is mixed with 1 mol/L Lanthanum (III) nitrate in $1x10^{-3}$ mol/L nitric acid by an ultrasonic homogenizer. It is modified with La (III) ions by contact. The modified zeolite is filtrated and washed with distilled water and dried at room temperature.

2.1.3. Zinc acetate, magnesium chloride and calcium chloride modification

The zeolite was added to 150 ml of 0.1 M soluble salts of Zn, Mg, and Ca. The solution was stirred at ambient temperature for 1 hour. Then it was filtered. 150 ml of 1 M ammonium oxalate solution was added to the supernatant. This is the ammonium oxalate gravimetric method. It was ensured that no further ion exchange would take place. Ion exchange zeolites were washed with distilled water and dried at room temperature.

2.2. Addition of modified zeolites to the plating bath

The laboratory scale of the alkaline zinc plating process was established in the laboratories of İleten Mühendislik Kaplama Ind.&Trade Inc. The plating process was performed with the addition of modified zeolites to the plating bath in a 2-liter glass beaker. The iron plate to be plated was placed as the cathode in the plating bath. Before plating, it is always necessary to pre-treat the metal to be plated, the tools and equipment required for this process are the parts that complete the plating process. The metal surface must be purified not only from oil and dirt but also from other remaining layers on the surface. The first step in cleaning is to remove oil and dirt using a suitable organic solvent. The plate is then thoroughly washed with water. During the study, one plate was plated in a plating bath where no modified zeolite was added. The purpose of this is to be able to observe how much longer the red rust formation time of the plating made with modified zeolite is than the plating made without the modified zeolite. Another reason to doing this is to make inferences about the effect of the experimental parameters on the corrosion resistance by comparing the modified and unmodified plates. During the plating process, the plating bath was stirred for both conditions. It was aimed to make the plating bath more homogeneous and to distribute the zeolites better into the bath by stirring. In the plating bath; 2 Ampere/dm^2, 3.5 Volt were applied for half an hour for each plate.

The plating thickness of the plates was measured by an X-ray device after the plating process. Whether the plates were properly plated, and the distribution of the plating was checked with the help of X-ray measurements. There should be no darkening, burning, or swelling in any part of the plated area of the plates.

2.3. Corrosion tests

The salt spray test is a standardized and popular corrosion test method, used to check the corrosion resistance of materials and surface plating. The purpose of this test is to measure the corrosion resistance of the metals used. The apparatus for testing consists of a closed testing cabinet, where a saltwater solution (5% NaCl) is atomized by means of spray nozzles using pressurized air. This method provides a possibility to check the plating quality of a metallic substance.

Before the plates were put to the salt test during the experiments, the type of modification used in the plating, the day of the experiment, the time when the plate was put to the salt test, and the plating thickness of the plate was noted. During the experiments, the plates were placed inside the cabinet in such a way that they were not located directly above the path of the sprayed fog and they did not come into contact with each other. In addition, the hanger material on which the plates are hung should in no case be metallic. Therefore, plastic hanger material was used in the experiments. The salt spray test was operated in the pressure range of 1-1.1 bar. During the test period, any pressure increase or pressure drop in the cabinet was avoided so that the results would not be affected. As a result of the tests carried out, the quality of the plating is understood according to the time of formation of red rust on the plate. The operating conditions of the device are determined according to the ASTM B117-Standard Practice for Operating Salt Spray (Fog) Apparatus and ISO 9227-Corrosion Tests in Artificial Atmospheres standards.

3. Results and discussion

This study aimed to increase the anticorrosive property of the alkaline zinc process by using modified zeolites. The results of the study can be examined in two main categories:
Evaluation of characterization results of zeolites,
Evaluation of zinc plating thickness values,
Evaluation of corrosion test results.

3.1. Characterization of modified zeolite

The modified zeolites were analyzed by Fourier-transform spectroscopy (FT-IR) in KBr pellets at room temperature using a Perkin Elmer FT-IR spectrophotometer with wavenumbers between 4000 cm^{-1} and 400 cm^{-1}. Characterization of the surface morphology of the modified zeolites was performed with a Thermo Scientific Apreo S scanning electron microscope (SEM).

3.1.1 FT-IR spectroscopy of modified zeolite

FT-IR analysis was performed to observe new peaks of all samples after modifications were made. The wavelength is between 4000 cm^{-1} and 400 cm^{-1}. The characteristic peak of the zeolite is seen at the wavenumber of 950 cm^{-1} -1200 cm^{-1}. Zeolites are microporous aluminosilicates, and it was observed in the graphs drawn as a result of the FT-IR analysis of the modified zeolites that the peak point was approximately 1000 cm^{-1} in Figure 1, which indicates that the Si/Al-O vibrations occur at 1000 cm^{-1} (Mozgawa, W.et al.1999).

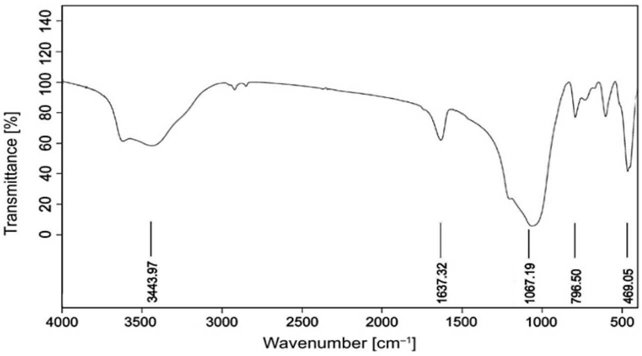

Figure 1. The clinoptilolite Fourier transform infrared spectroscopy (Mansouri, N. et al. 2013)

The characteristic peak of all samples is shown in about 1000 cm^{-1} wavenumber as seen in Figures 2, 3, 4, 5, 6. A broad and almost linear band is observed due to absorbed water between 3000-4000 cm^{-1} due to H-O-H bands of absorbed water. In addition, the peak transmittances of the zeolite samples in the wavenumber range of 1500-2000 cm^{-1} have become more obvious. This is due to the vibrations of strong ions in the modifications.

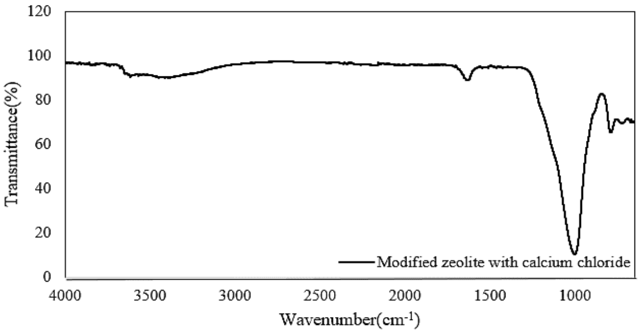

Figure 2. FTIR spectra of modified zeolite with calcium chloride, experiment 2

Figure 3. FTIR spectra of modified zeolite with magnesium chloride, experiment 3

3.1.2 Scanning electron microscopy (SEM) analysis of modified zeolite

Scanning electron microscopy (SEM) provided high-resolution images that clearly showed the surface properties of the modified zeolites. It was observed that the modified zeolites with good results had extremely porous structures and semi-platelet particles in Figure 7. Therefore, modified zeolites were found to be suitable for ion exchange.

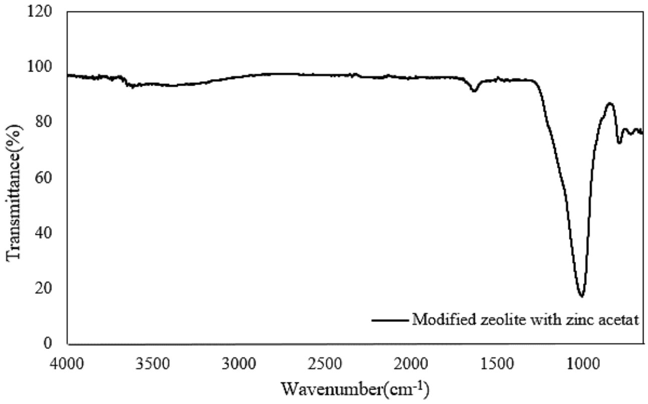

Figure 4. FT-IR spectra of modified zeolite with zinc acetate experiment 4

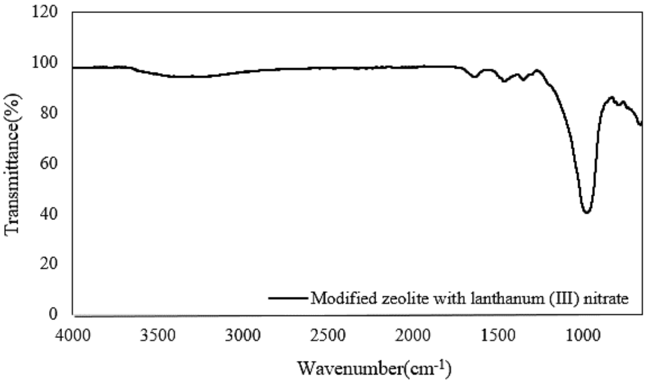

Figure 5. FT-IR spectra of modified zeolite with lanthanum (III) nitrate experiment 5

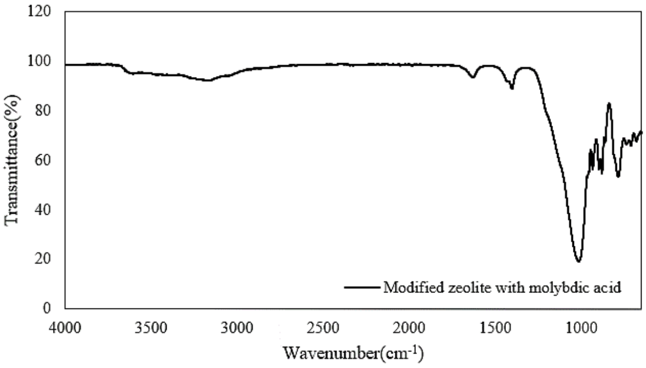

Figure 6. FTIR spectra of modified zeolite with molybdic acid experiment 6

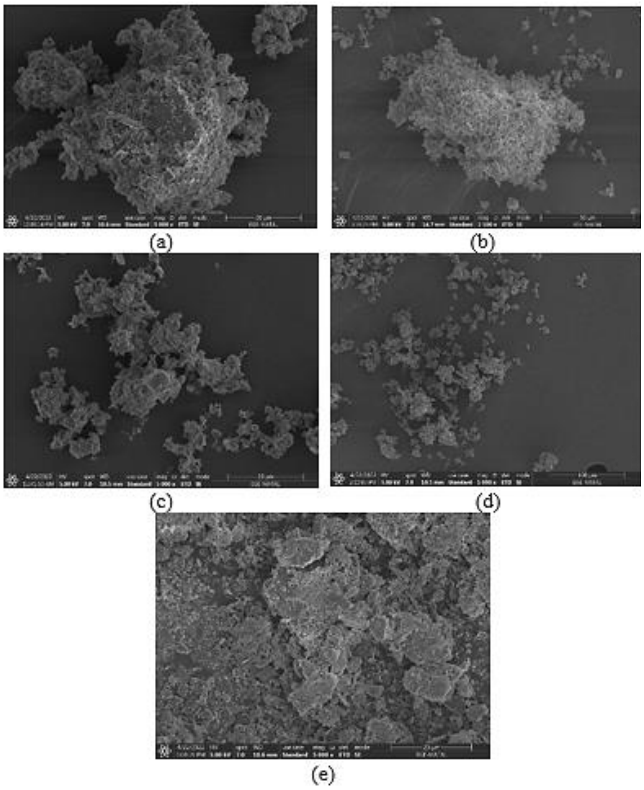
(a) (b) (c) (d) (e)

Figure 7. SEM micrograph of the modified zeolites for a) Experiment no. 2 b) Experiment no. 3 c) Experiment no. 4 d) Experiment no. 5 e) Experiment no. 6

Table 1. Average plating thickness values for each experiment

Experiment No	Average Plating Thickness (µm)	Experiment No	Average Plating Thickness (µm)
1	8.70	10	9.83
2	10.35	11	8.54
3	9.89	12	9.57
4	9.64	13	9.68
5	9.75	14	9.95
6	10.71	15	9.60
7	8.96	16	8.12
8	9.79	17	10.46
9	9.70		

3.2. Plating thickness results

According to the type of plating performed in each experiment, the plating thicknesses differed from each other. These differences are due to the type of chemical used in the experiments, the amount of zeolite, the particle size of the zeolite, and criteria such as pH and temperature contained in the baths used during the experiment. The average plating thickness values of the plates are shown in Table 1 and the red rust formation time for each plate in the experiment is shown in Table 2. When these two tables are compared with each other, it is seen that satisfactory and compatible results are obtained for both.

Table 2. Experimental Studies

Experiment No	Zeolite Particle Size (µm)	The Amounts of Zeolite (g)	Chemical Type	Red Rust Time (hour)
1	10	7	Unmodified	504
2	10	7	Calcium Chloride	720
3	10	7	Magnesium Chloride	648
4	10	7	Zinc Acetate	552
5	10	7	Lanthanum(III)Nitrate	600
6	10	7	Molybdic Acid	888
7	50	7	Calcium Chloride	528
8	100	7	Calcium Chloride	624
9	50	7	Magnesium Chloride	576
10	100	7	Magnesium Chloride	624
11	50	7	Zinc Acetate	504
12	100	7	Zinc Acetate	531
13	50	7	Molybdic Acid	576
14	10	14	Calcium Chloride	648
15	10	14	Magnesium Chloride	576
16	10	14	Zinc Acetate	480
17	10	14	Molybdic Acid	744

3.3. Corrosion test results

Corrosion tests are the most important part of this study. If the plate does not receive a sufficient amount of plating, the formation of red rust on the plate, the beginning of corrosion, occurs earlier and faster. Therefore, different factors were taken into account when comparing the results. The red rust formation time for each experiment is shown in Table 2.

When the micron values and the amount of the zeolite added to the plating bath were kept constant (experiments 1, 2, 3, 4, 5, and 6) it was observed that molybdic acid was the chemical that gave the best result among the chemicals used in the modification process. If a ranking is to be made between these different chemicals, Molybdic Acid showed the best results, followed by $CaCl_2$, $MgCl_2$, Lanthanum (III) Nitrate and Zinc Acetate. The reason why the plates with zinc acetate modification rust earlier than other chemicals may be due to the fact that the plating bath is also a zinc containing bath. The corrosion test duration of the best result in this study is the modification with Molybdic Acid. In this plate which was plated with 7 grams and 10 µm of zeolite (experiment 6), red rust formation was observed 384 hours - 16 days later, than the plate without using modified zeolite.

For each chemical used in the experiments (calcium chloride, magnesium chloride, zinc acetate and molybdic acid), it is observed that the formation time of red rust on the plates is shortened when the particle size of the zeolite is kept constant at 10 µm and only the amount used is increased from 7 grams to 14 grams (experiment 2-19, experiment 3-15, experiment 4-16, experiment 6-17). As the amount of zeolite increases, it makes it harder for the zeolites to hang in the plating bath, and accordingly, the tendency to collapse at the bottom of the plating bath increases. Based on these results, it can be said that increasing the amount of zeolite does not have a positive effect on corrosion resistance.

In addition, there is an inverse relationship between zeolite size and ion exchange capacity. Increasing zeolite size reduces the ion exchange capacity of the zeolite, resulting in lower corrosion resistance. The reason is that the larger the zeolite size, the more difficult it is to distribute the zeolites homogeneously in the plating bath. So larger sizes of zeolites can prevent the plates from getting the plating well.

It was observed that the corrosion resistance changed non-linearly as the zeolite size increased. Modifications which have 50 µm zeolite size (experiment 7-9-11-13) are not as durable as modifications that have 100 µm zeolite size (experiment 8-10-12) to corrosion. It is not clear what caused this result because a precise correlation between corrosion inhibition and zeolite particle size has not been reached.

The results of this study are very promising. In the experiments, the best effect in improving corrosion resistance was achieved when the amount of zeolite was kept at 7 grams and the zeolite size was kept at 10 µm. The most efficient results were obtained from the modifications made with molybdic acid (experiment 6 and experiment 17) and the corrosion resistance of the process increased significantly. This proves that the study has reached its goal and that it has succeeded in delaying the formation of red rust by increasing the anticorrosive property of the alkaline zinc process.

4. Conclusions

It can be stated that zeolites are of great interest to the chemical industry, especially for their ability to ion exchange. Exchangeable cations of zeolites could be changed by corrosion inhibiting ions. In this study, this property of zeolite has been utilized and it has been tried to be used in delaying the formation of corrosion on materials, and accordingly, positive and promising results have been obtained.

Anticorrosive applications of modified zeolite are a new method and less harmful to the environment. In addition to that, cation-exchanged zeolites can be considered a safe and efficient alternative. With the help of our study, it will be possible to produce more resistant materials against corrosion by using the world's natural resources in the plating process.

According to the results obtained, the best anticorrosive effect was observed on the plate that was plated with 7 grams and 10 µm zeolite with molybdic acid in experiment 6. Considering the effects of corrosion in terms of equipment, operation, and cost, it is very valuable to be able to delay the rusting of the material by 384 hours-16 days. This means that it extends the service life of the material and makes the material more durable from corrosion.

As the conclusion of the study, reducing the size of zeolite is increase the weight percent of exchanged cation due to the results of analysis because the increasing the surface area of zeolite material. The reduced size of zeolites provides a more effective ion exchange procedure. Therefore effective corrosion prevention is observed.

It is very promising for future corrosion studies, that it has been achieved to increase the corrosion resistance of the alkaline zinc plating process, which is a process with not very high corrosion resistance, with the zeolite modification prepared using different chemicals. These procedures could be developed by using solutions with different concentrations, different amounts and different sizes of clinoptilolite.

Acknowledgments

The authors acknowledge the financial support by the İleten Mühendislik Kaplama Ind. & Trade Inc., Scientific and Technological Research Council of Turkey (TUBITAK-2209 A) under project number 19192012110275 and Ege University Scientific Research Fund under project number FLP-2022-23588.

References

[1] Ahmed, N. M., Hassan, S.E., and Selim, M. M. (2011), “Anticorrosive performance of ion-exchange zeolites in alkyd-based paints”, *Pigment & Resin Technology*, 40(2), 91-99 pp. https://doi.org/10.1108/03699421111113747

[2] Calabrese, L. (2018), “Anticorrosion behavior of zeolite coatings obtained by in situ crystallization: a critical review, materials”, *Materials*, 2019(12),1-25 pp. https://doi.org/10.3390/ma12010059

[3] Demir H., Polat E. (2003), “Zeolit (klinoptiloit) ve tarımda kullanımı”, *Hassad,* 221*,* 54-59 pp.

[4] Deyá, C., Romagnoli, R. and del Amo, B. (2007), “A new pigment for smart anticorrosive coatings”, *J. Coat. Technol. Res.*, 4 (2), 167–175 pp. https://doi.org/10.1007/s11998-007-9021-4

[5] Holland, R., and Larick, 2003, The Use of Alkaline Cyanide Free Zinc Plating Under Paint and Powder Coatings, Coating, 1 p.

[6] Kaesche, H. (2003), “Corrosion of metals”, *Physicochemical Principles and Current Problems,* 1-4 pp. ISBN-10: 3642056202, ISBN-13: 9783642056208.

[7] Mansouri, N., Rikhtegar, N., Panahi, H., Atabi1, F. and Shahraki, B. (2013), Porosity, characterization and structural properties of natural zeolite–clinoptilolite – as a sorbent, Environment Protection Engineering, 39(1), 139-152 pp. doi: 10.5277/EPE130111

[8] Mozgawa, W., Sitarz, M. and Rokita, M., (1999), “Spectroscopic studies of different aluminosilicate structures”, *Journal of Molecular Structure*, 511- 512, 251–257 pp. https://doi.org/10.1016/S0022-2860(99)00165-9

[9] Nezamzadeh-Ejhieh A., Raja G. (2012), “Modification of nanoclinoptilolite zeolite with hexadecyltrimethylammonium surfactant as an active ingredient of chromate-selective membrane electrode*”, Hindawi Publishing Corporation Journal of Chemistry*, 2013,1-13 pp. http://dx.doi.org/10.1155/2013/685290

[10] Pokhmurskii, V. I., Zin, I.M., Bily, L.M., Vynar, V.A. and Zin, Ya I. (2013), “Aluminum alloy corrosion inhibition by chromate-free composition of zinc phosphate and ion-exchanged zeolite*”, Surf. Interface Anal.*, 45, 1474–1478 pp. https://doi.org/10.1002/sia.5275

[11] Roselli, S., Bellotti, N., Deyá, C., Revuelta, M., del Amo, B. and Romagnoli, R. (2014), “Lanthanum-exchanged zeolite and clay as anticorrosive pigments for galvanized steel”, *Journal of Rare Earths,* 32(4), 352 p. https://doi.org/10.1016/S1002-0721(14)60078-8

[12] Schofield, M. J. (2002), “Corrosion”, *Plant Engineer's Reference Book (Second Edition),* 33*, 1-25 pp.* Hardcover ISBN: 9780750644525, eBook ISBN: 9780080497723.