

Synthesis & characterization of $Zn_3(VO_4)_2$ pigment for anti-corrosive coating application

Snehal Balbudhe^{a,b}, Debishree Khan^{a,b*}, Sachin Mandavgane^c, Gajanan Lakhawat^d & Vijay Pawade^d

^aCSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur 440 020, India

^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India

^cVisvesvaraya National Institute of Technology (VNIT), Nagpur 440 010, India

^dLaxminarayan Innovation Technological University, Nagpur 440 033, India

Received: 10 June 2024; accepted: 12 January 2025

This study has reported a simple and cost-effective method for the synthesis of the corrosion inhibitor zinc vanadate nano-pigment. Further, the prepared pigment has been well characterized by different techniques such as XRD, FESEM, FTIR, EIS, etc. The formation of zinc vanadate nanoparticles has been confirmed by the FESEM. Zinc vanadate nano-pigment-based anti-corrosive coating has been prepared in epoxy resin and has been compared with zinc phosphate-based epoxy coating for the anticorrosive properties using an electrochemical impedance test (EIS test). The result has indicated that zinc vanadate nano-pigments have exhibited better performance in coating applications and also have shown high inhibitor efficiency and a lower corrosion rate. Thus, it has found potential scope in anticorrosive coating applications.

Keywords: Anti-corrosive properties, Coating applications, Electrochemical impedance test, Nano-pigment, Precipitation technique

1 Introduction

Every year, various industries like chemicals, infrastructure, shipping and ports etc. across the globe are facing economic losses due to the corrosion of metals. Protecting and enhancing the life of metal structures from corrosion is still a matter of research to date, even after many researchers have made efforts to develop advanced materials and related anticorrosive coating technology. It is well known that once corrosion starts on the metal surface, it cannot be fully eliminated, but by applying anticorrosion protection to the surfaces of the metal, the effects of the material's deterioration can be prevented to some extent. Further, factors of risk due to corrosion can also be minimized at the stage of designing and fabrication, with the addition of some other element in the composition of the metal. However, the mechanical, physical, and chemical properties of the metal are also important for a variety of applications. Therefore, using organic coating on the metal surface is a more effective and sustainable approach to avoid corrosion¹⁻⁴. Anticorrosive pigment-based coatings can make a significant contribution to corrosion inhibition due to the three important mechanisms such as the shielding

effect, passivation, and electrochemical protection, etc.⁵⁻⁸. Some of the well-known anticorrosive pigments are phosphate, molybdate, chromate, zinc oxide, etc.^{9,10}. Additionally, vanadates, molybdates, or phosphates are also favourable inorganic inhibitors that are employed as economical alternatives to improve the quality and performance of the coating¹¹⁻¹⁵.

This study focuses on the promising material zinc vanadate, which is an ideal class of inorganic nanomaterials that can be synthesized by different techniques like the hydrothermal method¹⁶, sol-gel¹⁷, wet chemical approach¹⁸, coprecipitation¹⁹ and solid state^{20,21}. These methods are widely applicable for the preparation of anticorrosive nano pigments. In this study, zinc vanadate nano-pigments are synthesized by a hydrothermal precipitation method using four different zinc salts, i.e., zinc acetate, zinc chloride, zinc nitrate and zinc sulphate as precursors and ammonium meta-vanadate as the precipitant. Further, zinc vanadate is used to formulate an anti-corrosion coat and is compared with that of zinc phosphate using an electrochemical impedance test.

2 Materials and Methods

In this study, zinc acetate was obtained from Loba Chemi (Mumbai), zinc sulphate and zinc phosphate were obtained from Kemhasol, zinc chloride and zinc

*Corresponding author (E-mail: k.debishree@neeri.res.in)

nitrate were purchased from a local vendor and ammonium meta-vanadate (NH_4VO_3) from Hi Media (Mumbai). Ethanol is obtained from MEARCK, Epoxy resin is being prepared in the laboratory, Amine hardener is obtained from SDFCL, and Toluene is obtained from Ranboxy (Hyderabad). The raw materials taken were of analytical grade with 99.9% purity, so the analysis of the raw materials was not performed.

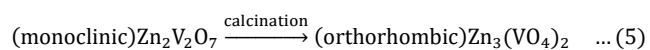
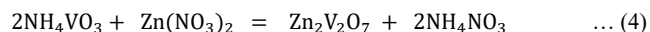
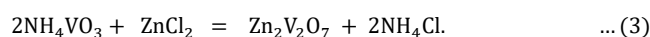
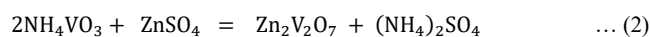
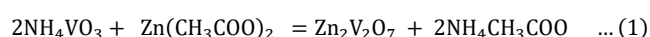
In this work, a synthesis of nanosized zinc vanadate pigment was successfully carried out by a hydrothermal controlled precipitation method using ammonium metavanadate as the common source of vanadium and four different salts of zinc, like sulphate, chloride, acetate and nitrate, all with 99.9% purity. The experimental setup consists of a 0.5L, round bottom flask with 3 necks, placed in a water bath for constant heating. The dropping funnel is attached to one neck of the 3-neck flask and a water condenser to the other. The thermometer pocket is attached to the remaining neck of the 3-neck flask. The assembly is fixed firmly with the help of clamps and a stand. A magnetic needle is placed inside the flask to facilitate stirring. The inlet of the water condenser is supplied with water from the motor and the outlet is kept in the bucket for continuous water circulation.

2.1 Synthesis of zinc vanadate pigment

For the preparation of zinc vanadate nano-pigment, an aqueous solution of 0.1 M zinc acetate was used, which acts as a zinc source in the reaction. An aqueous solution of 0.1 M NH_4VO_3 was taken in a 3-neck round-bottom flask, in which the prepared aqueous solution of zinc acetate was added dropwise with the help of a dropping funnel. This step was carried out at room temperature.

Further, a few drops of 1 N ammonium hydroxide (NH_4OH) were added to maintain the pH at the

neutral or alkaline side. The reaction of zinc acetate and ammonium meta-vanadate is shown in Eq. (1), which is a double displacement neutralization precipitation reaction. This mixture was simultaneously stirred and further heated for 45 mins in a water bath at $80^\circ C$ which resulted in a white precipitate. This precipitate was then filtered, and the impurities were washed out with an ethanol and water mixture. After washing it, the precipitate was dried in an oven for 2 hours at $105^\circ C$. Further, the synthesized material was calcined at $500^\circ C$ for 2 hours, producing the white pigment which was further characterized. Similarly, other zinc salts like chloride, nitrate and sulphate are used to synthesize zinc vanadate, keeping ammonium metavanadate as a common source for vanadium and the reactions are shown in Eqs (2-4). In the process of calcination, the monoclinic $Zn_2V_2O_7$ is converted to orthorhombic $Zn_3(VO_4)_2$, which is responsible for anticorrosion pigmentary properties, as shown Eq. (5)



The process block diagram of the preparation of zinc vanadate pigment is shown in Fig. 1.

Zinc salts used in this reaction are acidic and their acidic strength is given as zinc acetate < zinc chloride < zinc nitrate < zinc sulphate. These acidic salts, while reacting with weak basic salt ammonium metavanadate, dissociate into ammonia and vanadium pentoxide as given in Eq. (6).

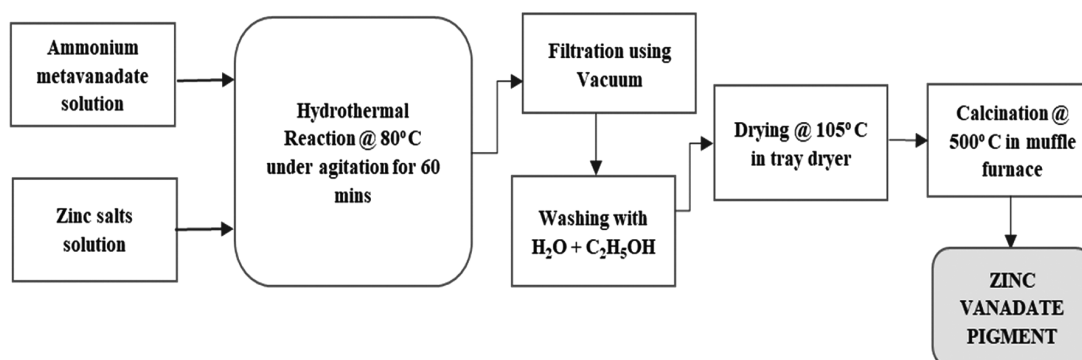


Fig. 1 — Process block diagram of zinc vanadate pigment.

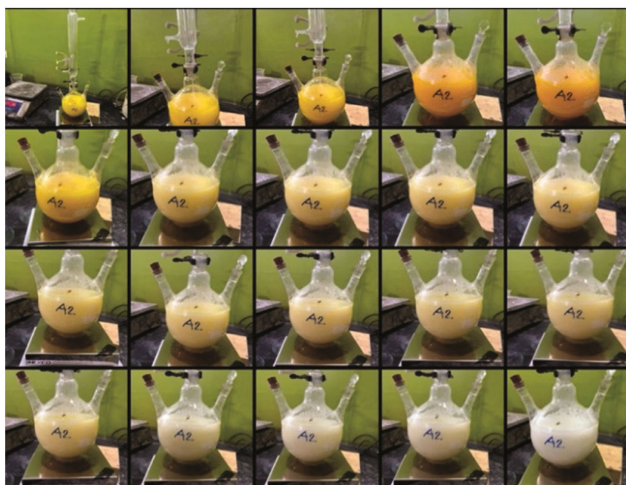


Fig. 2 — Orange slurry in the absence of NH_4OH turning white as NH_4OH is added.

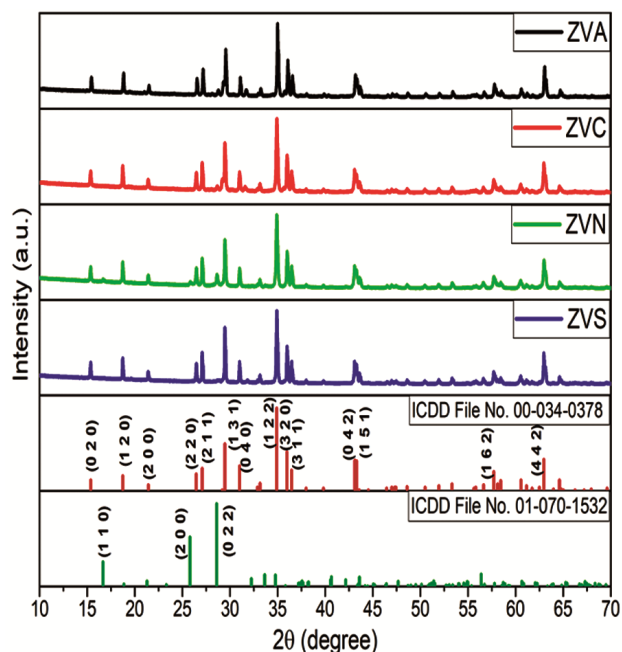


Fig. 3 — XRD pattern of $\text{Zn}_3(\text{VO}_4)_2$ nanoparticles-zinc vanadate synthesized by zinc acetate (ZVA), zinc chloride (ZVC), zinc nitrate (ZVN), zinc sulphate (ZVS).



This breakdown of ammonium metavanadate reduces the yield of the reaction and hence, the pH of the reaction system is maintained by the addition of NH_4OH . The same has been confirmed by carrying out the reaction in the absence of NH_4OH , showing an orange slurry, which confirms the presence of V_2O_5 as shown in Fig. 2.

2.2 Formulation of coatings

Coatings are formulated using four samples of zinc vanadate pigments with resinous epoxy polymer as the primary binder and toluene as a solvent to study its electrochemical impedance for analyzing its anticorrosive properties. The coating is loaded with 1% zinc vanadate pigment. These coatings were compared with a blank epoxy coating and a 1% zinc phosphate epoxy-based coating. The coatings were coated by brush on steel panels. Panels were made ready before the coating was applied by polishing it with 100-600 mesh of silicon carbide (SiC) sandpaper and then cleaned with ethanol. Coatings were cured for 48 hours at room temperature.

3 Results and Discussion

3.1 Characterizations

3.1.1 XRD

Figure 3 shows the X-ray diffraction pattern of the zinc vanadate sample. The XRD results show that the nano zinc vanadate powder is composed of two phases: orthorhombic $\text{Zn}_3\text{V}_2\text{O}_8$, which accounts for 94.1% of the powder, and monoclinic $\text{Zn}_2\text{V}_2\text{O}_7$, which accounts for 5.9% of the powder. These phases match the JCPDS cards # 00-034-0378 and # 01-070-1532, respectively. The diffraction peaks are relatively sharp but low in intensity, indicating the good incorporation of vanadate ions into the zinc lattice. This may affect the band gap and the optical properties of the nano zinc vanadate, which is a metal vanadate nanomaterial with various applications in catalysis, photoluminescence, antibacterial, and energy storage. After comparison of the empirically derived pattern, it doesn't show any other phases and hence confirms the formation of the product and its purity.

3.1.2 SEM and EDS

From the SEM image, it is seen that the prepared pigment has varying particles of different sizes and shapes, few of them are spherical, observed under 100 nm resolution. The observed spherical-shaped nanoclusters of $\text{Zn}_3(\text{VO}_4)_2$ nano pigment are of various sizes between 140-949 nm as shown in Fig. 4 (a). The large grain size results from long-range order and consequently have higher crystallinity. Thus, the SEM investigation confirmed that the hydrothermally controlled precipitation method is a well-suited technique for the preparation of $\text{Zn}_3(\text{VO}_4)_2$ nanopigment.

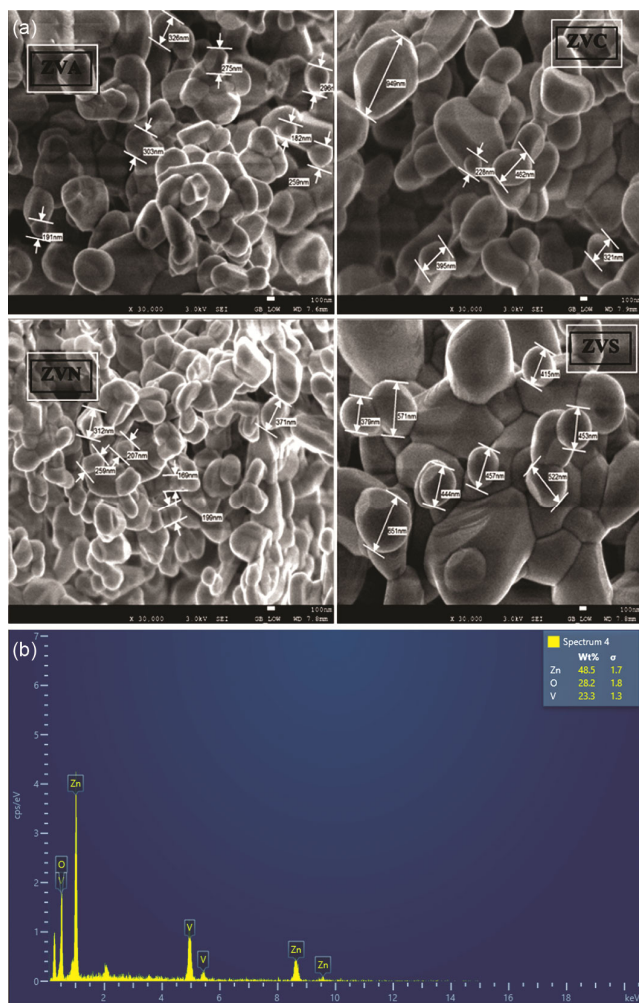


Fig. 4 — (a) SEM images zinc vanadate synthesized by zinc acetate (ZVA), zinc chloride (ZVC), zinc nitrate (ZVN) & zinc sulphate (ZVS) and (b) EDS spectrum indicating elemental composition of zinc vanadate.

Further, for the presence of elemental composition of the synthesized flakes shaped $Zn_3(VO_4)_2$ nanoparticles were studied using EDS analysis as shown in Fig. 4 (b). From the EDS spectrum, it is seen that the prepared samples consist of different elements such as Zn, V, O etc. The atomic wt/wt percentage of $Zn_3(VO_4)_2$ is also shown in Fig. 4 (b).

Hence, elemental mapping confirms that all 3 elements are uniformly distributed. The composition of Zn, V and O present in the $Zn_3(VO_4)_2$ sample was found to be 29% O, 23% V and 46% Zn. No other evidence of impurity elements was observed in the images.

3.1.3 FTIR

FTIR spectrum confirmed the presence of metal-oxygen bonding as well as stretching and bending

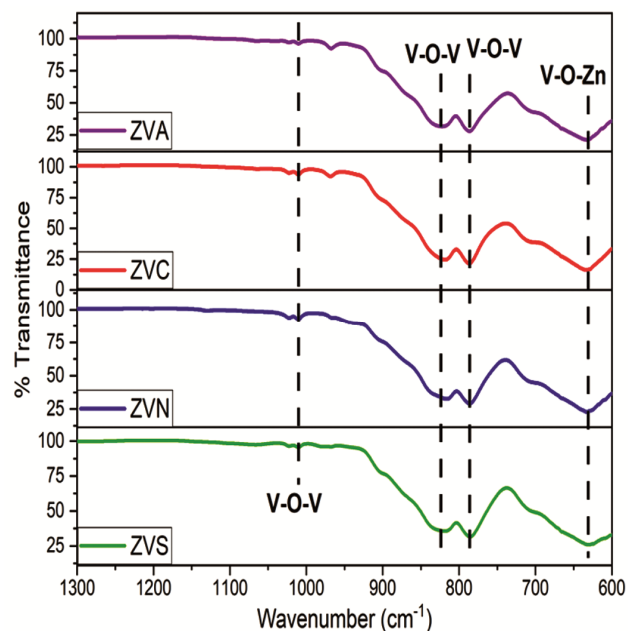


Fig. 5 — FTIR spectrum of $Zn_3(VO_4)_2$ nanoparticle.

vibrations in the prepared sample. Here, Fig. 5 shows the comparative FTIR spectra of $Zn_3(VO_4)_2$ nanoparticles synthesized by using zinc acetate (ZVA), zinc chloride (ZVC), zinc nitrate (ZVN), zinc sulphate (ZVS), respectively. The presence of peaks at 408, 840 cm^{-1} are represents the stretch and vibration of V-O-Zn band and VO_4^{3-} , respectively. Other intense peaks that appeared at 1080.14, 840.96 and 663.51 cm^{-1} are due to the presence of metal group V-O-V stretching in tetrahedral rocking vibration modes of VO_4 . A weaker peak at 794 cm^{-1} is assigned due to the sharing of the bond by the corner atoms of (VO_4) in a tetrahedral structure. And there are no traces of additional peaks that were found in the FTIR spectrum. Hence, it confirms that the synthesized sample is of higher purity. Further, the occurrence of peaks at the fingerprint region revealed that only zinc and vanadium metal oxides exist in the synthesized zinc vanadate, which has also been confirmed from XRD and EDS analysis.

3.2 Anti-corrosion performance of $Zn_3(VO_4)_2$ -based epoxyres in coating

Electrochemical impedance spectroscopy (EIS) is a widely used method to measure the anticorrosive performance of pigment-based epoxy-coated metal surfaces. It works in 3- 3-electrode modes, *viz*: a coated metal electrode acts as the working electrode and a platinumized titanium/graphite solid rod acts as the counter electrode, and a standard calomel electrode

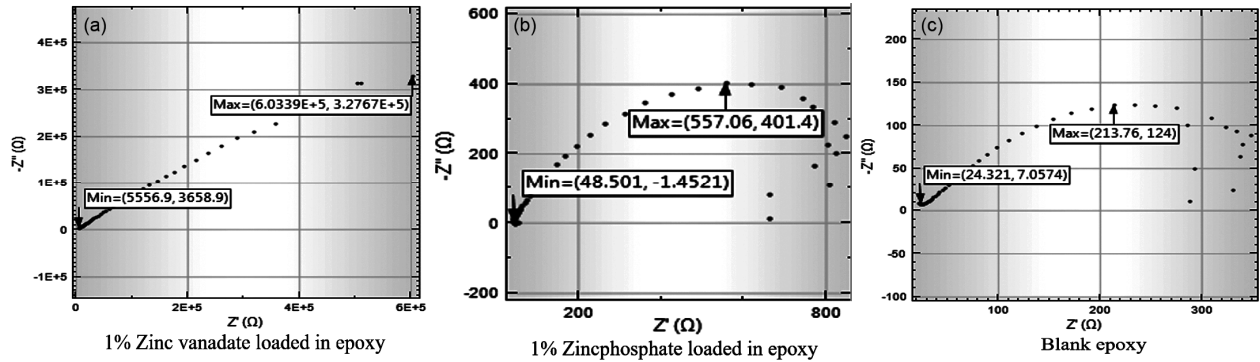


Fig. 6 — Nyquist plot for the coatings of (a) 1% zinc vanadate loaded in epoxy, (b) 1% zinc phosphate loaded in epoxy and (c) Blank epoxy.

(SCE) acts as the reference electrode. Here, the coating is applied in a 1cm by 1cm area on the surface of the working electrode, which is 1cm by 2cm in dimension. A portion of the bare metal must be exposed to make an electrical connection to the working electrode. The electrodes must be submerged in 3.5 % w/w sodium chloride electrolyte solution to perform EIS measurement.

Thus, corrosion resistance of zinc vanadate, zinc phosphate and blank epoxy coating has been carried out from the EIS test. In the region of higher frequency, the Nyquist plots of phosphate coating and blank epoxy coating exhibited a semi-circular arc in the impedance range of 200-800Ω. However, the impedance spectra for the zinc vanadate coating are inclined and linear in the wide impedance range of 300 to 5E⁺⁵Ω as shown in Fig. 6. Usually, for the ideal anti-corrosive coating the Nyquist plot shows a vertical line and the slope of the vertical line is infinite hence the corrosion current will be zero. If the Nyquist plot exhibits an inclined line which explains the impact of other parameters like diffusion of the solution, hydration of coating materials, an anomaly in material and processing of the coating, etc. However, if the slope of the line observed is between zero and infinity, then a standard Nyquist plot for a corrosion rate of 1 mm/year is observed in a semicircle. Coating those fail in anti-corrosion performance the corresponding Nyquist plot of a particular coating exhibits two semicircles. In the present work, the anti-corrosive performance of the zinc vanadate, zinc phosphate and blank epoxy coating has been investigated from the Nyquist plot as shown in Fig. 6. Here, blank epoxy coating shows poor corrosion resistance, proving that there is physical damage in the coat, and it loses the

Table 1 — The anti-corrosive performance of different coatings.

Coating type	Corrosion current I _{corr} (amp/cm ²)	Corrosion rate (mm/year)	Inhibition efficiency%
1% zinc vanadate loaded in epoxy	1.0449E-06	1.2272E-02	99.996
1% zinc phosphate loaded in epoxy	2.1850E-03	2.5663E+01	91.256
Blank epoxy	2.4970E-02	2.9328E+02	-

protective action as shown in Fig. 6(c). Whereas the addition of zinc phosphate in epoxy coating (1% load) increases the resistance to corrosion in the final coat and gives comparatively moderate service life. However, the addition of zinc vanadate in epoxy coating (1% load) gives better anti-corrosive performance and could increase the service life of the coated surface. Table 1 shows the different parameters such as corrosion current (I_{corr}), corrosion rate and inhibition efficiency that deal with corrosion, which can be calculated using some empirical formulas as mentioned in Eq. (7) and Eq. (8).

The corrosion rate was evaluated as:

$$Corrosion\ rate = \frac{I_{corr} \cdot K \cdot b \cdot EW}{d \cdot A} \quad \dots (7)$$

where, I_{corr} = the corrosion current

K = 3272 mm / (amp-cm-year),

EW = the equivalent weight in grams/equivalent,

d = Density (g/cm³)

A = Sample area (cm²)

The corrosion inhibition efficiency was calculated according to the Eq. (8),

$$\% \text{ inhibition efficiency} = \frac{(i_0 - i_i)}{i_0} \times 100 \quad \dots (8)$$

where, i_i and i₀, are the corrosion rates with and without inhibitor, respectively. The inhibition

efficiency of 99.99% and 91.25% on mild steel panels was seen for zinc vanadate nano pigment and zinc phosphate pigment.

4 Conclusion

This paper summarizes the synthesis and characterization of zinc vanadate nanoparticles by precipitation under hydrothermal conditions. It was observed during the reaction that the acidic zinc salts break down the ammonium metavanadate into ammonia and vanadium pentoxide giving orange coloured slurry, hindering the formation of zinc vanadate, hence the pH of the reaction was controlled to have an optimum output of zinc vanadate nano pigment. Zinc vanadate obtained from the reaction is dried to produce a powder which consists of monoclinic $Zn_2V_2O_7$. Here, the transformation of $Zn_2V_2O_7$ to orthorhombic $Zn_3(VO_4)_2$ was observed in post-calcination at $500^\circ C$ due to the realignment of atoms in the lattice structure, producing two-dimensionally large flaky grains. The prepared pigment was thoroughly characterized by XRD, SEM-EDS & FTIR analysis to confirm phase purity, morphology, presence of elemental composition, and metal-oxygen bonding. The XRD pattern shows a high degree of crystallinity of the synthesized zinc vanadate samples. The FTIR spectra do not show any vibration at 8486 cm^{-1} and 1621 cm^{-1} which indicates good dehydration and dehydroxylation in the process of calcination. The absence of OH and HOH in zinc vanadate ensures better stability against rehydration in coatings and hence provides better anti-corrosion properties, which can be confirmed from a linear Nyquist plot with a greater slope value. Thus, zinc vanadate shows excellent anticorrosion characteristics with an efficiency of 99.9% in coating applications. Further, it provides a comparative analysis of the anticorrosive performance of zinc phosphate and zinc vanadate nano pigment, and it concludes that zinc vanadate nano pigment is a superior material for anticorrosive coating.

Acknowledgements

Authors thankfully acknowledge the Council of Scientific and Industrial Research (CSIR), India and its constituent laboratory National Environmental Engineering Research Institute (NEERI) for supporting the research under AcSIR Ph. D. Programme in Engineering Science. The manuscript is checked for plagiarism using licensed iThenticate software through CSIR-NEERI Knowledge Resource Centre.

References

- 1 Sonawane S H, Bhanvase B A, Jamali A A, Dubey S K, Kale S S, Pinjari D V, Kulkarni R D, Gogate P R & Pandit A B, *Chem Eng J*, 189e190 (2012) 464.
- 2 Abdel-Gaber A M, Nabey BAAE, Khamis E, Abdelattef O A, Aglan H & Ludwick A, *Prog Org Coat*, 69 (2010) 402.
- 3 Zang D, Zhu R, Zhang W, Yu X, Lin L, Guo X, Liu M & Jiang L, *Adv Funct Mater*, 27 (2017) 1605446.
- 4 Askari F, Ghasemi E, Ramezanzadeh B & Mahdavian M, *Dyes Pigments*, 124 (2016) 18.
- 5 Łuczka K, Sibera D, Smorowska A & Grzmil B, *Chem Pap*, 67 (2013) 1210.
- 6 Benda P & Kalendova A, *Phys Proc*, 44 (2013) 185.
- 7 Deya C, Blustein G, del Amo B & Romagnoli R, *Prog Org Coat*, 69 (2010) 1.
- 8 Yabuki A, Shiraiwa T & Fathona I W, *Corrosion Sci*, 103 (2016) 117.
- 9 Yasakau K A, Tedim J, Montemor M F, Salak A N, Zheludkevich M L & Ferreira M G S, *J Phys Chem C*, 117 (2013) 5811.
- 10 M'hiri N, Veys-Renaux D, Rocca E, Ioannou I, Boudhrioua N M & Ghoul M, *Corrosion Sci*, 102 (2016) 55.
- 11 Yasakau K A, Zheludkevich M L, Karavai O V & Ferreira M G S, *Prog Org Coat*, 63 (2008) 352.
- 12 Du J Y, Damron M, Tang G, Zheng H, Chu C-J, Osborne J H, *et al.*, *Prog Org Coat*, 41 (2001) 226.
- 13 Huang X & Li N, *Appl Surf Sci*, 254 (2007) 1463.
- 14 Palanivel V, Huang Y & Van Ooij W J, *Prog Org Coat*, 53 (2005) 153.
- 15 Mora N, Cano E, Polo J L, Puente J M & Bastidas J M, *Corros Sci*, 46 (2004) 563.
- 16 Shi R, Wang Y, Zhou F & Zhu Y, *J Mater Chem*, 21 (2011) 6313.
- 17 Xiao L, Zhao Y, Yin J & Zhang L, *Chem Eur J*, 15 (2009) 9442.
- 18 Mondal C, Ganguly M, Sinha A K, Pal J, Sahoo R & Pal T, *Cryst Eng Comm*, 15 (2013) 6745.
- 19 Gan L H, Deng D, Zhang Y, Li G, Wang X & Jiang L, Wang C R, *J Mater Chem A*, 2 (2014) 2461.
- 20 Li T, Luo J, Honda Z, Fukuda T & Kamata N, *Adv Mater Phys Chem*, 2 (2012) 173.
- 21 Wang D, Tang J, Zou Z & Ye J, *Chem Mater*, 17 (2005) 5177.