

# One-step synthesis and performance evaluation of zinc metavanadate pigments as highly anticorrosive primers

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## **Abstract:**

Recently, the vanadate species have been considered as promising inhibitor agents used for metal protection. Various metallic materials were treated in a vanadate solution in order to form a passivation coating. However, the use of solid vanadate compounds as inhibitor pigments in the formulation of anticorrosive primers is still limited. Therefore, in this work, solid zinc metavanadate pigments for application in paint primers were prepared by a simple route at various pH values and concentrations of monovanadate. According to the results, all samples showed a characteristic hexagonal structure with high anticorrosive abilities. Both the pH and monovanadate concentration strongly affected the morphology, the particle size, and the anti-corrosion power. Among the prepared samples, the best anticorrosive pigment was the sample prepared at pH 8 with a vanadate concentration of 0.2 M.

**Keywords:** anticorrosive pigment, electrochemical impedance, primers, steel plate, Zinc metavanadate.

**Classification number:** 2.2

## **Introduction**

Due to the planet's oxidizing atmosphere, metal corrosion is considered one of the most severe problems across various industries and causes not only material destruction but also tremendous economic damages. Over the past few decades many anti-corrosion methods have been proposed, which can be divided into two groups: active corrosion protection and passive corrosion protection. The former mechanism is based on the fabrication of corrosion-resistant alloys and the application of inhibitors on the metallic surface, whereas the latter mechanism relies on the development of coating films that isolate the underlying metal from its corrosive environment [1, 2]. In fact, corrosion can be effectively and economically prevented by using suitable anti-corrosion coatings. Among the available coating materials, chromate coatings have been widely used to passivate steel, aluminum, and other metals. Chromate was also used as an inhibitive pigment in the formulation of protective paint [3, 4]. However, due to the presence of hexavalent chrome, this type of coating and pigment is highly toxic and carcinogenic [3-7]. Thus, it is exceedingly necessary to develop novel materials that are both adequately anti-corrosive and environmentally benign [8, 9].

Recently, various works have proved that vanadate ions can play as an alternative coating for the protection of steel, aluminum alloy or Mg-Zn alloys [10-13]. In these studies, the metallic surface was treated in  $\text{NaVO}_3$  solution with different concentration of vanadate ion and different pH values. For example, when zinc foil was dipped in an aqueous solution of  $\text{NaVO}_3$  (4 mM), a polymerized vanadate film was successfully formed on the metallic surface [12], which can cause the two-order magnitude decrease in corrosion current density. Likewise, Feng, et al. (2018) [13] successfully created a dense vanadate film on the surface of AZ31 Mg alloy by immersing this alloy in the 4 mM solution of  $\text{NaVO}_3$  at pH 7.7-9.2. Owing to this vanadate film, the

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corrosion current density was dramatically decreased while the breakdown potential was effectively increased. In the presence of the vanadate film, the corrosion current density was dramatically decreased. It was also observed that the variation of vanadate concentration and solution pH may result in various types of vanadate ions, affecting the corrosion inhibition of coating films. In his work, Frankel noticed that the anti-corrosion power of metavanadate coating is better than decavanadate coating for the protection of Al alloy [14]. Moreover, when the vanadate concentration increased from 0.1 to 4.15 mM, the corrosion current density was found to be declined, proving that the concentration of vanadate plays an important role for the development of protective layers. Especially, Morks, et al. (2012) [10] proposed to embed  $\text{Na}_3\text{VO}_4$  in a modified zinc phosphate coating with Mn-Mg additives. At the vanadate concentration of  $10^{-3}$  M and the pH of 4, the inhibition efficiency for pipeline steel of this as-prepared coating can reach 99%.

These previous works have shown that vanadate is a promising inhibition agent for metal protection. However, up to now, the use of solid vanadate compounds as inhibitor pigments in the formulation of anticorrosive primers is still limited. There are only several papers reporting the application of ion-exchangeable pigments based on hydrotalcite/vanadate [15, 16] to passivate low carbon cold rolled steel plates. On the other hand, the solid vanadate compounds prepared by solid-state reactions or hydrothermal methods have been usually applied as catalysts [17, 18] for oxidation reactions or antibacterial additives [19]. Therefore, in this work, we proposed to synthesize solid zinc metavanadate pigment by using a simple precipitation method at various pH values and concentrations of vanadate in order to form anticorrosive paint primers for steel plates.

## Experimental

### Preparation of zinc vanadate

The starting materials,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$  and NaOH ( $\geq 97\%$ , reagent grade), were purchased from Guanghua Sci-tech (Guangdong, China). These chemicals were used as received without further purification. Firstly,  $\text{NH}_4\text{VO}_3$  was dissolved into distilled water to form the metavanadate solutions with various monovanadate concentrations (0.1, 0.2 and 0.5 M) and the pH of these solutions was adjusted to 6, 8, or 10 by NaOH solution. Then a  $\text{ZnSO}_4$  solution was slowly added to the above  $\text{NH}_4\text{VO}_3$  solutions under continuous magnetic stirring. The mixed solutions were magnetically stirred for 1 h. After that, the pigment products were filtered, washed with distilled water, and finally dried at  $80^\circ\text{C}$  for 2 h. In this manuscript, the samples are labelled as in Table 1.

**Table 1. Synthesis conditions of pigment samples.**

Samples	$\text{ZnSO}_4$ solution	$\text{NH}_4\text{VO}_3$ concentration	pH of $\text{NH}_4\text{VO}_3$ solution
ZV-5.8	1 M	0.5 M	8
ZV-2.6	1 M	0.2 M	6
ZV-2.8	1 M	0.2 M	8
ZV-2.10	1 M	0.2 M	10
ZV-1.8	1 M	0.1 M	8

### Characterization

The structure and phase composition of our pigments were characterized by powder X-ray diffraction (XRD) on a D8-ADVANCE (BRUKER) using  $\text{Cu K}_\alpha$  radiation with an accelerating voltage of 40 kV and an applied current of 40 mA. The XRD patterns were recorded from  $10^\circ$  to  $70^\circ$ . The morphology and particle size were investigated by field emission scanning electron microscopy (FESEM) on a S4800 (HITACHI, Japan) with an accelerating voltage of 10 kV.

### Electrochemical impedance measurements

Pigments with a total mass of 0.25 g were dispersed into 250 ml of NaCl 3.5% w/w solution and magnetically stirred for 24 h. Then, the solid pigments were removed from the solution to obtain the leaching solutions. Meanwhile, steel plates ( $2.5 \times 5$  cm) were surface-treated and afterwards covered by insulating tape leaving only a surface with the area of  $1 \text{ cm}^2$ . These steel plates were immersed in the leaching solutions and the electrochemical impedance was measured versus time by using a Versastat 3 with 3 electrodes: the treated steel plates as working electrode, the silver electrode as reference electrode, and the platinum electrode as the counter electrode. For comparison, steel plates were immersed in a 3.5% w/w NaCl solution without monovanadate and their electrochemical impedance was also measured on a Versastat 3 (AMETEK Scientific Instruments).

### Corrosion resistance of zinc vanadate pigments on steel

Firstly, 0.50 g of zinc monovanadate pigment was dispersed in a mixture containing 30.0 ml of commercial epoxy paint and solidifier. The painting mixture was subsequently applied on the surface of the steel plates ( $2.5 \times 8$  cm) that were previously surface-treated. After that, the steel plates were exposed to ambient atmosphere for 40 h in order to dry the paint coating. Finally, the steel plates were dipped into the NaCl 3.5% solution for 480 h to investigate their corrosion resistance. The blank sample

(without zinc monovanadate pigment) was also immersed in the NaCl solution for comparison. The steel plates coated with the paint mixture containing zinc monovanadate were also exposed to air at 30°C for 480 h to test their corrosion resistance in atmosphere.

## Results and discussion

### Crystal structure and morphology

Figure 1 presents the XRD patterns of the zinc monovanadate samples prepared with different monovanadate concentrations and different pH values. According to these patterns, all samples revealed the presence of the  $\alpha$ - $Zn_3(VO_4)_2$  hexagonal phase (space group of P-6) identified by the characteristic diffraction peaks at 12.2, 16.6, 20.6, 29.5, 31.4, 33.5, 35.6, 41.6, 50.3, and 60.9°, which is the same as the results of D.A.H. Ayala, et al. (2001, 2002) [20, 21]. When both the concentration of monovanadate and the solution pH increase, the XRD baselines become less stable and the diffraction peaks become asymmetrical, which indicates the decrease in crystallinity in these samples.

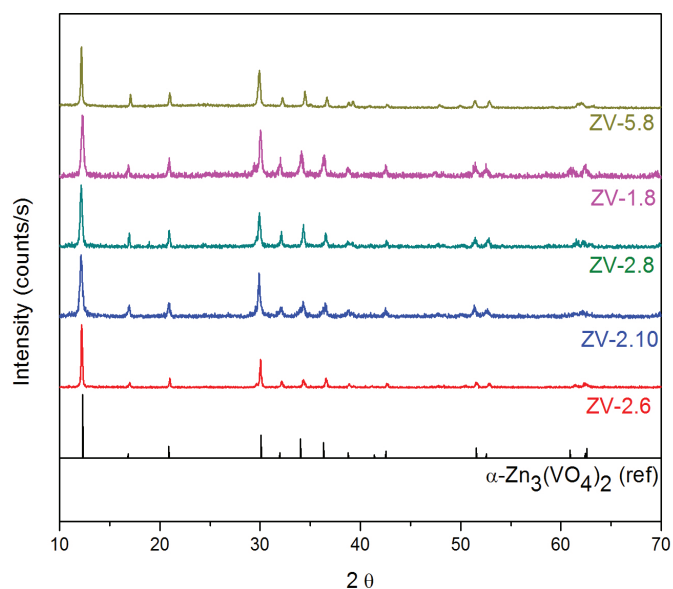


Fig. 1. XRD patterns of ZV samples.

Figure 2 presents the FESEM images of the pigment samples. It was observed that all samples were composed of multi-dispersed particles. For the samples prepared with low monovanadate concentrations (0.1 M and 0.2 M), the particles were tabular in shape with the particle size varying from 10 to 40 nm. When the monovanadate concentration was up to 0.5 M, the particle size greatly increased (100–2000 nm) with the appearance of very large polyhedral particles. The pH values of the  $NH_4VO_3$  solutions also affect the morphology of zinc monovanadate pigments.

At a monovanadate concentration of 0.2 M and pH of 6, the particle size can reach 1000 nm whereas at pH 8, the particle size decreases to 320 nm. Furthermore, the pigment particles of the ZV-2.8 sample were found to be more homogeneous in size than in other samples.

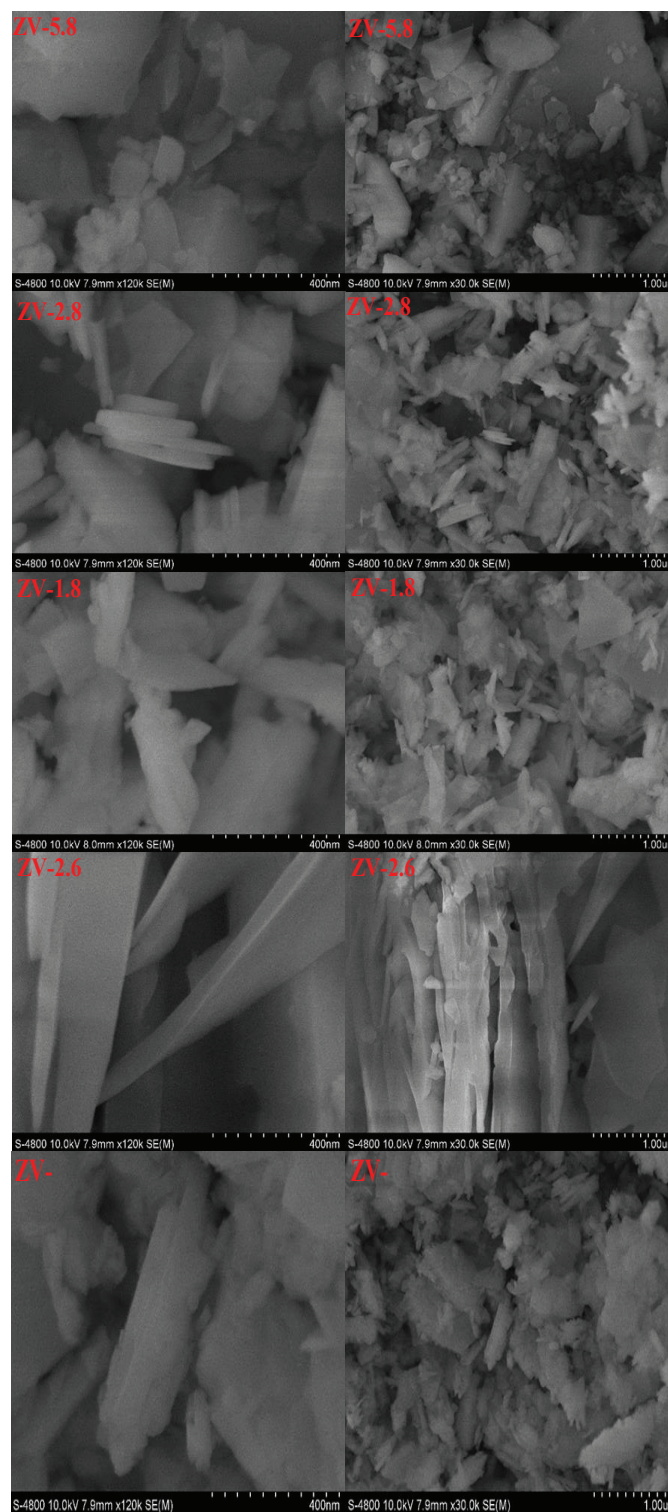


Fig. 2. SEM images of the ZV samples.

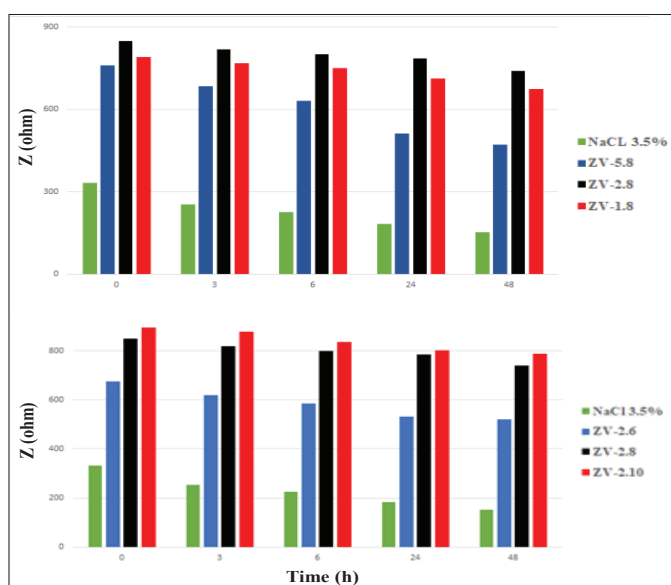
**Table 2.** The pH and electric conductivity values of pigment leaching solutions after 24 h in NaCl 3.5% solution.

	NaCl 3.5% w/w solution	ZV-5.8	ZV-2.8	ZV-1.8	ZV-2.6	ZV-2.10
pH	6.035	7.012	6.964	6.991	6.984	7.033
Electric conductivity ( $\mu\text{S}/\text{cm}$ )	53523.0	54217.9	54108.3	54303.4	53687.6	53985.4

It should be noted that the evolution of particle size and particle shape in our samples did not modify the pH or the electric conductivity of leaching solutions. Due to hydrolysis of the monovanadate ions, all the leaching solutions showed a higher pH and conductivity than that of the NaCl 3.5% w/w solution (Table 2).

**Electrochemical impedance results**

For all the steel plates, the electrochemical impedance values,  $Z$ , decreased with soaking time in the leaching solution, indicating that the corrosion of steel takes place over time (Fig. 3). Nevertheless, at the same time interval, the steel plates immersed in the leaching solution of zinc monovanadate pigments always showed higher impedance values than the blank sample. In addition, the decreased rate of impedance with time of the steel plates in ZV leaching solutions was lower than that of blank sample. Hence, we can confirm that the ZV pigments can help protect the surface of the steel plates. Moreover, in the leaching solution prepared from a low concentration of  $\text{NH}_4\text{NO}_3$ , the steel plates did not only show a high impedance but also presented a slow decrease in impedance values. Likewise, when the pH of the monovanadate solution rose from 6 to 8 and 10, the impedance value tended to increase and the evolution of the impedance versus time slowed down. These results suggest that the tabular shape and the particle size of 300-400 nm seem to be the most important factors to enhance the anti-corrosion power of zinc monovanadate particles.

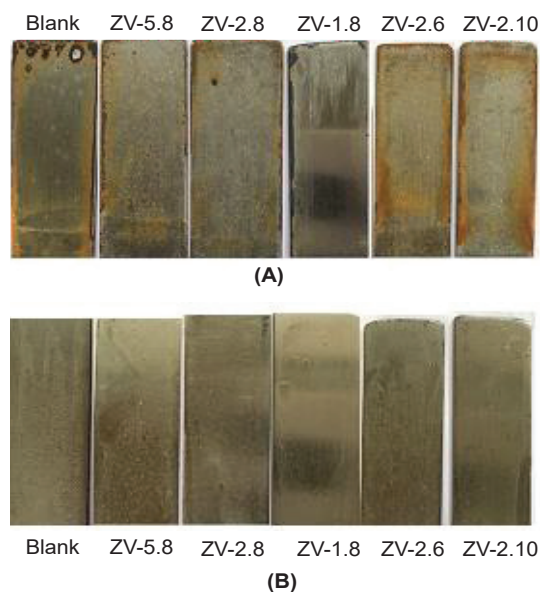


**Fig. 3.** The electrochemical impedance at 0.01 Hz as a function of immersion time in ZV extracts.

**Corrosion resistance of zinc vanadate pigments coated on steel**

According to Fig. 4A, after 480 h in NaCl 3.5% w/w solution, all the samples, including the blank sample and the steel plates coated with ZV-containing paints, suffered from corrosion that clearly occurred at their margins. Especially, corrosion strongly occurred at some spots on the surface of the blank sample. It was observed that the steel plates using ZV-2.6 and ZV-2.10 pigments in the primer also suffered from corrosion in a similar way to the blank sample. Among the samples, the steel plates using ZV-2.8 and ZV-1.8 pigments showed the best corrosion resistance in the NaCl solution.

In ambient atmosphere, all the steel plates coated with ZV-containing paints were less corrosive than the blank sample (Fig. 4B). The steel plates using ZV-2.8 and ZV-1.8 pigments were still the best anti-corrosive samples. However, the remaining samples showed several spitting areas on the surface, proving that the paint-containing ZV particles prepared under other conditions did not adhere well to the metallic surface. Thus, it can be stated that a monovanadate concentration of 0.2 M and pH of 8 were the optimal conditions to prepare zinc monovanadate pigments with high anti-corrosive power in this work.



**Fig. 4.** Steel plate surfaces with primer paint after 480 h in (A) NaCl 3.5% solution and (B) ambient atmosphere.

## Conclusions

In this work, we successfully prepared zinc monovanadate particles as inhibitor pigments used in the formulation of anticorrosive primers. When mixed with primer painting components, these pigments provided beneficial corrosive resistance for steel plates. The experimental results also demonstrated the influences of pH and starting concentration of  $\text{NH}_4\text{VO}_3$  on the crystal structure, morphology, and anti-corrosive power of the pigments. Among all the samples, the pigments prepared with a monovanadate concentration of 0.2 M and pH of 8 show the best anti-corrosive performance for steel plates in both ambient atmosphere and NaCl solution.

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The authors declare that there is no conflict of interest regarding the publication of this article.

## REFERENCES

- [1] C. Verma, E.E. Ebenso, M.A. Quraishi (2017), "Corrosion inhibitors for ferrous and non-ferrous metals and alloys in ionic sodium chloride solutions: a review", *J. Mol. Liq.*, **248**, pp.927-942.
- [2] S.B. Ulaeto, R. Rajana, J.K. Pancrecioua, T.P.D. Rajana, B.C. Pai (2017), "Developments in smart anticorrosive coatings with multifunctional characteristics", *Prog. Org. Coat.*, **111**, pp.294-314.
- [3] S.A. Katz, H. Salem (1993), "The toxicology of chromium with respect to its chemical speciation: a review", *J. Appl. Toxicol.*, **13(3)**, pp.217-224.
- [4] S. Langård, T. Norseth (1975), "A cohort study of bronchial carcinomas in workers producing chromate pigments", *Br. J. Ind. Med.*, **32(1)**, pp.62-65.
- [5] R.G. Buchheit, H. Guan, S. Mahajanam, F. Wong (2003), "Active corrosion protection and corrosion sensing in chromate-free organic coatings", *Prog. Org. Coat.*, **47(3-4)**, pp.174-182.
- [6] N. Granizo, J.M. Vega, D. de la Fuente, J. Simancas, M. Morcillo (2012), "Ion-exchange pigments in primer paints for anticorrosive protection of steel in atmospheric service: cation-exchange pigments", *Prog. Org. Coat.*, **75(3)**, pp.147-161.
- [7] L. Fachikov, D. Ivanova (2012), "Surface treatment of zinc coatings by molybdate solutions", *Appl. Surf. Sci.*, **258(24)**, pp.10160-10167.
- [8] S. Alinejad, R. Naderi, M. Mahdavian (2016), "The effect of zinc cation on the anticorrosion behavior of an eco-friendly silane sol-gel coating applied on mild steel", *Prog. Org. Coat.*, **101**, pp.142-148.
- [9] M. Zubielewicz, W. Gnot (2004), "Mechanisms of non-toxic anticorrosive pigments in organic waterborne coatings", *Prog. Org. Coat.*, **49**, pp.358-371.
- [10] M.F. Morks, P.A. Corrigan, I.S. Cole (2012), "Mn-Mg based zinc phosphate and vanadate for corrosion inhibition of steel pipelines transport of  $\text{CO}_2$  rich fluids", *Int. J. Greenhouse*, **7**, pp.218-224.
- [11] L. Niu, S.H. Chang, X. Tong, G. Li, Z. Shi (2014), "Analysis of characteristics of vanadate conversion coating on the surface of magnesium alloy", *J. Alloy Compd.*, **617**, pp.214-218.
- [12] B.L. Hurley, K.D. Ralston, R.G. Buchheit (2014), "Corrosion inhibition of zinc by aqueous vanadate species", *J. Electrochem. Soc.*, **161(10)**, pp.C471-C475.
- [13] Z. Feng, B. Hurley, J. Li, R. Buchheit (2018), "Corrosion inhibition study of aqueous vanadate on Mg Alloy AZ31", *J. Electrochem. Soc.*, **165(2)**, pp.C94-C102.
- [14] M. Iannuzzi, T. Young, G.S. Frankela (2006), "Aluminum alloy corrosion inhibition by vanadates", *J. Electrochem. Soc.*, **153(12)**, pp.B533-B541.
- [15] J.M. Vega, D. de la Fuente, B. Chico, M. Morcillo, N. Granizo (2013), "Ion-exchange pigments in primer paints for anticorrosive protection of steel in atmospheric service: anion-exchange pigments", *Prog. Org. Coat.*, **76**, pp.411-424.
- [16] N. Granizo, J.M. Vega, I. Díaz, B. Chico, D. de la Fuente, M. Morcillo (2011), "Paint systems formulated with ion-exchange pigments applied on carbon steel: effect of surface preparation", *Prog. Org. Coat.*, **70**, pp.394-400.
- [17] H. Sameie, A.A.S. Alvani, N. Naseri, S. Du, F. Rosei (2018), "First-principles study on  $\text{ZnV}_2\text{O}_6$  and  $\text{Zn}_2\text{V}_2\text{O}_7$ : two new photoanode candidates for photoelectrochemical water oxidation", *Ceram. Int.*, **44(6)**, pp.6607-6613.
- [18] L.Z. Pei, N. Lin, T. Wei, H.D. Liu, H.Y. Yu (2015), "Zinc vanadate nanorods and their visible light photocatalytic activity", *J. Alloys. Compd.*, **631**, pp.90-98.
- [19] A.S.K. Heer (2017), "Simple and direct synthesis of zinc vanadate ( $\text{ZnV}_2\text{O}_5$ ) nanocrystals for its electrocatalytic and antimicrobial activity", *J. Chem. Pharm. Res.*, **9(12)**, pp.18-24.
- [20] D.A.H. Ayala, A. Echavarría, C. Saldarriaga (2001), "Synthesis and structure of a porous zinc vanadate,  $\text{Zn}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ ", *J. Mater. Sci.*, **36**, pp.5515-5518.
- [21] D.A.H. Ayala, A. Echavarría, L.A. Palacio, C. Saldarriaga (2002), "Structural characterization of a porous zinc vanadate:  $\text{Zn}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ ", *Powder Diffr.*, **17(4)**, pp.320-321.