Monitoring metal ion leaching in oil-ZnO paint systems with a paramagnetic probe

Alessia Artesani*[1,2], Laurent Binet[3,4], Francesca Tana[5], Daniela Comelli[1], Luigi De Nardo[5], Austin Nevin[6,7], Nadia Touati[3,4], Gianluca Valentini[1], Didier Gourier[3,4]

1. Politecnico di Milano, Physics Department, Milano, Italy
2. Center for Cultural Heritage Technology (CCHT), Italian Institute of Technology (IIT), Italy
3. Chimie-ParisTech, PSL University, CNRS, Institut de Recherche de Chimie-Paris (IRCP), Paris, France
4. Centre de Recherche et de Restauration des Musées de France (C2RMF), Palais du Louvre, Paris, France
5. Politecnico di Milano Chemistry, Materials and Chemical Engineering Department "G. Natta", Milano, Italy
6. Istituto di Fotonica e Nanotecnologie – Consiglio Nazionale delle Ricerche (IFN-CNR), Milano, Italy
7. Department of Conservation, University of Gothenburg, Gothenburg, Sweden

Abstract. Zinc oxide (ZnO), used as a pigment since the 19th C., is highly reactive when mixed with drying oils. Indeed, the combination of metal-based pigments and drying oils may react to form metal complexes in paint, which may lead to the aggregation of metal carboxylates or soaps. Whereas the mechanism and chemistry behind metal soap formation has been studied in depth, little research has focused on the changes that affect the inorganic pigment particles. In this work, we concentrate on the first phase of these reactions and monitor the evolution of an oil-ZnO paint system through Electron Paramagnetic Resonance (EPR) spectroscopy. By employing Cu^{II} as a paramagnetic probe, the progression of metal ion leaching from ZnO is followed through the switching of Cu^{II} from a silent tetrahedral coordination in ZnO bulk to an EPR active pseudo-octahedral coordination. Complementarily, the effective concentration of dissolved or extracted Zn and Cu is quantified through Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The experiment probes the spontaneous metal ion release in oil-based paint films and demonstrates that the kinetics of this phenomenon proceeds with a very steep increase in the first hours after mixing. This is followed by the saturation of the grow rate after a few days that we ascribe to the passivation of the ZnO pigment surface by carboxylate groups, which hinders the further leaching of metal ions, leading to a steady-state before the complete hardening or oxidation of the paint film.

Manuscript

1. Introduction

Curators and scientists are acutely aware of the importance of chemical reactions between pigments and binders since these govern the stability/instability of oil paints. Among modern pigments considered to be reactive in drying oil media, zinc white (ZnO) is one of the most alarming. In Zn-based paint, it has been shown that the reaction between pigment particles and drying oils leads to the formation of a metal carboxylate network (1)(2)(3). While during the initial stage this network results in the advantageous rigidity of paint film, in the long-term the crystallization of metal carboxylate complexes can be a problematic issue because of the formation of metal soaps that may compromise the adhesion and cohesion of paint (3)(4)(5). Despite the wide consensus on the principal chemical reactions leading to the formation of these crystalline complexes, only few studies have provided insight into the mechanisms which initiate the formation of the metal carboxylate network (3)(4). For this purpose, in this work we focus on the changes that occur to the inorganic pigment particles and we specifically concentrate on the first phase of the pigment-binder reaction, monitoring the evolution of the leaching of metal ions in paints with a novel approach.

In detail, we use Electron Paramagnetic Resonance (EPR) spectroscopy coupled with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), to investigate metal ion leaching and measure its temporal evolution in paint films. We have studied the first stage of the reaction between ZnO and linseed oil by using a paramagnetic probe diluted in ZnO crystallites. Cu^{II} ($3d^9$ configuration) was chosen as a paramagnetic probe since its EPR spectrum strongly depends on its coordination and on the symmetry of its environment, hence providing information on changes of the Cu^{II} environment.

Cu^{II} has an imposed tetrahedral coordination in ZnO, and the degenerate (or nearly degenerate) $^2T_2$ ground state gives an EPR spectrum (with g∥=0.74 and g⊥=1.53) that is detectable only at low temperature (around 4 K)

(6). In contrast, if Cu^{II} is free to achieve a six-fold or four-fold planar coordination, as would be the case for copper ions bound to carboxylates (in the following quoted as Cu^{II}–carboxylate complexes), the orbitally non-degenerate ground state would invariably give an EPR spectrum detectable at room temperature with typical g-factors equal to g∥≈2.25-2.40 and 2.00<g⊥< g∥ (see for example (7) (8)). For this reason, no Cu^{II} EPR signal is expected at room temperature in ZnO, whereas on the contrary, if mixing with binder induces a surface modification of ZnO and a metal ion extraction, the EPR spectrum of Cu^{II}–carboxylate complexes should appear.

In this work, we have monitored EPR over time in a mixture of 0.8% Cu-doped ZnO powder and linseed oil. The system mimics the progression of metal ion leaching in oil-based paint films and the EPR spectroscopy signal is used to monitor the evolution of metal ions. Finally, since EPR spectroscopy is silent with respect to the coordination of Zn ions (note that Zn^{II} is diamagnetic), ICP-OES was used on the oil extracted from the ZnO:Cu-oil mixture, to confirm the migration of metal ions into the oil medium and to measure the concentrations of Zn and Cu ions.

2. **Materials and Methods**

2.1 Materials

The Cu-doped ZnO powders, labelled as ZnO:Cu, were synthesized by the co-precipitation method. The synthetic procedure is summarized as follows (9): 25 ml solution (aq) of $1.49\cdot10^{-2}$ mol zinc acetate dihydrate (Sigma Aldrich, Milano, Italy) is mixed with 10 ml water solution of $0.018\cdot10^{-2}$ mol copper acetate monohydrate (≥98% Sigma Aldrich, Milano, Italy). After the addition of 25 ml of KOH ($4.99\cdot10^{-2}$ mol) drop by drop under constant stirring, the mixture is heated at 80°C for 1 hour, until a precipitate is formed. The dispersion is washed and centrifuged (4000 rpm, 15 min) twice with distilled water followed by ethanol to remove impurities. Finally, the ZnO:Cu is calcined at 1000°C for 3 hrs in a muffle furnace. In this way a ZnO:Cu doped at 0.8% is obtained (as demonstrated by ICP-OES measurements). The same procedure was applied for the preparation of pure ZnO, without the addition of the Cu-dopant. Historical recipes suggest heating (without boiling) of commercial cold-pressed linseed oil (supplied by Laverdure); in this work the linseed oil was heated for about 3 hours at 120 °C prior to mixing with pigment. It is noted that the starting linseed oil is pure and does not contain siccative compounds (such as litharge, PbO) or other detectable metal ion impurities.

2.2 Methods

X-ray powder diffraction. The phase evolution of synthesized powders was monitored by X-ray diffractometry (XRD, (Panalytical Empyrean)) using a Bragg Brentano diffractometer and Cu-Kα1 radiation (λ= 0.154056 nm). The X-ray diffraction patterns were collected at room temperature in the 10-70° 2θ range with a scan step size of 0.02°.

Electron Paramagnetic Resonance Spectroscopy. For EPR spectroscopy measurements a sample containing 50 mg of ZnO:Cu powder mixed with 50 mg of linseed oil was prepared. EPR spectra were recorded at room temperature with a Bruker Elexsys E500 spectrometer operating at X-band (9.69 GHz) in a continuous-wave mode and equipped with a Bruker 4122SHQE/0111 resonator. A magnetic field modulation at 100 kHz was applied with an amplitude of 0.8 mT. The microwave power was 20 mW. Simulations of EPR spectra were performed with the Easyspin software (10). The mass m_{Cu} of Cu^{II} detected by EPR was estimated by comparing the intensities I_{Cu} of the Cu^{II} spectra with the intensity I_{ref} of a reference sample made of 40.0 mg of CaCuSi$_4$O$_{10}$, corresponding to 6.4×10^{19} Cu^{II} ions, mixed with 45 mg of linseed oil, according to:

$$m_{Cu} = 6.4 \times 10^{19} \times \frac{I_{Cu}}{I_{ref}} \times \frac{M_{Cu}}{N_A} \qquad (1)$$

with M_{Cu}=63.55 g.mol^{-1} the molar mass of Cu and N_A=6.02x10^{23} the Avogadro number.

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The amount of Cu doping in the synthesized powder was evaluated by ICP-OES (Perkin Elmer Optima 3200) spectrometry as 0.8 ± 0.1 w%. ICP-OES measurements were further exploited to measure on leaching (Zn and Cu) from the metal oxide pigment particles into the binding medium. The synthetized ZnO:Cu powder was mixed 1:1 (wt.) with linseed oil and kept in closed vessels in the dark. The obtained white paste was washed with diethyl ether and centrifuged

at 4000 rpm (Universal 32 R, Hettich Zentrifugen) to separate the organic components in supernatant from the ZnO powder. Linseed oil-ether solution was then analysed by ICP-OES after an acid water extraction (water/HNO_3), multiple extractions were carried out to maximize the final recovery. The acidic conditions employed during extraction lead to the dissolution of any residual ZnO:Cu particles. For this reason, ZnO:Cu powder was analysed separately in the same conditions and used as a control to validate the efficiency of the centrifuging procedure in ZnO:Cu particle removal, since the presence of residual ZnO:Cu particles in the supernatant solution could invalidate the final Zn and Cu quantification. As a further control, the same measurement was carried out on pure linseed oil binder. A schematic representation of the entire procedure is summarized in Figure S1. The results obtained by different tests are consistent and the concentration of detected ions was above the detection limit of ICP-OES (approximately 0.05 µg/l).

3. Results

3.1 Monitoring reactions with a paramagnetic probe

Figure 1(A) shows the X-band (9.693 GHz) EPR spectra at room temperature recorded for the ZnO:Cu powder at different times after mixing it with linseed oil. The EPR spectrum of pure ZnO:Cu powder shows a very weak signal in the range 310-350 mT. Its shape and position and the fact that it is detected at room temperature leads us to infer that the signal corresponds to Cu^{II} in a distorted octahedral coordination (8), possibly in perturbed sites at the surface of the particles. In addition, signals from transition metal impurities present in the zinc acetate used during the synthesis of the powder can be observed: Mn^{II} ($3d^5$, S=5/2) is clearly recognizable thanks to the classical hyperfine pattern of the EPR transition between the M_S=-1/2 and M_S=+1/2 electron spin manifolds labelled by asterisks in Figure 1(A) (11). In addition, a symmetrical line at g = 2.14, labelled by a cross, is typical of Ni^{II} in octahedral symmetry ($3d^8$, $^3A_2$ ground state) (8), which could correspond to the cation interstitial site in the ZnO structure. Our interpretation of a six-fold coordinated Ni^{II} for the line at g=2.14 is supported by a recent study of Ni-doped ZnO nanopowders reporting a signal at g=2.19 attributed to Ni^{II} in octahedral coordination (12). Indeed, Ni^{II} with $3d^8$ configuration has an integer spin S=1. Generally, ions with integer non-zero spin are not detectable in EPR at X-band unless the Zero-Field Splitting (ZFS) interaction is very small (8). This can however be the case in a high symmetry environment such as the interstitial octahedral site of ZnO. A possible Ni^{II} substituting in the tetrahedral cation site of ZnO with a then a degenerate orbital state ($^3T_1$) should not be detectable at room temperature, owing to spin-orbit coupling, which would induce a strong relaxation broadening of its EPR signal. An undetermined signal at g = 2.55 labelled by a square in Figure 1(A) is also observed.

Figure 1 - (A) Room temperature X-band (9.693 GHz) EPR spectra of the ZnO:Cu powder sample (black line) compared with the spectra of the same powder mixed with linseed oil, at different time-points. (B) Experimental and simulated EPR spectra of ZnO:Cu mixed with linseed oil after ten days and simulated contributions of Cu^{II}, Mn^{II}(*), Ni^{II} (†) and undetermined species (g = 2.55).

Linseed oil does not present any paramagnetic signal at room temperature. The EPR spectrum of ZnO:Cu is not modified immediately after mixing with linseed oil, as only Mn^{II}, Ni^{II} and the g=2.55 signals are detected and the weak Cu^{II} signal is unchanged. Over time the Cu^{II} signal grows progressively in the 335-345 mT region, achieving significant intensity values after a few hours (Figure 1(A)). As this signal increases at different time delays after mixing with oil, we conclude that it is due to the conversion of EPR silent Cu^{II} in four-fold tetrahedral environment into EPR active Cu^{II} in six-fold or square-planar environment. This EPR signal is simulated with spin Hamiltonian parameters (g_z = 2.3, g_x = 2.045, g_y = 2.1, A_z = 483 MHz, A_x =27 MHz, A_y =88 MHz for ^{63}Cu), as shown in Figure 1(B). Values of the spin-Hamiltonian and, more specifically, of the hyperfine parameters A_x, A_y and A_z are fairly inaccurate due to the lack of spectral resolution but are in the range of values for Cu^{II} coordinated to oxygen ions (7). All simulation parameters, including g- and A-strain (effect of ligand field disorder), are given in Table S1.
The variation with time of the amount of Cu^{II} detected by EPR is depicted in Figure 2 (filled red circles). The increase in EPR active Cu^{II} is very steep in the first hours after mixing, but after a few days the growth rate significantly decreases, and the intensity reaches saturation level (note that the binding oil is still liquid at this time). Small variations in the Ni^{II} and Mn^{II} EPR intensities are within experimental errors.
Figure 2 - Ratio of the mass of released cation to the initial mass of ZnO:Cu in linseed oil, at different time delays after mixing and detected either by EPR or by ICP-OES. Red line: simulation with equation (2).

3.2 Concentration of metal ions extracted in oil

In order to demonstrate that Zn^{II} ions are also released in the investigated system, together with the leaching of Cu^{II} ions, we have tested the presence of both metal ions in the oil extracted from ZnO:Cu-linseed oil with ICP-OES. In order to employ ICP analyses on isolated linseed oil, the ZnO:Cu is dispersed in linseed oil forming a white paste, which is then washed with diethyl ether and centrifuged (Figure S1). This procedure allows the separation of the organic components in supernatant from the ZnO:Cu powder, allowing us to measure the metal content released in the extracted linseed oil. For pure linseed oil, a residual Zn content of 0.18 mg.L^{-1} is detected. In the case of ZnO:Cu powder alone (not mixed with oil) we have detected residual amounts of 62 mass ppm and 5 mass ppm for Zn and Cu, respectively. Zn and Cu ions in the ZnO:Cu powder mixed with linseed oil have been measured up to 7 days after mixing and results are shown in Figure 2. ICP-OES analysis reveals a significant increase in the concentration of both Cu and Zn ions after only few minutes of mixing ZnO:Cu with linseed oil, followed by saturation. Zn or Cu released in oil after 3 days correspond to about 0.1 % and 0.06 %, respectively, of Zn and Cu in the ZnO:Cu powder.

4. Discussion

EPR analyses show that the environment of Cu^{II} changes due to the reaction of ZnO:Cu with linseed oil. The Cu^{II} metal ions switch from tetrahedral CuO_4 coordination to octahedral CuO_6 or CuO_4 planar coordination. It is worth stressing that the detected EPR spectrum of Cu^{II} does not show the usual four-line hyperfine pattern of the parallel component of the spectrum. The "smoothing" is due to a strong broadening of the hyperfine lines, typically produced by ligand field strain and disorder that in turn induces a distribution of g and A parameter values, as reported also in (13). Although the measured g and A parameter values are typical of Cu^{II} with oxygen ligands (7), evidence of strong disorder suggests that the EPR spectrum is most probably the sum of several types of Cu^{II} environments, which differ in their symmetry and/or in the nature of the coordinating ligands. We propose at least two different situations to account for this observation. The first one is the coordination of Cu^{II} at the perturbed ZnO surface. In this case, the oxygen ligands of the Cu^{II} complex can belong to both ZnO and oil carboxylate groups with different configurations. For example, Cu^{II} can be bound with four O ligands from ZnO and two additional ligands from carboxylates, or with two ligands from ZnO and four from carboxylates. In the second situation, Cu^{II} ions are extracted from ZnO and bound only to carboxylate groups. Hence, the superposition of these different spectra with different g_z and A_z parameters considerably distorts the low field part of the spectrum (14).

The evolution of the amount of Cu^{II} detected by EPR and illustrated in Figure 2, can be empirically interpolated with a power law

$$M(t) \cong M_0 + At^n \quad (2)$$

with $M_0 \cong 3.9$ ppm (the initial Cu^{II} amount corresponding to Cu^{II} at the surface of the raw particles), $A \cong 6$ ppm.h^{-n} and $n \cong 0.30$. It follows that the kinetics of the released Cu^{II} ions deviates form a simple first order kinetics, which would give an exponential rise. In metal oxide dissolution, such a power law can be affected by several factors such as particle shape (15), heterogeneous diffusion (16) and chemical processes at the solid/liquid interface (17). An important result of our measurement is that the complete dissolution of Cu^{II} ions is not reached even after several days in oil. One possible explanation could be related to a combination of pH effect and passivation phenomenon. Acidity is known to be a major parameter controlling dissolution (17). In an acidic medium, as is the case of linseed oil, Zn-O bonds are weakened by adsorption of carboxylic –COOH groups. Acid groups bond to Zn-O via dissociative adsorption (bidentate mode) and hydrogen ions migrate from –COOH to oxygen sites. Therefore, the dissolution occurs rapididly directly after mixing ZnO particles with oil, *i.e.* when pH is low. As dissolution proceeds, protons are consumed, and pH increases. In this process, the dissolution slows because the ZnO surface approaches its zero-charge point (neutral surface condition) and becomes less reactive (17). In addition, COO- groups covalently bind to the ZnO surface and lead to passivation (18) (19), halting ion leaching.

It can be noticed that the rate of copper release detected by ICP-OES is much faster than that detected by EPR (Fig.2). A possible explanation of this effect is to that Cu^{II} are first liberated in the form of EPR silent tetrahedral complexes, which then slowly convert to square planar or (and) six-fold coordinated EPR active complexes. For example, this may happen if the reaction with binding oil proceeds first by extracting very small (nanometer size) ZnO aggregates, containing Cu^{II} in tetrahedral coordination, which are then completely dissolved in the binding oil, as depicted in Figure 3. If these particles are small enough to remain in the liquid phase after centrifugation (Fig. 3), ICP-OES detects all Cu^{II} produced during the two steps, *i.e.* both EPR silent Cu^{II} still bound to small ZnO particles and the Cu^{II} ions dissolved in oil. Instead, EPR can detect only Cu^{II} produced during the second step. The dissolution of ZnO in oil thus shares similarities with the dissolution of oxide particles in aqueous solutions that lead to a release of metal ions in the liquid phase [20] [21] [22] [23].

Figure 3 – (a) Pristine ZnO particle containing EPR silent Cu^{II} (black dots). (b) Partial dissolution of smaller ZnO particles and releasing EPR active Cu^{II} in oil (red dots). (c) Full dissolution of the smaller particles and formation of outer passivation layer (orange) which hinders the dissolution phenomenon.

Because of the partial dissolution process, the ZnO surface structure is strongly modified after the dispersion in oil medium. This should in turn change the photoluminescence properties of ZnO grains. Indeed, in other research [24] [25] we have clearly detected an enhancement of the photoluminescence intensity from trap state levels of zinc oxide mixed with oil with respect to unmixed zinc oxide. This change can be attributed to the adsorption of carboxylate groups to the ZnO surface, which affects the electronic structure at ZnO surface and its luminescence properties [26]. The changes in luminescence have been shown to be significant in the first days after mixing of pigment powders and oils, but stable in time once the paint film become dried [24] [25].Results of EPR analysis allow us to better explain this evolution in time of the photoluminescence signal as a consequence of the passivation of ZnO which reaches a steady-state after a few days after mixing.

Conclusion

In this work, we applied for the first time EPR spectroscopy combined with ICP-OES to probe the release of metal ions in paint films, and in particular we considered the case of ZnO particles dispersed in oil medium. The most remarkable results are related to the determination of the kinetics of the metal ion leaching. Firstly, the results show that the pigment particles dissolve in drying oil following a trend comparable to dissolution of metal oxides in aqueous solutions, which is steep in the first stage and then slows because the passivation of the ZnO surface by carboxylate groups. A steady-state condition is reached in ten days, significantly preceding the complete hardening of the paint film.

The second important result regards the strong tendency of metal-based pigments to react with acid groups of drying oils. The latter are governed by the surface pigment reactivity towards the adsorption of acids and by the tendency of the pigment particles to dissolve in the oil medium. The reactivity of metal-based pigments can be controlled by adjusting their surface characteristics, by applying a surface coating, or by controlling the pH of the mixture in order to limit the metal ion leaching.

The method applied in this study for monitoring the metal ion leaching in paint mixing could be employed to study the effect of particle size on reactivity, and to investigate other oil-based paints, in which metal ion leaching phenomena and migration of metal complexes are implicated in paint degradation, as in the case of lead white oil paint.

Acknowledgment

Conflicts of interest

There are no conflicts to declare.

References

1. Osmond G, Boon JJ, Puskar L, Drennan J. Metal stearate distributions in modern artists' oil paints: Surface and cross-sectional investigation of reference paint films using conventional and synchrotron infrared microspectroscopy. Appl Spectrosc. 2012;66(10):1136–44.

2. Gabrieli F, Rosi F, Vichi A, Cartechini L, Buemi LP, Kazarian SG, et al. Revealing the nature and distribution of metal carboxylates in Jackson Pollock's alchemy (1947) by micro-attenuated total reflection FT-IR spectroscopic imaging. Anal Chem. 2017;

3. Hermans JJ, Keune K, Van Loon A, Iedema PD. The crystallization of metal soaps and fatty acids in oil paint model systems. Phys Chem Chem Phys. 2016;18(16):10896–905.

4. Baij L, Hermans JJ, Keune K, Iedema P. Time-Dependent ATR-FTIR Spectroscopic Studies on Fatty Acid Diffusion and the Formation of Metal Soaps in Oil Paint Model Systems. Angew Chemie - Int Ed. 2018;57(25):7351–4.

5. Mecklenburg MF, Tumosa CS, Vicenzi EP. The Influence of Pigments and Ion Migration on the Durability of Drying Oil and Alkyd Paints. New Insights into Clean Paint Proc from Clean 2010 Int Conf Univ Politec Val Museum Conserv Inst. 2013;

6. Dietz RE, Kamimura H, Sturge MD, Yariv A. Electronic structure of copper impurities in ZnO. Phys Rev. 1963;132(4):1559–69.

7. Peisach J, Blumberg WE. Structural implications derived from the analysis of electron paramagnetic resonance spectra of natural and artificial copper proteins. Arch Biochem Biophys. 1974;165(2):691–708.

8. de Boer E. Electron Paramagnetic Resonance. Elementary Theory and Practical Applications, J.A. Weil, J.R. Bolton and J.E. Wertz, John Wiley, U.S.A., 1994 xxi + 568 pp., £66.00, ISBN 0-471-57234-9. Recl des Trav Chim des Pays-Bas. 2010;

9. Baskar G, Gurugulladevi A, Nishanthini T, Aiswarya R, Tamilarasan K. Optimization and kinetics of biodiesel production from Mahua oil using manganese doped zinc oxide nanocatalyst. Renew Energy. 2017;103:641–6.

10. Stoll S, Schweiger A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. J Magn Reson. 2006;

11. Li GL, Wu SY, Hu XF, Kuang MQ. Theoretical studies on the spin Hamiltonian parameters and local environment of Mn2+ in ZnO nanocrystal and bulk. Phys B Condens Matter [Internet]. 2015 Jun 1 [cited 2019 Feb 3];466–467:64–7. Available from: https://www.sciencedirect.com/science/article/pii/S0921452615300016

12. Babu B, Sundari GR, Ravindranadh K, Yadav MR, Ravikumar RVSSN. Structural, spectroscopic and magnetic characterization of undoped, Ni 2+ doped ZnO nanopowders. J Magn Magn Mater [Internet]. 2014 Dec 1 [cited 2019 Feb 3];372:79–85. Available from: https://www.sciencedirect.com/science/article/pii/S0304885314006775

13. Gourier D, Vivien D, Thery J, Livage J, Collongues R. ESR of copper-doped β-alumina localization of Cu2+ and linewidth effect. Phys Status Solidi. 1978;45(2):599–606.

14. Marquardt CL, Giuliani JF, Gliemeroth G. A study of copper ions in silver-halide photochromic glasses. J Appl Phys. 1977;48(9):3669–79.

15. Kline WE, Fogler HS. Dissolution kinetics: The nature of the particle attack of layered silicates in HF. Chem Eng Sci. 1981;

16. Macheras P, Dokoumetzidis A. On the heterogeneity of drug dissolution and release. Pharmaceutical Research. 2000.

17. Stumm W. Reactivity at the mineral-water interface: Dissolution and inhibition. Colloids Surfaces A Physicochem Eng Asp. 1997;

18. Taratula O, Galoppini E, Wang D, Chu D, Zhang Z, Chen H, et al. Binding studies of molecular linkers to

ZnO and MgZnO nanotip films. J Phys Chem B. 2006;

19. Moreira NH, Da Rosa AL, Frauenheim T. Covalent functionalization of ZnO surfaces: A density functional tight binding study. Appl Phys Lett. 2009;

20. Yoon TH, Johnson SB, Brown GE. Adsorption of Organic Matter at Mineral/Water Interfaces. IV. Adsorption of Humic Substances at Boehmite/Water Interfaces and Impact on Boehmite Dissolution. Langmuir. 2005;

21. Sakallioglu T, Bakirdoven M, Temizel I, Demirel B, Copty NK, Onay TT, et al. Leaching of nano-ZnO in municipal solid waste. J Hazard Mater. 2016;

22. Petrochenko PE, Zhang Q, Bayati R, Skoog SA, Phillips KS, Kumar G, et al. Cytotoxic evaluation of nanostructured zinc oxide (ZnO) thin films and leachates. Toxicol Vitr. 2014;28(6):1144–52.

23. Bian SW, Mudunkotuwa IA, Rupasinghe T, Grassian VH. Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: Influence of pH, ionic strength, size, and adsorption of humic acid. Langmuir. 2011;27(10):6059–68.

24. Artesani A, Gherardi F, Nevin A, Valentini G, Comelli D. A photoluminescence study of the changes induced in the zinc white pigment by formation of zinc complexes. Materials (Basel). 2017;10(4).

25. Artesani A, Gherardi F, Mosca S, Alberti R, Nevin A, Toniolo L, et al. On the photoluminescence changes induced by ageing processes on zinc white paints. Microchem J. 2018;

26. Zhang Z, Yates JT. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. Vol. 112, Chemical Reviews. 2012. p. 5520–51.