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Inorganic-based phytohormone delivery vector of 2-chloroethylphosphonate nanohybrid: a new stimulating compound with controlled release property to increase latex production

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New inorganic-based phytohormone delivery system, a stimulating compound to increase latex production was developed through hybridisation of 2-chloroethylphosphonic acid (ethephon) into the interlayer of Zn–Al-layered (ZAL) double hydroxide. The hybridisation product, ZADO, was synthesised using co-precipitation technique at pH 7.5, 0.08 M ethephon and initial molar ratio of Zn to Al, $R = 4$. The resulting material has a basal spacing of 11.5 Å and Fourier transform infrared spectra further supported the hybridisation episode of ethephon into the ZAL. The release behaviour of the active agent, ethephon from the nanohybrid was found to be of controlled manner, governed by pseudo-second order kinetics. These results indicate that it is possible to design and develop a new delivery system of a phytohormone, [ethephon (2-chloroethylphosphonate)] with controlled release property to increase latex production of rubber tree (*Hevea brasiliensis*).

Keywords: intercalation; nanohybrid; self-assembly; controlled release formulation; layered double hydroxide

1. Introduction

The natural rubber sector has been expanding tremendously due to overwhelming demand worldwide. Natural rubber exhibits unique physical and chemical properties, which makes it reliable in making useful products. In aid to this sector, the application of nanotechnology offers vast improvement to conventional devices, methods and materials exploited in the natural rubber latex industries. Research in rubber nanotechnology areas, in an attempt to maintain the natural rubber latex supply, will potentially help the industries to meet the increasing demands at present.

Two-chloroethylphosphonic acid or ethephon is a well known latex stimulant agent, which is commonly used to increase the latex yield of the rubber tree (*Hevea brasiliensis*)

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[1–3]. Ethephon could modulate plant growth and metabolism by releasing ethylene, which affects the latex production of the rubber tree. In the physiological medium with pH >3.5, ethephon releases ethylene, a phytohormone, which facilitates the aqueous transfers within the *Hevea* trunk's outer tissues, cambium, and thus prolong the latex flow duration and increase the latex production [2].

Hybridisation of the active agent, ethephon with layered inorganic structure, such as layered double hydroxides (LDHs) is believed to be useful, as our previous study has shown that the resulting hybridised active agent can be released in a controlled manner [4,5]. Similar studies on drugs show that this is the case [6–8]. Studies on phosphonic-based layered material using various methods for various applications have been done by few researchers [9–12]. However, no work on intercalation of ethephon into LDHs has been reported in the open literature.

LDHs are of anionic clays family, which includes the naturally occurring hydrotalcite mineral, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$. LDH can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{b+}[A^{m-}_{b/m}]\cdot nH_2O$ where M^{II} represent divalent cations (Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, etc.), M^{III} represent trivalent cations (Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, La^{3+}) and A^{m-} represent anions (CO_3^{2-}, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-) in the interlayer [13].

In recent years, LDHs have been widely used as the host material to produce new organic–inorganic hybrid material. This is due to their unique properties, such as the flexibility to incorporate various anions into the interlayer. This particular property of LDH has attracted considerable attention to create new compounds, which is called nanohybrid or nanocomposite through hybridisation of the organic and the inorganic component via the intercalation process. Intercalation is the insertion of a guest species into the interlayer region of a layered solid with preservation of the layered structure. It is expected that from intercalation of various anions into the interlayer of LDH, the resulting materials have enhanced or tailor-made properties with novel functionality and applications [14–16].

This study is focused on synthesising phase-pure, well-ordered layered nanohybrid material containing an active agent, ethephon or 2-chloroethylphosphonate as guest anion. The guest is encapsulated into the interlayer of the layered host, Zn–Al–LDH (ZAL), to form an organic–inorganic nanohybrid (ZADO). This hybrid material is expected to have controlled release property in which the active agent, ethephon (molecular structure is given in the inset of Figure 1) can be released from the inorganic interlayer in a controlled manner, and subsequently modulate metabolism by slowly releasing ethylene, the phytohormone, which in turn will increase the latex production and further boost the production of rubber plantation industry. From this study, it is hoped that the application of ethephon in the form of slow release formulation (nanohybrid) could be used as a starting point for new generation of agrochemicals which is safer and user as well as environment friendly.

2. Materials and methods

All of the chemicals used in this synthesis were obtained from different chemical suppliers and were used as received. Both ZAL and ZADO were synthesised by co-precipitation method. For the formation of ZAL, the mother liquor solutions of Zn and Al was set at Zn

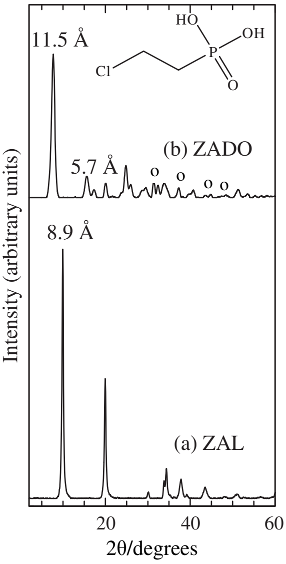

Figure 1. PXRD patterns for ZAL (a) and its nanohybrid with ethephon, ZADO (b). The reflections marked with O are due to $ZnAlO_4$. The molecular structure of ethephon is given in the inset.

to Al initial molar ratio, $R = 4$, and the pH was brought to 7.5 by drop-wise addition of 2 M NaOH. The same method was adopted to synthesise the LDH nanohybrid, ZADO, in which the solution of 0.08 M ethephon was added alternatively with the 2 M NaOH. During the addition, the solution was stirred under nitrogen atmosphere to avoid contamination from atmospheric carbon dioxide. The resulting slurry was aged for 18 h with continuous agitation. The ZAL and ZADO formed were cooled, centrifuged and washed several times, dried and kept in sample bottles for further use and characterisations.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained using filtered Cu-Kα radiation in a Shimadzu diffractometer D-600. Fourier transform infrared (FTIR) spectra were recorded by a PerkinElmer 1750 spectrophotometer. KBr pallet of 1% sample was used to obtain the FTIR spectra. The elemental analyses were done by using a CHNS-932 (LECO) and the inductively coupled-plasma atomic emission spectrometry (ICP-AES), with a PerkinElmer spectrophotometer model Optima 2000DV under standard condition. The release of ethephon was studied by measuring the concentration of carbon in the release media using a SGE ANATOC series II total organic carbon analyser.

3. Results and discussion

3.1. *Powder X-ray diffraction*

The ZAL with nitrate as the counter anion in the interlayer shows a well-ordered LDH material with basal spacing of 8.9 Å (Figure 1(a)). On the other hand, the resulting nanohybrid, ZADO in which ethephon has been intercalated into the LDH inorganic

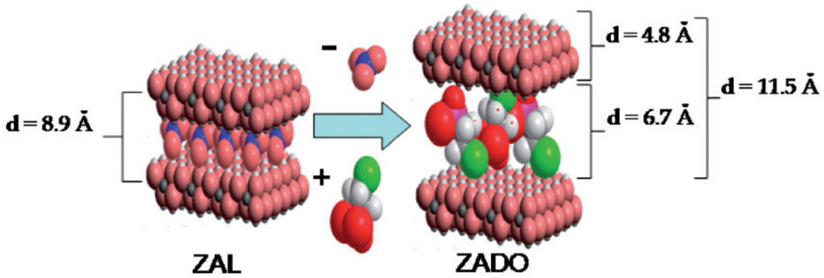

Figure 2. The formation of Zn–Al–ethephon nanohybrid, ZADO shows monoanion arrangement of ethephon between the inorganic LDHs.

interlayers shows the decrease in the PXRD intensity with basal spacing of 11.5 Å. The optimum condition in which a well-ordered layered nanohybrid could be synthesised was by using 0.08 M ethephon with Zn to Al molar ratio of 4 and pH 7.5.

The insertion of ethephon occurred in the interlayer of ZAL, resulting in the expansion of basal spacing to 11.5 Å. The expansion indicated that the interlayer has been expanded in order to accommodate the ethephon moieties, which are bigger in size compared to nitrate. In addition, the expansion is also due to spatial orientation of ethephon in the inorganic intergallery to achieve the most stable configuration. Based on the molecular calculation using ChemOffice software, the monoanion of ethephon molecule has to be tilted at about 45° inside the inorganic interlamellae space, resulting in the dimension of about 6.7 Å, so that the basal spacing of 11.5 Å could be obtained by adding the thickness of ZAL, which is 4.8 Å [13] (Figure 2).

The interlayer spacing of ZADO is 11.5 Å, and this is consistent with the previous study on the intercalation of $C_nH_{2n+1}PO_3H^-$ and $C_nH_{2n+1}PO_3^{2-}$ anions ($n = 0, 1, 2, 3, 4$) into LDH which are in a range of 11.9–15.9 Å, taking into account the slightly different organic moieties, sizes and their spatial orientation in the inorganic interlayers [9]. In addition, the Zn to Al molar ratio also plays a role in determining the basal spacing. The Zn to Al molar ratio determined in this work is around 3.5 compared to around 2.0 reported earlier for the *n*-alkyl phosphonates [9].

The PXRD pattern for ZADO also shows the presence of unknown phase/s (Figure 1(b)). The non-LDH phases may be zinc or aluminium salts of 2-chloroethylphosphonic acid [12]. Attempt has been made to remove the unknown phase by washing procedure, but the effort was not successful. Fortunately, the presence of this phase has no effect on the release property of the ethephon from the interlamellae of the nanohybrid. This will be discussed later.

3.2. *FTIR spectroscopy*

Figure 3 shows the FTIR spectra for ZAL, ethephon and their hybridisation product, the nanohybrid, ZADO. The broadbands at 3442 and 3438 cm^{-1} for ZAL and ZADO, respectively, are dominated by the OH stretching of both the structural OH groups in the hydroxide layers and the interlayer water in the material. The band at 3390 cm^{-1} in

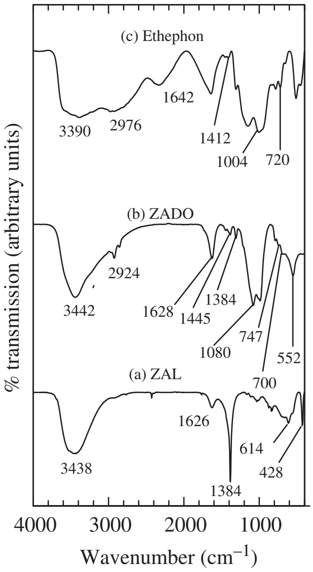

Figure 3. FTIR spectra of ZAL (a), ZADO (b) and the guest anion, ethephon (c).

ethephon is due to the OH stretching of the two OH bonds of the R-PO_3H_2 groups. The bands observed at 2924 cm^{-1} in ZADO can be attributed to the C–H stretching, which also appears in the FTIR spectrum of the guest anion, ethephon at around 2976 cm^{-1}. The presence of $\nu_{\text{H–O–H}}$ bending vibration can be observed in the range 1626–1642 cm^{-1}. The CH_2P stretching band in ethephon could be observed at 1412 cm^{-1}, compared to 1445 cm^{-1} in ZADO.

A band at 1384 cm^{-1} appears in the FTIR spectrum of ZADO suggesting that nitrate is present either as adsorbed and/or co-intercalated species. This is expected, as PXRD technique is not sensitive enough to detect trace amounts of nitrate. A band at 1080 cm^{-1} in ZADO is due to the P=O stretching of ethephon in which it appeared at around 1004 cm^{-1}. The C–Cl stretching which appeared at 720 cm^{-1} in ethephon could be seen in ZADO at 747 cm^{-1}. The other two bands that appeared at 700 cm^{-1} and 552 cm^{-1} can be attributed to the Al–OH and Zn–Al–OH bonding vibrations, respectively, and these bands could also be seen in the spectra of ZAL, the parent material at 614 cm^{-1} and 428 cm^{-1}, respectively.

The FTIR spectrum of ZADO shows that it resembles a mixture of each spectrum of ZAL and ethephon. This indicates that both functional groups of the host and the guest are simultaneously present in the nanohybrid, which confirmed the intercalation episode of ethephon into the interlamellae, as indicated by the PXRD pattern shown in Figure 1.

3.3. *Elemental analysis*

Elemental analysis shows that the final Zn to Al molar ratio, R_f for ZAL is 3.6. Due to the presence of little amount of unknown phase, the Zn to Al molar ratio for ZADO was estimated to be about 3.5. The initial molar ratio of Zn to Al in the mother liquor for both ZAL and ZADO is 4. The R_f values show that they are lower than the original value, and the new values reflect the values that are required to compensate the negatively charged nitrate counter anion and organic guest ethephon, respectively [19]. The CHNS results show that ZAL contains 3.5% nitrogen. This is in agreement with the presence of a strong, sharp band at 1384 cm^{-1}, which is due to the nitrate group in the FTIR spectrum of ZAL, as shown in Figure 3. From the CHNS result, it could be observed that ZADO contains about 0.3% nitrogen, which indicates that the nitrate groups are still present in the resulting nanohybrid either as co-intercalant and/or adsorbed species. The content of ethephon in ZADO was estimated to be about 39.5%, and this is expected, which is due to the intercalated ethephon in the interlayer, together with some unknown phase.

3.4. *Release of phytohormone, ethephon from the nanohybrid*

The release profile of ethephon from the nanohybrid, ZADO into distilled water is shown in Figure 4. The release was found to be fast at the beginning (<200 min) and more sustained thereafter up to 1000 min, which when extended up to 3000 min, the percentage release was only increased by about 5%. The maximum accumulated saturated release of ethephon is around 90%.

In order to obtain some insight into the release behaviour of ethephon from the nanohybrid into distilled water, the data of the amount of ethephon released were fitted to various kinetic models; zeroth [18], first [19] and pseudo-second [20] order kinetics as well as parabolic diffusion [21]. The fitting was done for the data obtained in a range of 0–2880 min, as given in Figure 5 and the parameters obtained from the fitting are summarised in Table 1.

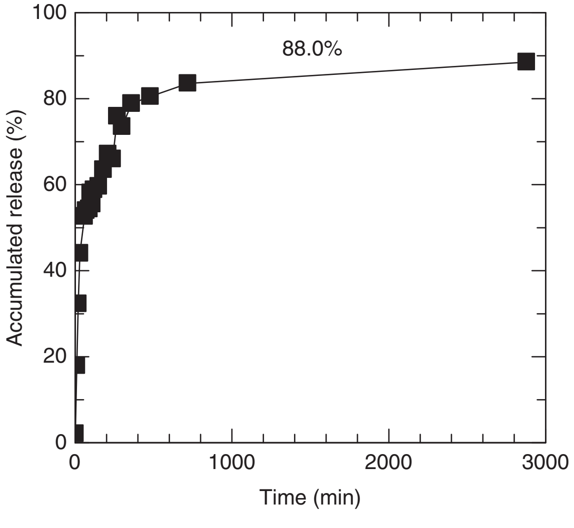

Figure 4. Release profile of ethephon from its nanohybrid into distilled water.

Compared to the other models used in this work, it is clear that pseudo-second order kinetics gives the best fit to the experimental data as indicated by the higher correlation coefficient, $r^2 = 0.999$. The $t_{1/2}$ values, i.e. the time taken for ethephon concentration to be at half of the accumulated saturated release were calculated to be 56 min, consistent with

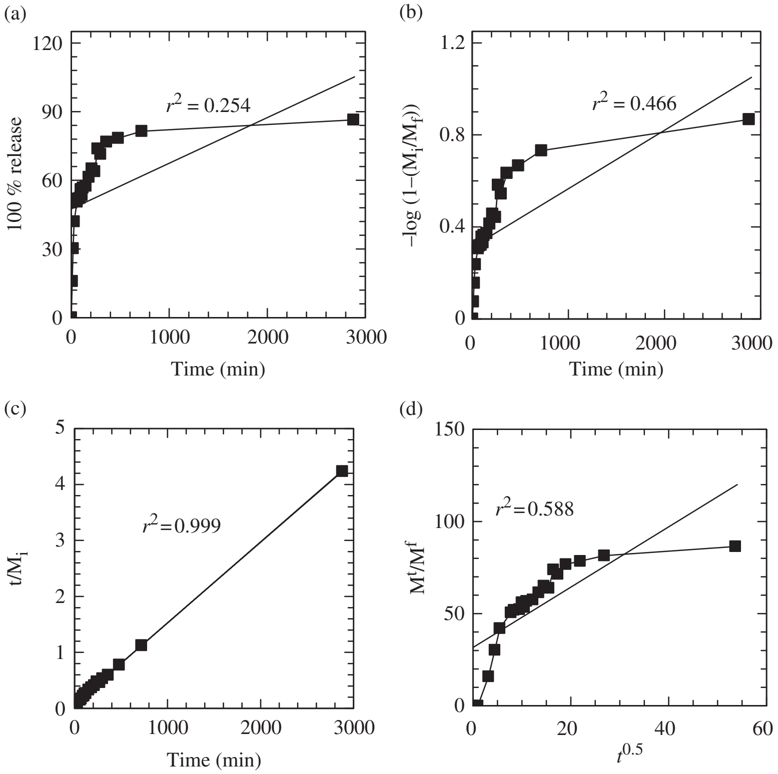

Figure 5. Fitting of the data of ethephon released from the nanohybrid into distilled water to various models at 0–2880 min; zeroth order (a) first order (b) pseudo-second order (c) and parabolic diffusion (d).

Table 1. The parameters obtained from the fitting of the release data of ethephon from the nanohybrid to various models, and their correlation coefficient, r^2 is also given.

	Zeroth order	First order	Pseudo-second order	Parabolic diffusion
k	$2.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}\,s^{-1}}$	$2.5 \times 10^{-4}\,\mathrm{s^{-1}}$	$2.6 \times 10^{-5}\,\mathrm{mol^{-1}\,L\,s^{-1}}$	$1.6\,\mathrm{s^{-0.5}}$
$t_{1/2}$	19669.0 min	2772.0 min	56.0 min	360.0 min
C	47.5	3.1×10^{-1}	8.1×10^{-2}	31.6
r^2	2.5×10^{-1}	4.7×10^{-1}	1.0	5.9×10^{-1}
Equations	$C = kt + \mathrm{c}$	$-\log(1 - C) = kt + \mathrm{c}$	$t/C_t = 1/k_2 C_{eq}^2 + (1/C_{eq})t$	$C_t/C_{eq} = \mathrm{c} + kt^{0.5}$

Notes: C_{eq}, concentration of anion at equilibrium; C_o, initial concentration of the anions; C_t, concentration of anion at time t; C, percentage release of anion; k is the rate constant; k_2 is the rate constant of pseudo-second order; c, a constant.

very steep release profile, as shown in Figure 4. This is within the fast release stage of the active agent, ethephon.

4. Conclusions

New inorganic-based nanohybrid compound containing ethephon, a phytohormone to stimulate latex production of rubber tree, *H. brasiliensis* was designed and synthesised. The resulting material acts as a delivery vector of the phytohormone, which can be released in a controlled manner. The release was found to be fast at the beginning (<200 min), followed by a more sustained release thereafter up to 1000 min and can be extended to around 3000 min. The release is governed by pseudo-second order kinetics with accumulated saturated release of ethephon of around 90%. The co-precipitation method was found suitable to generate the new nanohybrid material.

Acknowledgements

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References

[1] D. Derouet, L. Cauret, and J.C. Brosse, *Synthesis of 1,4-polyisoprene support of 2-chloroethylphosphonic acid (ethephon), a stimulating compound for the latex production by the Hevea brasiliensis*, Eur. Polym. J. 30 (2003), pp. 671–686.

[2] D. Derouet, L. Cauret, and J.C. Brosse, *Synthesis of poly(silyenephosphate)s incorporating 2-chloroethylphosphonic acid (ethephon), a stimulant for the latex production by the Hevea Brasiliensis*, Eur. Polym. J. 40 (2004), pp. 1953–1966.

[3] J. Auzac, J.L. Jacob, and H. Chrestin, *Physiology of Rubber Tree Latex*, CRC Press, FL, 1989.

[4] M.Z. Hussein, Z. Zainal, A.H. Yahaya, and D.W.V. Foo, *Controlled release of a plant growth regulator, 1-naphthaleneacetate from the lamella of Zn-Al-layered double hydroxide nanocomposite*, J. Controll. Release 82(2–3) (2002), pp. 417–427.

[5] M.Z. Hussein, S.H. Sarijo, A.H. Yahaya, and Z. Zainal, *Synthesis of 4-chlorophenoxyacetate-zinc-aluminium-layered double hydroxide nanocomposite: Physico-chemical and controlled release properties*, J. Nanosci. Nanotechnol. 7 (2007), pp. 2852–2862.

[6] V. Ambrogi, G. Fardella, G. Grandolini, L. Perioli, and M.C. Tiralti, *Intercalation compounds of hydrotalcite-like anionic clays with anti-inflammatory agents-II. Uptake of diclofenac for a controlled release formulation*, AAPS Pharm. Sci. Tech. 3(3) (2001), pp. 1–6.

[7] M. Trikeriotis and D.F. Ghanotakis, *Intercalation of hydrophilic and hydrophobic antibiotics in layered double hydroxides*, Int. J. Pharm. 332 (2007), pp. 176–184.

[8] J.H. Yang, Y.S. Han, M. Park, T. Park, S.J. Hwang, and J.H. Choy, *New inorganic based-drug delivery system of indole 3-acetic acid-layered metal hydroxide nanohybrid with controlled release rate*, Chem. Mater. 19 (2007), pp. 2679–2685.

[9] U. Constantino, S. Clementi, M. Nocchetti, and R. Vivani, *Intercalation and grafting of n-alkyl phosphonates into synthetic hydrotalcites*, Mol. Cryst. Liq. Cryst. 311 (1998), pp. 207–212.

[10] M. Edgar, V.J. Carter, D.P. Tunstall, P. Grewal, V.F. Nicolin, P.A. Cox, P. Lightfoot, and P.A. Wright, *Structure solution of a novel aluminium methylphosphonate using a new simulated annealing program and powder X-ray diffraction data*, Chem. Commun. (2002), pp. 808–809.

[11] B. Meena and I.J. Shannon, *Synthesis and characterization of new layered mixed metal phosphonate materials magnesium–zinc phosphonates* $Mg_{1-x}Zn_x(O_3PR)\cdot H_2O$ *and nickel–zinc phosphonates* $Ni_{1-x}Zn_x(O_3PR)\cdot H_2O$ *using mixed divalent magnesium–zinc and nickel–zinc hydroxides*, J. Mater. Chem. 12 (2002), pp. 350–355.

[12] P. Gerbier, C. Guerin, B. Henner, and J.R. Unal, *An organometallic route to zinc phosphonates and their intercalates*, J. Mater. Chem. 9 (1999), pp. 2559–2565.

[13] F. Cavani, F. Trifiro, and A. Vaccari, *Hydrotalcite-type anionic clays: Preparation, properties and applications*, Catal. Today 11(2) (1991), pp. 173–301.

[14] A. Aguzzi, V. Ambrogi, U. Constantino, and F. Marmottini, *Intercalation of acrylate anions into the galleries of Zn–Al layered double hydroxide*, J. Phys. Chem. Solids 68 (2007), pp. 808–812.

[15] T. Markos and D.T. Ghanotakis, *Intercalation of hydrophilic and hydrophobic antibiotics in layered double hydroxides*, Int. J. Pharm. 332 (2007), pp. 176–184.

[16] S. Aisawa, N. Higashiyama, S. Takahashi, H. Hirahara, D. Iketmatsu, H. Kondo, H. Nakayama, and E. Narita, *Intercalation behavior of L-ascorbic acid into layered double hydroxides*, J. Appl. Clay Sci. 35 (2007), pp. 145–154.

[17] M.Z. Hussein, J.M. Amin, Z. Zainal, and A.H. Yahaya, *Self-assembled nanocomposite of organic–inorganic hybrid: 2,4-dichlorophenoxyacetate in Zn–Al hydrotalcite-like layers*, J. Nanosci. Nanotechnol. 2(2) (2002), pp. 143–146.

[18] P. Costa and J.M.S. Lobo, *Modelling and comparison of dissolution profiles*, Eur. J. Pharm. Sci. 13 (2000), pp. 123–133.

[19] J.G. Wagner, *Interpretation of percent dissolved-time plots derived from in vitro testing of conventional tablets and capsules*, J. Pharm. Sci. 58 (1969), pp. 1253–1257.

[20] L. Ling, J. He, M. Wei, D.G. Evans, and X. Duan, *Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies*, Water Res. 40 (2006), pp. 735–743.

[21] T. Kodama, Y. Harada, M. Ueda, K.I. Shimizu, K. Shuto, and S. Komarneni, *Selective exchange and fixation of strontium ions with ultrafine Na-4-mica*, Langmuir 17 (2001), pp. 4881–4886.