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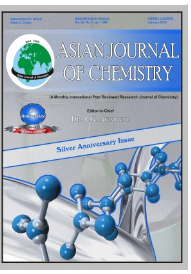

Release Kinetics of Lawsone from the Layer of Zn-Al Layered Double Hydroxide

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A drug-inorganic nanostructure material involving a pharmaceutically active compound lawsone intercalated Zn-Al layered double hydroxide (Law-LDHs) with Zn/Al = 4 has been assembled by the co-precipitation method. The deintercalation or the release of lawsone was found to be rapid initially followed by a more sustained release thereafter and this behaviour was found to be dependent on the pH of the release medium. The release kinetic of lawsone from the layer of layered double hydroxide was found to be governed by the first order kinetic. The release profile data and the results from the kinetic study indicate that the dissolution mechanism is mainly contributed to the release behaviour of lawsone from the layer of layered double hydroxides. It is suggested that the layered double hydroxides may have an application as the basis of a drug delivery medium.

Key Words: Layered double hydroxides, Lawsone, Intercalation, Release kinetics.

INTRODUCTION

Recently, the synthesis of organic-inorganic layered double hydroxides hybrid containing drug molecules have becoming the area of research that get more attention from many researchers due to its enhanced in properties of resulting compound such as dissolution property[1], thermal stability[2] and an increased in controlling the rate of release[3]. The unique properties of layered double hydroxides such as anion exchange property also contributed a huge opportunity in industrial and environmental research in preparing a catalyst[4,5], antacid[6], controlled release formulation[7] and pharmaceuticals products[8].

Layered double hydroxides are layered solids that have positively charged layers and an interlayer charge compensating of anions that can be interleaved with an organic moiety, especially of an anionic type to balance the net charge of the layered double hydroxides sheets. The chemical composition of layered double hydroxides can be represented by the general formula $[M^{II}_{(1-x)}M^{III}(OH)_2]^{x+} A^{z-}_{x/z}.yH_2O$ or $[M^{I}M_2^{III} (OH)_2]^{+} A^{z-}_{1/z}.yH_2O$, where M^{I}, M^{II} and M^{III} are mono and di- and trivalent cations, respectively, occupying octahedral positions in the hydroxide layers and A^{z-} is an interlayer charge-compensating anion.

Lawsone (law) [2-hydroxy-1,4-naphtaquinone] is a red orange dye present in the leaves of the *henna* plant. The *henna* extracts containing lawsone use by human being for hair and skin pigments for many years. Lawsone strongly absorbs UV light and aqueous extracts can be effective sunless tanning sunscreens. Nowadays, lawsone is becoming more and more popular due to its profound effect on human health[9,10]. The insertions of lawsone into a layer of layered double hydroxides can be done by two routes namely direct and the indirect methods. In the direct route, lawsone can be intercalated by the co-precipitation technique[11]. By using this technique, the host and guest species (lawsone) are included in the mother liquor, followed by the aging process to form a well ordered nanolayered structure. In the indirect route method, the insertion of the guest can be done by first preparing the host followed by the modification of the host and finally insertion of the guest molecule into the interlayer[11].

In the present study, lawsone was selected as the biological active species and intercalated into the Zn and Al layered double hydroxide by co-precipitation technique. In the authors' previous paper, the characterizations of this compound using powder X-ray diffraction (PXRD) and Fourier transform infrared (FTIR) was reported[11]. In addition to the previously reported paper, further investigation will be carried out on the release kinetics of lawsone from the layer of layered double hydroxides as well as to study and discuss the controlled release property of the resulting intercalated compound.

EXPERIMENTAL

Synthesis of intercalated compound using co-precipitation method (ZAN-Law): An aqueous solution (100 mL) of sodium hydroxide (NaOH) (1.52 g, 0.003 mol) and lawsone (1.03 g, 0.003 mol) was added with dropwise to a solution (250 mL) containing zinc nitrate (1.53 g, 0.006 mol) and aluminium nitrate (0.75 g, 0.002 mol) under the nitrogen atmosphere with vigorous stirring until the final pH of 10. The resulting slurry was aged at 28 ºC for 48 h in an oil batch shaker. The resultant slurry was then filtered, washed with de-ionized water until the final pH of 7 and finally dried at room temperature for 12 h.

Controlled release study: Phosphate buffer solution at pH 7.0, 4.0 and pH 10 were used as the aqueous release medium in this study. The release of lawsone from the interlayer of the layered double hydroxides was performed by adding 0.025 g of ZAN-law into 200 mL of aqueous release medium at room temperature. The paddle rotation speed was set at 125 rpm. 2 mL of the sample was withdrawn at pre-determined intervals and passed through 0.45 μm membrane filter before the concentration of lawsone released into an aqueous release medium was measured using UV-VIS spectrometer which performed at 265 nm wavelength.

RESULTS AND DISCUSSION

Controlled release study of lawsone: Lawsone can be de-intercalated from the interlayer of layered double hydroxides through an ion-exchange with the surrounding anions, such as phosphate. A series of phosphate buffer solutions with different pH values were used to observe the pH effect on the release rate of the lawsone from the interlayer of the layered double hydroxides. Fig. 1 shows the release profile of the lawsone from the interlayer of the layered double hydroxides into the release medium at different initial pH values.

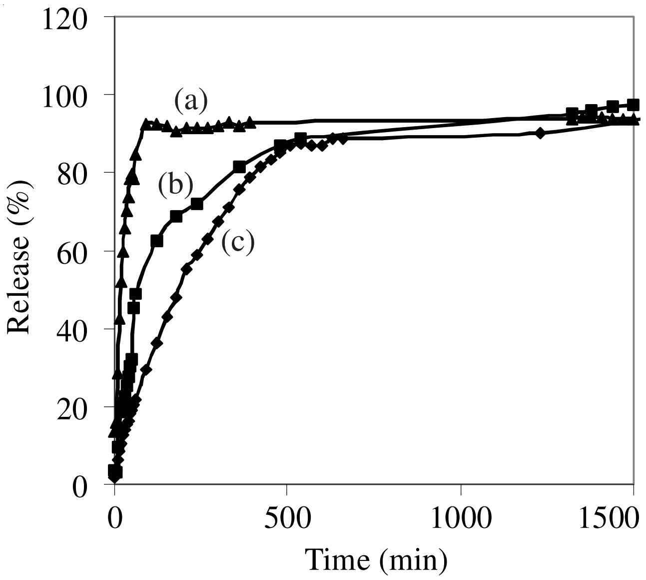

Fig. 1. Release profile of lawsone from ZAN-Law at different pH values (a) pH = 10, (b) pH = 7 and (c) pH = 4

As shown in the figure, the released rate of lawsone into an aqueous release medium increased with the increase in contact time between the intercalated compound and aqueous release medium. The release rate was found to be rapid for the first one hour for all pH and this was followed by a more sustained released thereafter. Equilibrium was achieved after 1 h. This is true for all released medium with the initial pH of 4, 7 and 10. The release rate was found to be rapid for the first one hour but it recorded a slower rate thereafter and the release process still continued after 3 h. A maximum percentage of release was achieved at 90 min for pH 10, 480 minutes for pH 7 and 540 min for pH 4.

The percentage of lawsone released from the ZAN-Law into the aqueous release medium solutions at the initial pH 10 was found to be the lowest (Fig. 1). The highest percentage of lawsone released was achieved in a neutral and acidic aqueous release medium solution. At equilibrium it was estimated that 90 % and 82 % of lawsone could be released from the ZAN-Law into the aqueous release medium solution with an initial pH of 7 and 4 respectively. The results were in agreement with the previous report studied[12], which explained that the intercalation drug was unionized in the acidic environment and ionized in the neutral and alkaline environment. The explanation reflected the results that were obtained from the released study which showed that the lowest percentage of release was recorded at the pH of 4. This might be due to the remaining lawsone that was still in the interlayer of the layered double hydroxides which was unable to be ionized and thus performed an ion exchange while in the neutral and alkaline aqueous release mediums the lawsone was ionized and was able to perform ion exchange which contributed to the high percentage of release.

Release kinetics of lawsone: The release of intercalated compounds from the layer of layered double hydroxides have been previously studied by many researchers and various model such as Freundlich[13], zeroth[14], first[15], second[15] and Bhaskar *et al.*[16] were used to study the release kinetics. As reported by many researchers, the released of drugs from the layer of layered double hydroxides can be controlled either by dissolution of layered double hydroxides particles[7] or by diffusion through the layered double hydroxides particle[3]. The release profile of the drugs from the layer of layered double hydroxides can be determined from the fitted selected various models as stated above.

In the present study, in order to get some insights into the mechanism that governs the release of lawsone into aqueous release medium at different pH, first order and Bhaskar equations were used. Bhaskar equation as shown in equation (1) can be used to evaluate whether the diffusion through the particle is the rate limiting step[16] whereas first order equation as shown in equation (2) can be used to describe the phenomenon of dissolution.

$$-\log(1-X) - t^{0.65} \tag{1}$$

$$-\log(1-X) - t \tag{2}$$

From the equations as stated above, X and t are the release percentage and time, respectively.

The fitting results for both equations are given in Fig. 2 and the resulting correlation coefficients are given in Table-1. As shown in Fig. 2(a), the release profile of lawsone into an aqueous release medium at pH of 4, did not follow both equations very well. The r^2 values of 0.9298 and 0.9069 were obtained for first order and Bhaskar equations, respectively. The results might be due to the possibility that the lawsone

TABLE-1
CORRELATION COEFFICIENT VALUES OBTAINED FROM THE FITTING OF THE RELEASE DATA OF LAWSONE FROM THE LAYER OF LAYERED DOUBLE HYDROXIDES INTO AN AQUEOUS RELEASE MEDIUM AT DIFFERENT PH USING FIRST ORDER AND BHASKAR EQUATIONS

Aqueous release medium (pH)	Full release period (minutes)	r^2 value (First order)	r^2 value (Bhaskar)
4	360	0.9298	0.9069
7	540	0.9978	0.9939
10	60	0.9798	0.9573

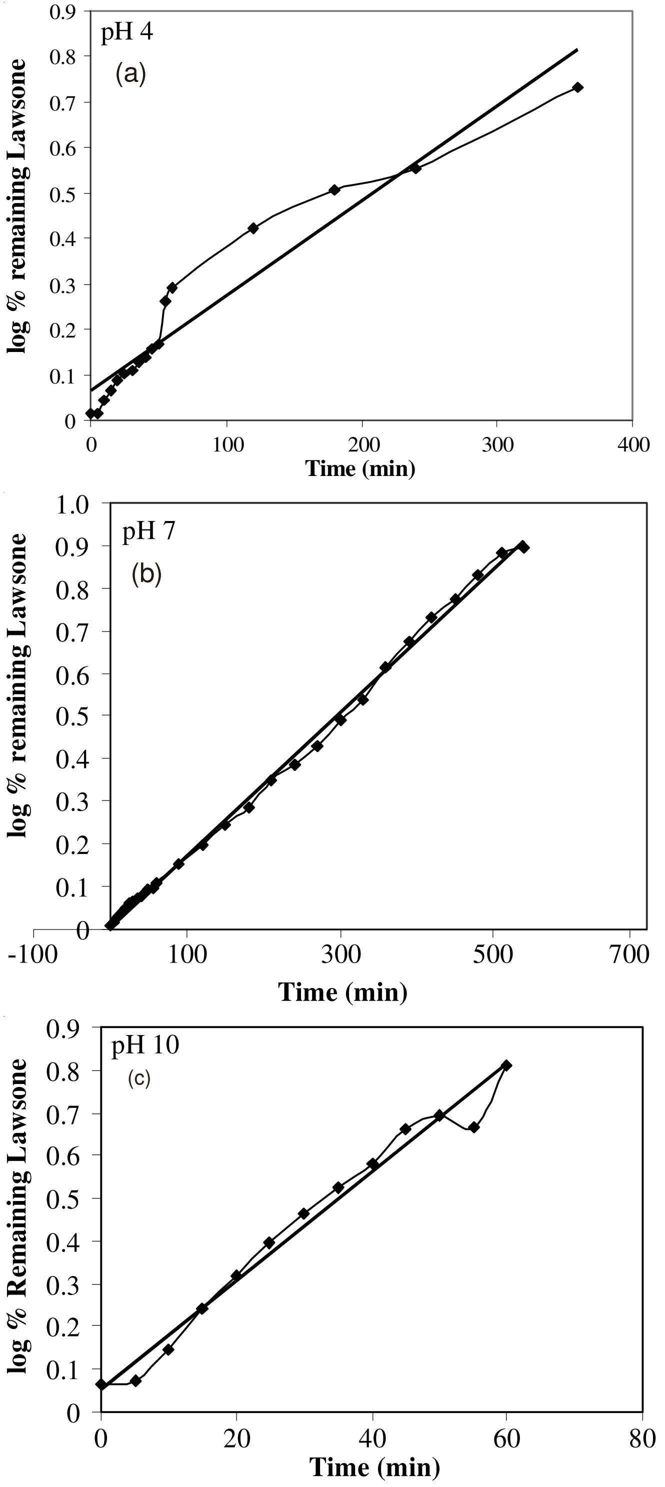

Fig. 2. Fitting of the lawsone release data at different pH to first order equation (a) at pH 4 (b) at pH 7 and (c) at pH 10

released is a co-effect behaviour including dissolution of nano-composites and ion exchange between the intercalated lawsone in the layer of layered double hydroxides and the phosphate anions in the buffer solutions[17]. From the r^2 values that obtained from both equations, it can also be deduced that the dissolution of nano-composites mainly contribute to the co-effect in this process.

The release profile of lawsone into an aqueous release medium at a pH of 7 is well fitted for both equations as shown in Fig. 2(b). The r^2 value in the first order model for a release period of 540 minutes was 0.9978 and the r^2 value for Bhaskar equation was recorded at 0.9939. The resulted release profile from both equations deduced that the dissolution of nano-composites is the limiting step for the release of lawsone in this study. The same release data with the same kinetic model was applied for aqueous release medium at a pH of 10 as given in Table-1. Thus, based on the r^2 values as given in Table-1, it can be deduced that the first order kinetics is better than Bhaskar equation to describe the release of lawsone into an aqueous release medium at different pH from the layer of layered double hydroxides.

Conclusion

The release study of lawsone from the layer of layered double hydroxides was found to be dependent on the pH of the release medium. The highest percentage of release was achieved in acidic and neutral release mediums. Application of the release data to two kinetic models namely first order and Bhaskar equations showed that the first order kinetics is better than Bhaskar equation to describe the release of lawsone into an aqueous release medium at different pH from the layer of layered double hydroxides. From the r^2 values that obtained from both equations, dissolution of nano-composites mainly contribute to the co-effect in this process.

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