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Carbamate insecticide release kinetics for controlled release formulation of isoprocarb insecticide from modified zinc layered hydroxide nanocomposite

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Abstract

A controlled release formulation for carbamate insecticide, isoprocarb was successfully developed using zinc layered hydroxide modified with sodium dodecyl sulphate (ZLH-SDS) as host material, resulted in the formation of inorganic-organic nanocomposite material with sustained release properties. The controlled release study was found that phosphate solution yielded highest percentage release compared to sulphate and chloride solutions. The release of isoprocarb from its nanocomposite was found to occur in a controlled manner, governed by first order (phosphate solution) and pseudo-second order (sulphate and chloride solutions). The maximum amount of isoprocarb released from the nanocomposite into solutions was found to be 90.1 %, 59.1 % and 54.0 % for phosphate, sulphate, and chloride solutions, respectively. This formulation allow the automatic release of the active agent to the target at a controlled rate and maintain its concentration in the system within the optimum limits over a specified period of time, thereby providing great specificity and persistence without diminishing efficiency.

1. Introduction

In the last centuries, the pesticide manufacturer made big effort developing fresh, more efficient, biodegradable pesticides, and to produce new kinds of formulations such as concentrated in suspension, concentrated emulsion-like, granules, and soluble liquids [1,2]. Anyhow, there are still significant issues arising from the immediate release of the active ingredients which leads to toxicity risks.

There are some studies which show that the losses of effectiveness of pesticides [3,4]. The result of trying to compensate such losses is a tendency showing the use of excessive quantities of these dangerous chemical substances which leads to residual risks [1]. The presence of residual pesticide in soil has many possible causes. Sometimes it is due to aerial treatments applied directly to the plant foliage in order to control pests and diseases, following which approximately 50% of the used product finally deposits in soil. Another case, it occurs by pesticide drift from the host by rain or wind. The pesticide residue may come from excess amount of pesticide applied to the soil and derive from plant

residues remaining in the soil after harvest [5]. Kamble, (2007) has reported that the total percentage abnormalities in pollen mother cells increase with increased in concentration of pesticide on meiosis of *Cannabinus Lin* [6]. The uses of pesticides can also risk human via drinking water. Pesticides are conceived to present a bigger menace because they are highly concentrated in the water supply due to runoff from the agricultural use. The prevalent exposure of the world population to this substance has caused concern over their potential health consequences. Idris et al. (2013) has reported that residue of pesticides has a significant environmental impact on aquatic ecosystems and mammals [7]. These uncontrolled released pesticides may flow into the drainage and irrigation canal that may lead to pollution. This situation is an important economic loss and, even so, it is harmful both to human health and to the environment [1]. Controlled delivery can be defined as a technique or method in which active chemicals are made available at a specified rate and duration to achieve the intended effect [8]. The controlled release system is expected to provide the active ingredient with a constant supply, usually at zero order, by continuously releasing it for a certain period of time [9]. Controlled release of agrochemicals (pesticides, herbicides, nutrients) is used to maintain the local concentration of active ingredients in the soil and to reduce runoff [10].

In agricultural, particular attention has been also focused on controlled release formulation of pesticides. There are profoundly cases of pesticides that have been intercalated into ZLH interlamellae such as 3-(4-methoxyphenyl)propionic acid [11], cetyltrimethylammonium bromide [12], chloroacetic acid [13], 2-(2,4-dichlorophenoxy)butyric acid [14], and 4-chlorophenoxyacetic acid [15]. These anionic active agents is easier to be intercalated into the interlayer of ZLH due to positively charged ZLH layers that promotes the attraction force between the guest anion and the host.

In a previous study [16], we analyzed the physico-chemical properties of zinc layered hydroxide-sodium dodecyl sulphate-isoprocarb nanocomposite (ZLH-SDS-ISO) by intercalating isoprocarb into the interlayer ZLH modified with sodium dodecyl sulphate (SDS) surfactant. The previous study showed the successful intercalation of isoprocarb into the ZLH interlayer by an ion exchange method. The SDS surfactant provided a great impact in order to intercalate the poor water-soluble insecticide, like isoprocarb, into the interlayer of ZLH. The crystallinity of the resulting nanocomposite is increase by increasing the amount of isoprocarb anion. The thermal stability of isoprocarb also increased after the intercalation, compared to its pure form. Besides, the resulting nanocomposite showed a mesoporous-like characteristic. This study also showed that ZLH can be an excellent host for isoprocarb. Continuing from that work, we now report on the release and kinetic study of ZLH-SDS-ISO nanocomposite as controlled release formulation for isoprocarb pesticide. Herein, we pursue our previous synthesized ZLH-SDS-ISO nanocomposite with controlled release properties.

2. Experimental

2.1 Preparation of ZLH-SDS-ISO Nanocomposite

The synthesis of ZLH-SDS-ISO nanocomposite was published elsewhere [16]. Briefly, ZLH-SDS was synthesized using a co-precipitation method by the slow addition of 1.0 M NaOH and 40 mL of 0.5 M of $Zn(NO_3)_2 \cdot 6H_2O$ into a solution containing 40 mL 0.25 M SDS under magnetic stirring. The pH value was adjusted to 6.5. The slurry was then centrifuged and dried in an oven at 70 °C [17].

Preparation of isoprocarb (ISO) intercalated into the interlayer of ZLH-SDS (indicated as ZLH−SDS-ISO) was achieved by an ion exchange method. Various concentrations of isoprocarb solution were prepared at 0.001 M, 0.0025 M and 0.005 M. Then 0.5 g of ZLH-SDS was dissociated in an isoprocarb solution and keep under magnetic stirring for 2 ½ hours. The slurry was then aged for 24 hours in an oil bath shaker at 70 °C. Then the slurry was centrifuged and the final white solid was dried in an oven for 24 hours.

2.2 Release Study of Pesticides

All three solutions, Na_3PO_4, Na_2SO_4, and NaCl solutions were prepared with various concentrations which are 0.10 M, 0.20 M, and 0.30 M. This solution is chosen because sulfate, phosphate and chloride ion is present in the rain water and the soil composition [18]. The releases of isoprocarb from the layered

material nanocomposites were studied by adding a 0.6 mg sample into the cuvette which is the optimum mass for ion exchange capacity as already be done in previous study [19]. The instrument of UV-Vis was set up with correct data for analysis. The quantity of pesticides released into the solution was measured at the preset time at λ_{max} = 270.0 nm. The release behavior was then determined by fitting the release data into five model of kinetic order which are zeroth order, first order, pseudo-second order, parabolic diffusion, and Fickian diffusion model. The data was calculated by Microsoft excel and EasyPlot software.

3. Results and discussion

3.1 Release study

The release profiles of isoprocarb from ZLH-SDS-ISO nanocomposite into sodium phosphate, sodium sulphate, and sodium chloride solution are shown in Figure 1 (a), (b), and (c) respectively. For phosphate solution (Figure 1(a)), the release was found to be rapid for the first 700 min followed by a sustained release thereafter until reach equilibrium at around 1500 min. Meanwhile, Figure 1 (b) shows the release rate of isoprocarb from interlayer of ZLH in sulphate solution faster at the first 1000 min and slower release until 1500 min before reach equilibrium at around 2500 min. The release of isoprocarb into chloride solution showed a faster release at the first 1500 min and slower release until 2500 min before reached equilibrium at around 3000 min (Figure 1 (c)).

The high density of phosphate, sulphate, and chloride ions lead to the faster release of isoprocarb anion into the solutions. This was due to rapid ion exchanged between the incoming anions in the solutions and isoprocarb anion in the interlayer of ZLH. Whereas, the slower release was due to the strong host-guest interaction resulting to much slower release process [18,20].

As shown in Figure 1 (a) to (c), the release profile of isoprocarb from ZLH-SDS-ISO nanocomposite in phosphate solution dominated the accumulate release percentage with 67.8 %, 75.1 %, and 90.1 % in 0.1 M, 0.2 M, and 0.3 M, respectively. Meanwhile, the percentage accumulated releases of isoprocarb into sulphate solution were 44.8 %, 50.1 %, and 59.1 % in 0.1 M, 0.2 M, and 0.3 M respectively which was higher than the percentage of accumulate release of isoprocarb into chloride solution with percentage release of 41.6 %, 46.4 %, and 54.0 % in 0.1 M, 0.2 M, and 0.3 M respectively.

All figures showed that the maximum accumulated release increased with increasing solutions concentration. This was due to the presence of high concentration of incoming anion in the release solutions that boost the ion exchange process between isoprocarb and the incoming anion [21]. Ion exchange occurred when the incoming anion had a high affinity towards the ZLH hence increased the accumulated release of isoprocarb anion. The percentage releases of isoprocarb into all solutions are listed in Table 1.

As shown in Table 1 a high percentage release could be observed for isoprocarb release into phosphate solution compared to sulphate and chloride solutions for all concentrations. This was due to the phosphate ion that had a higher affinity towards ZLH compared to sulphate and chloride ion. Besides, the tetrahedron (Td) point group of phosphate ion will contributed to increase the electrostatic attraction toward the positively charged ZLH layers [22]. There were two possible ideal configurations; the pyramidal configuration (with its C_3 axis perpendicular to the hydroxide layer) had three oxygen atoms closer to hydroxyl groups in one brucite-like layer and the fourth one pointing toward the opposite hydroxyl plane, and the other configuration (with its C_2 axis perpendicular to the hydroxide layer) places two oxygen atoms toward the opposite hydroxyl planes in each of two adjacent brucite-like layers [23]. Therefore phosphate was most preferred ion to be exchanged with isoprocarb anion and incorporated into the interlayer of ZLH for the formation of new ZLH with phosphate as a counter ion [24–26].

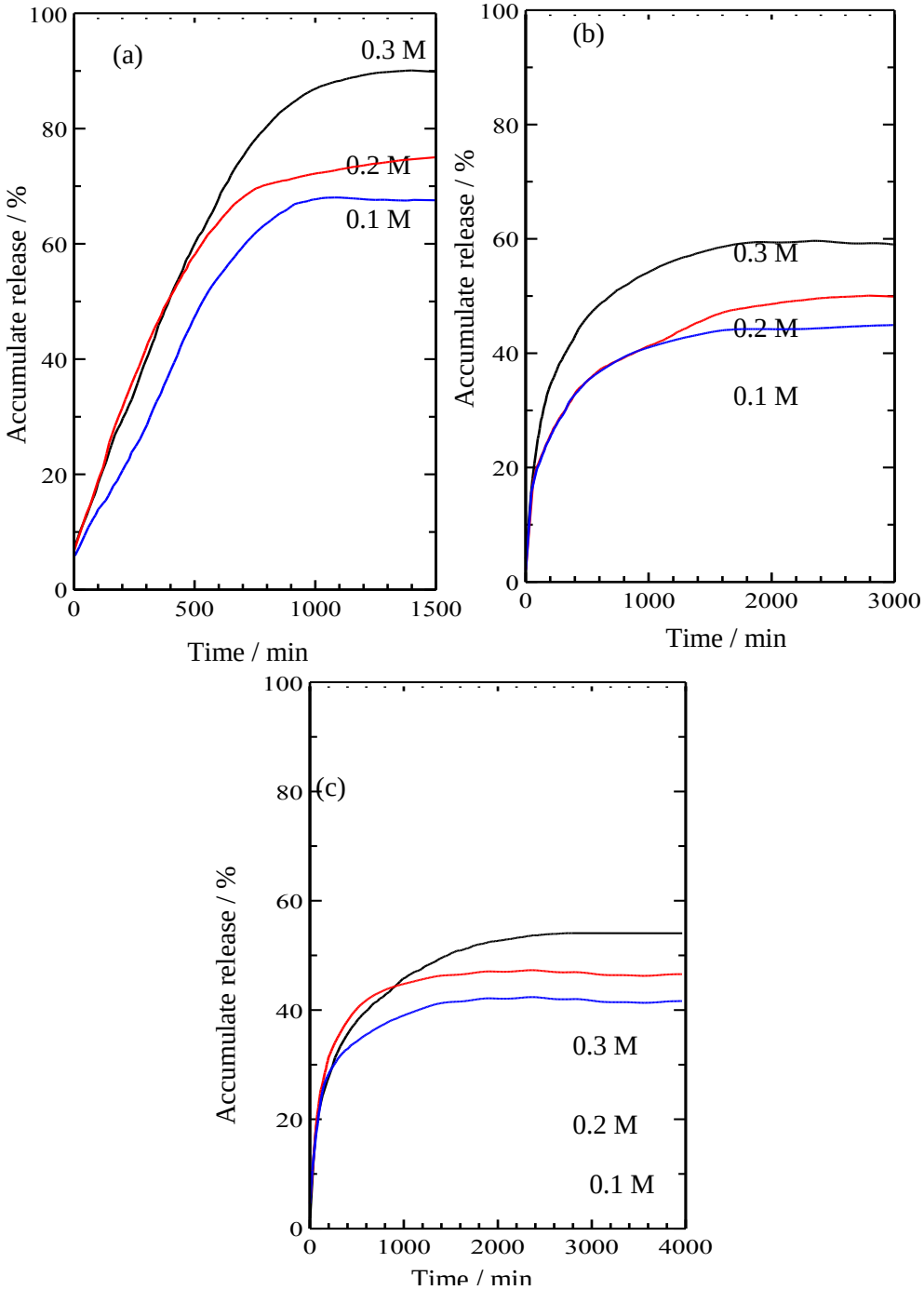

Figure 1: Release profile of isoprocarb from ZLH-SDS-ISO nanocomposite into 0.1 M, 0.2 M and 0.3 M concentration of aqueous (a) sodium phosphate, (b) sodium sulphate, and (c) sodium chloride solutions

Table 1: Percentage release of isoprocarb anion from ZLH-SDS-ISO nanocomposite into various solutions

Concentration (M)	Na_3PO_4 solution (%)	Na_2SO_4 solution (%)	NaCl solution (%)
0.1	67.8	44.8	41.6
0.2	75.1	50.1	46.4
0.3	90.1	59.1	54.0

3.2 Kinetic study

In order to understand the release behaviour of isoprocarb, a kinetic study of isoprocarb releases from the interlayer of ZLH-SDS-ISO nanocomposite was further performed. The controlled release data of ZLH-SDS-ISO nanocomposite was fitted to several kinetic models namely, zeroth order (eq. 4.5)) [27], first order (eq. 4.6))[28], pseudo-second order (eq. 4.7)) [29], parabolic diffusion model (eq. 4.8)) [30] and Fickian diffusion model (eq. 4.9)) [31] for which the equation is given below.

$$x = t + C \quad \text{(eq.4.5)}$$

$$-log\ (1 - M_i/M_f) = t + C \quad \text{(eq. 4.6)}$$

$$t/M_i = 1/M_f^2 + t/M_f \quad \text{(eq.4.7)}$$

$$M_i/M_f = kt^{1/2} + C \quad \text{(eq. 4.8)}$$

$$M_i/M_f = kt^n \quad \text{(eq. 4.9)}$$

The x is the percentage release of the isoprocarb anion at time t, M_i and M_f are the initial and final concentration of isoprocarb anions respectively and C is a constant. Whereas M_i/M_f represent the fraction of release anion at time, t, and n is an empirical parameter describing the release mechanism. The rate constant k, and $t_{1/2}$ are calculated from the corresponding equation where $t_{1/2}$ is the time required for 50 % of isoprocarb to be released from ZLH-SDS-ISO nanocomposite. The diffusional exponent, n and k for Fickian diffusion model have been evaluated from the slope of the plot $ln(M_i/M_f)$ versus $\ln t$.

The kinetic study of isoprocarb release from ZLH-SDS-ISO nanocomposite was analyzed by plotting the cumulative release data versus time by fitting to the equation as represented previously. The release data of ZLH-SDS-ISO nanocomposite in phosphate, sulphate, and chloride solutions was fitted between 0 to 500 min and presented in Figure 2 to Figure 4 respectively. The corresponding linear correlation coefficient, r^2 with value closest to 1, was considered as the best fit. The correlation coefficient, r^2 for the release of isoprocarb anion into phosphate solution, was best fitted to the first order. Whereas the release of isoprocarb anion in sulphate and chloride solution followed by pseudo-second order. The evaluated rate constants, half life ($t_{1/2}$), and correlation coefficients (r^2) obtained from the fitting of the data of ZLH-SDS-ISO are listed in Table 2.

The first order kinetic model demonstrated that the dissolution rate of the release system depends only on one reactant concentration [32,33]. Meanwhile, the pseudo-second order was the best model to describe the release behavior of isoprocarb from the ZLH-SDS-ISO into sulphate and chloride solution. This showed that the release of the isoprocarb from the inorganic ZLH interlayer involved dissolution of nanocomposite as well as ion exchange between the intercalated anions in the interlayer ZLH and the incoming anions in the aqueous solution which was controlled by pseudo-second order [34]. Based on the release profile for ZLH-SDS-ISO nanocomposite in all three solutions, the release rate was increased while $t_{1/2}$ is decreased with increasing concentration of release solution. These results showed that the higher concentration of the incoming anion, the faster the ion-exchange process, the more isoprocarb could be released and generally a shorter time is taken to reduce the concentration of the isoprocarb to one half of its saturated value. The pattern for k constant and $t_{1/2}$ values was similar to the previous study reported elsewhere [18,34,35].

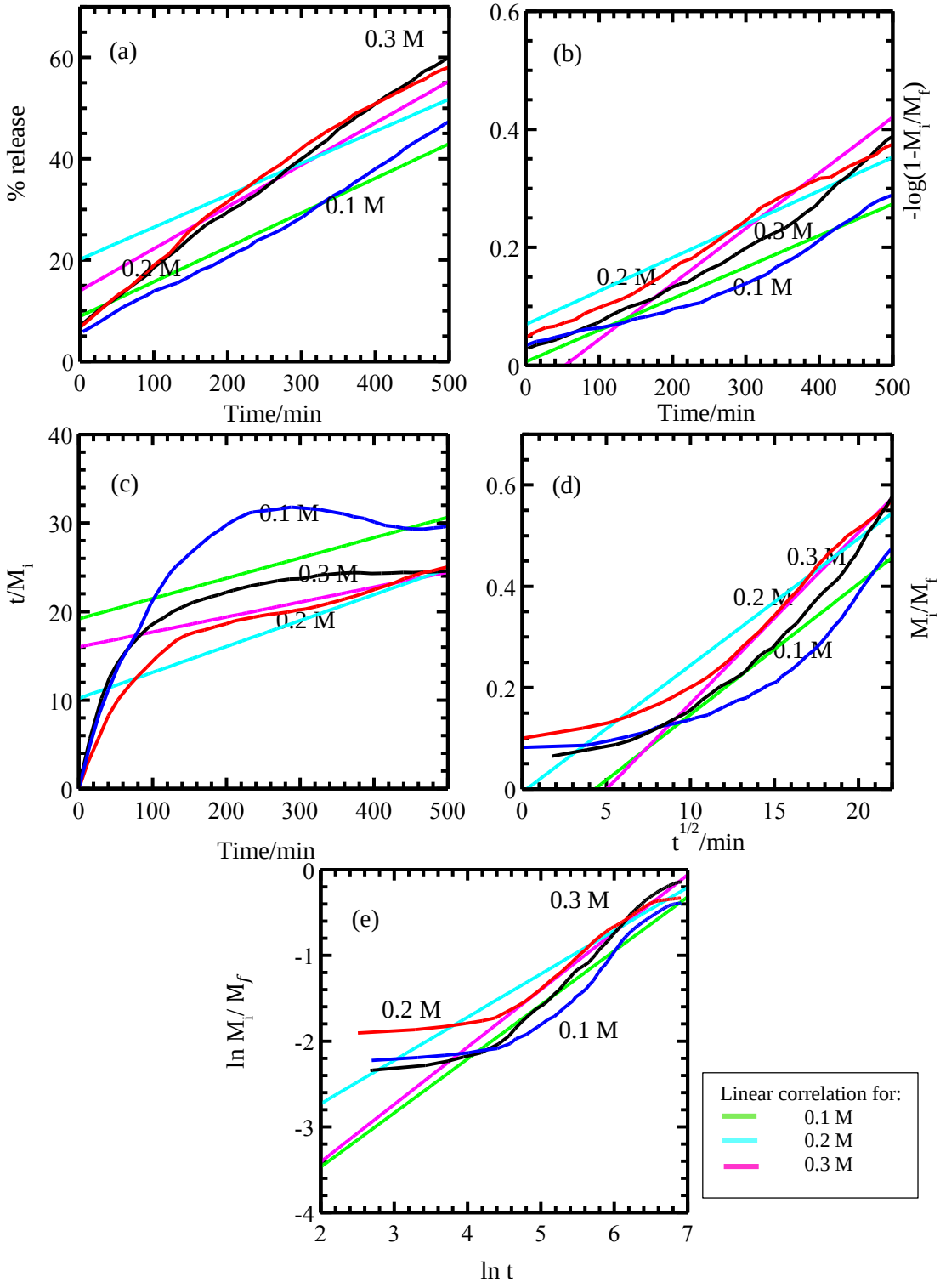

Figure 2: Fitting of the isoprocarb release data from ZLH-SDS-ISO nanocomposite to the (a) zeroth, (b) first, (c) pseudo second order, (d) parabolic diffusion, and (e) Fickian diffusion into various concentrations of aqueous sodium phosphate solutions.

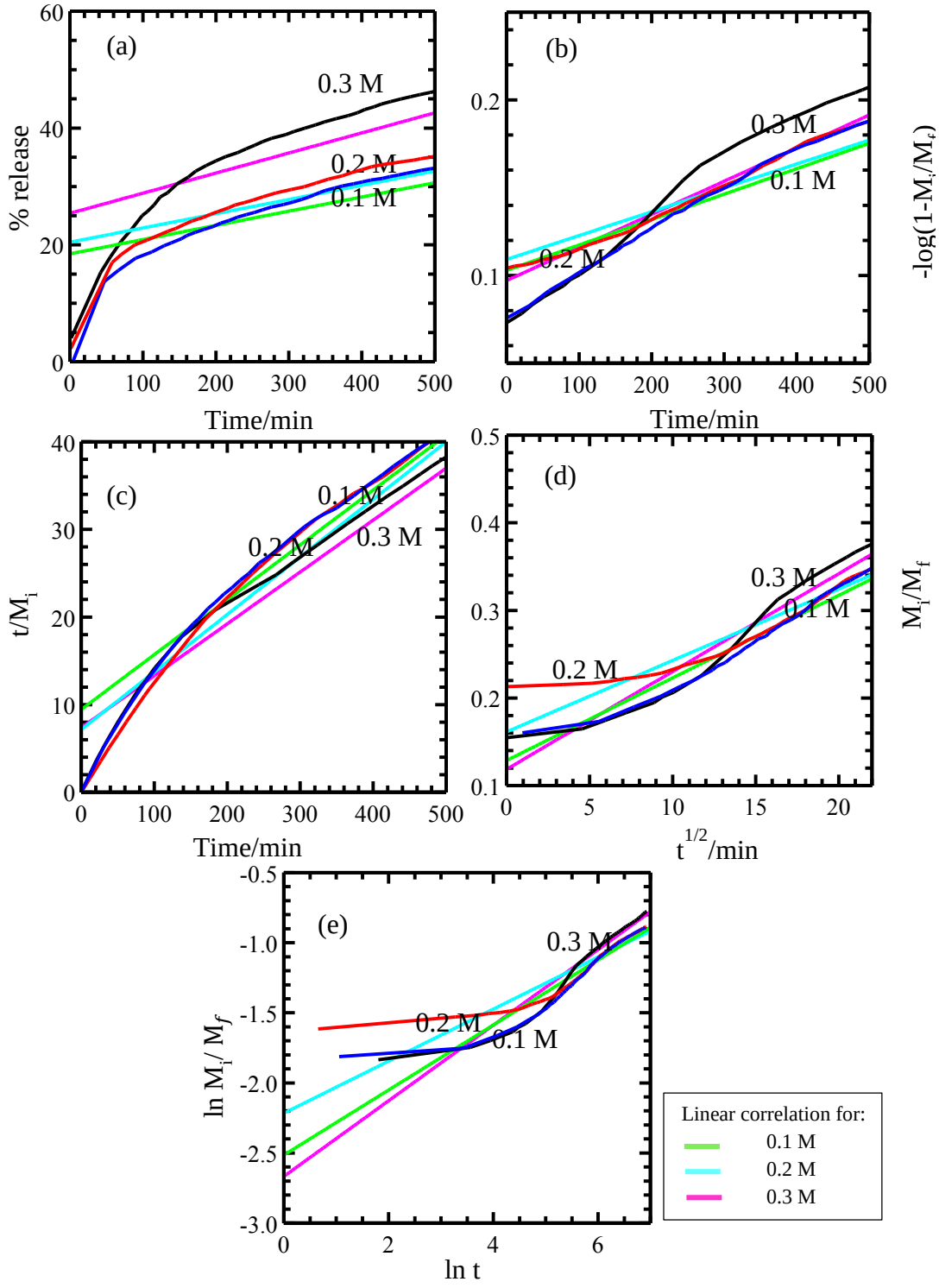

Figure 3: Fitting of the isoprocarb release data from ZLH-SDS-ISO nanocomposite to the (a) zeroth, (b) first, (c) pseudo second order, (d) parabolic diffusion, and (e) Fickian diffusion into various concentrations of aqueous sodium sulphate solutions.

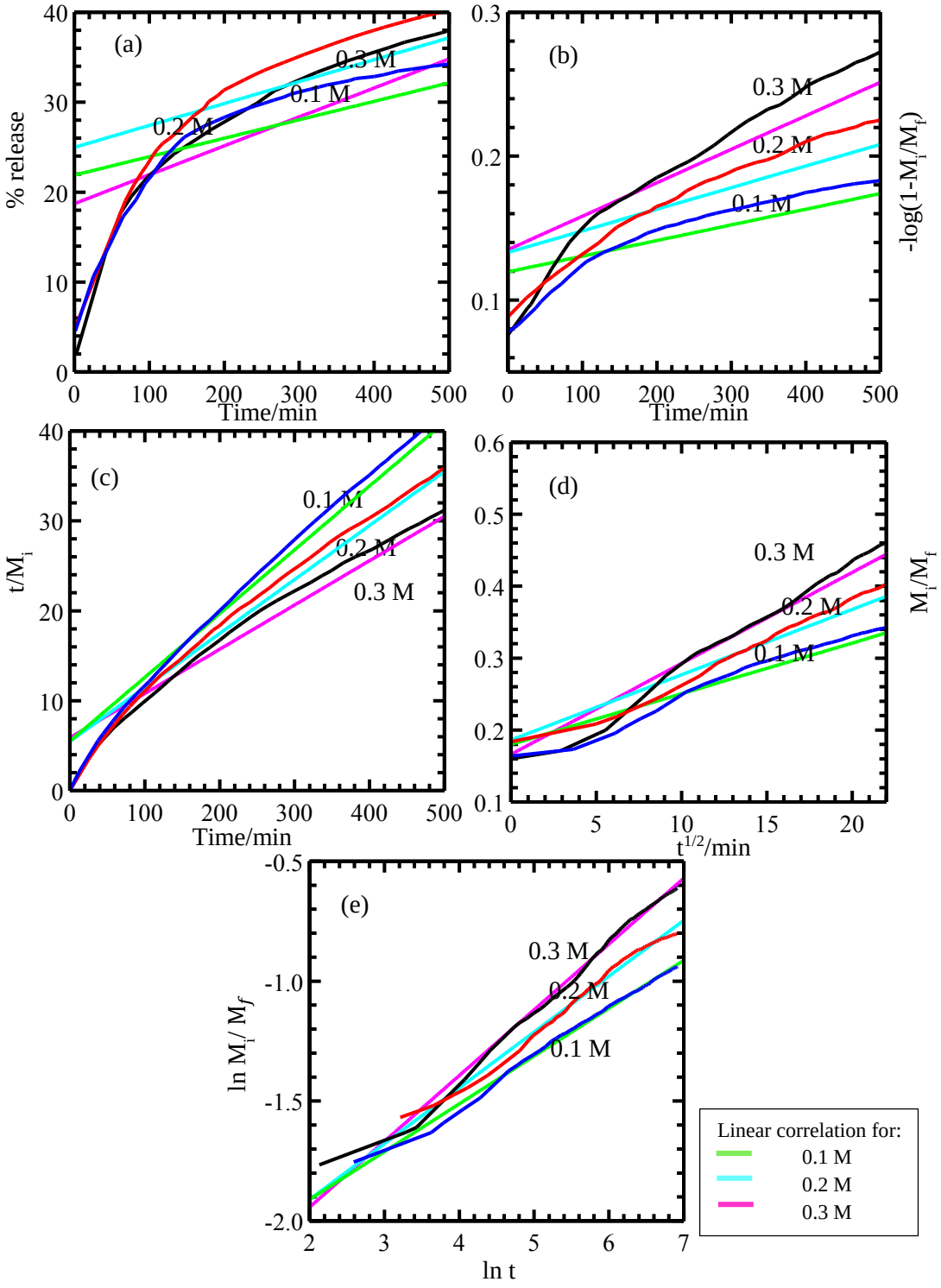

Figure 4: Fitting of the isoprocarb release data from ZLH-SDS-ISO nanocomposite to the (a) zeroth, (b) first, (c) pseudo second order, (d) parabolic diffusion, and (e) Fickian diffusion into various concentrations of aqueous sodium chloride solutions.

Table 2: Rate constants, half life ($t_{1/2}$), and correlation coefficients obtained from the fitting of the data of isoprocarb release from ZLH-SDS-ISO nanocomposite into sodium phosphate, sodium sulphate, and sodium chloride solutions.

Na_3PO_4 (M)	Zeroth order	Pseudo second order	Parabolic diffusion	Fickian	First order			
			r^2		r^2	k ($\times 10^{-4}$) ($mol^{-1}L\ s^{-1}$)	$t_{1/2}$ (min)	c ($\times 10^{-3}$)
0.1	0.972	0.698	0.957	0.925	0.987	5.34	304.9	6.32
0.2	0.908	0.947	0.970	0.948	0.962	5.66	300.7	9.40
0.3	0.974	0.771	0.978	0.956	0.989	9.41	298.1	5.10
Na_2SO_4 (M)	Zeroth order	First order	Parabolic diffusion	Fickian	Pseudo second order			
			r^2		r^2	k ($\times 10^{-4}$) ($mol^{-1}L\ s^{-1}$)	$t_{1/2}$ (min)	c
0.1	0.839	0.937	0.980	0.894	0.991	4.15	174.3	9.44
0.2	0.841	0.964	0.974	0.853	0.989	4.75	160.8	7.15
0.3	0.837	0.935	0.978	0.931	0.986	6.03	158.8	7.37
NaCl (M)	Zeroth order	First order	Parabolic diffusion	Fickian	Pseudo second order			
			r^2		r^2	k ($\times 10^{-4}$) ($mol^{-1}L\ s^{-1}$)	$t_{1/2}$ (min)	c
0.1	0.752	0.890	0.969	0.996	0.996	4.14	191.4	5.50
0.2	0.790	0.892	0.966	0.990	0.996	6.56	189.6	5.48
0.3	0.840	0.931	0.981	0.992	0.991	9.13	184.3	5.87

Conclusion

A ZLH-SDS-ISO nanocomposite as a controlled release formulation was successfully prepared and the pesticide release behavior has been studied. The release study have shown that: (i) the release pattern was rapid at first and followed by slower release until reach equilibrium, (ii) the percentage accumulated release was highest in phosphate solution followed by sulphate and chloride solutions. Whereas, the kinetic study have conclude that the isoprocarb release into phosphate solution was governed by first order, and the release into sulphate and chloride solutions governed by pseudo-second order. From both release and kinetic study, the use of this formulation could optimize the efficiency of delivery of isoprocarb pesticide and this study could be useful for designing systems which control the isoprocarb release, according to the plant requirements.

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Conflict of interest: The authors declare that they have no conflict of interest.

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