

Synthesis and Characterization of Imidacloprid/ Hydrotalcite-like Compound Nanohybrids

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Hydrotalcite-like compounds (HTlc) were first modified by sodium dodecyl sulfate (SDS), then the intercalation of imidacloprid (IM) into modified HTlc was carried out in mixed solvent of toluene/ethanol by an evaporating solvent enhanced intercalation method, obtaining IM-SDS-HTlc nanohybrids. It was found that the nanohybrids could well control the release of imidacloprid, demonstrating that the nanohybrids are a potential pesticide controlled-release formulation. The release of imidacloprid from IM-SDS-HTlc nanohybrids is dependent on the pH and the presence of electrolyte in release medium. Acidic medium and the presence of electrolytes induce the higher release rate of imidacloprid. The release process of imidacloprid from IM-SDS-HTlc nanohybrids can be described by pseudo-second-order release kinetics.

Keywords imidacloprid, hydrotalcite-like compound, nanohybrid, controlled-release formulation, pesticide

Introduction

Controlled-release formulations (CRFs) of pesticides have several advantages over standard pesticide formulations, including higher application rates, increased safety to the user and non-target organisms, and lower impact on the environment. Great deals of studies have been focused on the development of formulations for the controlled release of chemicals in agriculture, and many materials such as clay,^{1,2} polymer³⁻⁷ or both⁸ were used as carriers. Recently, hydrotalcite-like compounds (HTlc) have been reported as controlled-release carriers for many pesticides.^{9,10}

HTlc, or the so-called layered double hydroxides (LDHs), are a family of layered inorganic materials with structurally positively charged layers and interlayer balancing anions.¹¹⁻¹⁵ HTlc may be represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$, where M(II) and M(III) are di- and trivalent metal cations, respectively, A^{n-} is the gallery anion with charge $-n$, x is the number of moles of M(III) per formula weight of the compound, and z is the number of moles of co-intercalated water per formula weight of the compound. HTlc may be widely used in many fields, for example, catalyst,¹⁶ anion-exchanger,¹⁷ biology nanohybrids,^{18,19} photo protection²⁰ and anion adsorb-

ents.^{21,22} The interlayer region (or gallery) of HTlc may be considered as a microvessel in which pesticide molecules may be stored, *i.e.*, some pesticide molecules may be intercalated into the gallery of HTlc to form pesticide-HTlc nanohybrids. The nanohybrids may evidently inhibit the release of pesticide molecules stored in HTlc, therefore, the pesticide-HTlc nanohybrids may be potentially used in pesticide controlled-release.²³

Some anionic pesticides can be directly intercalated into the interlayer of HTlc by anion exchange,²⁴ coprecipitation¹⁸ and reconstruction,²⁵ while for charge-neutral pesticides, it is usually needed to modify HTlc with surfactants to form a hydrophobic region in the gallery of HTlc,^{26,27} then target pesticide molecules are intercalated into the hydrophobic region of HTlc. In this paper, a charge-neutral and poorly water-soluble pesticide, imidacloprid (IM), was chosen to synthesize the nanohybrids (IM-SDS-HTlc) of IM and sodium dodecyl sulfate (SDS) modified HTlc. According to our previous work, in water medium IM could not be effectively intercalated into the gallery of SDS modified HTlc (SDS-HTlc), the loading amount of IM in modified HTlc was too low, which may be due to the too low solubility of IM in water. In order to increase the solubility of IM in the intercalating medium, toluene-ethanol mixed organic solvent was chosen as the intercalating

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medium. In addition, a new method, enhanced intercalation by evaporating solvent (ethanol), was carried out in order to raise the loading amounts of IM in the nanohybrids. The release behavior of IM from the nanohybrids was investigated, demonstrating that pesticide-HTlc nanohybrids are potential CRFs of pesticides.

Experimental

Materials

Imidacloprid (technical grade, 96.5% purity) used in the experiments was friendly supplied by Shandong Pesticide Institution (Jinan, China) and used as received. Its molecular structure is shown in Figure 1. It is effective for controlling aphids, whiteflies, thrips, scales, psyllids, plant bugs and other various harmful pest species including resistant strains, often used as seed dressing, soil treatment and foliar treatment in various crops. Water solubility (20 °C) is 0.5 g/L.

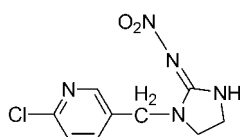


Figure 1 Molecular structure of imidacloprid.

All other chemical reagents used were of A. R. grade. Deionized water was prepared by ion exchange system.

Synthesis and characterization of modified HTlc and IM-SDS-HTlc nanohybrids

Modified HTlc Modified HTlc was synthesized by a coprecipitation method. Under stirring, 45 mL of solutions containing 0.03 mol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.015 mol of $Al(NO_3)_3 \cdot 6H_2O$ were added to 83 and 167 mL of 0.09 mol/L SDS solutions, respectively. The molar ratios ($R_{SDS/Al}$) of SDS to Al^{3+} in the two systems were 0.5 and 1, respectively. Then the coprecipitation agent, 5 mol/L NaOH solution, was added to the systems under stirring till the pH values of the systems reached 10 ± 0.2 . The mixtures were stirred for 2 d at 70 °C, and then filtrated and washed with deionized water and ethanol, respectively. The filter cakes were dried in an oven for 1 d at 80 °C to obtain modified HTlc (SDS-HTlc) samples. The two modified HTlc samples obtained with $R_{SDS/Al}$ values of 0.5 and 1 are denoted as M1 and M2, respectively, seeing Table 1.

Table 1 Loading amount and *d*-space of modified HTlc and IM-SDS-HTlc nanohybrids

Modified HTlc	$R_{SDS/Al}$	$A_{SDS}/\%$	<i>d</i> -space/ nm	Nanohybrid	$A_{IM}/\%$	<i>d</i> -space/ nm
M1	0.5	22.2	2.81	N1	45.1	2.60
M2	1	38.6	2.64	N2	45.6	2.58

IM-SDS-HTlc nanohybrids 0.2 g of the SDS-HTlc samples were added into 50 mL of toluene/ethanol

mixed solvents containing 0.6 g of imidacloprid, and the volume ratio of toluene to ethanol was 4 : 1. The suspensions were kept for 4 d at about 70 °C during mechanical agitation. During this time, ethanol was evaporated gradually. Then the suspensions were centrifuged at 3000 r/min for 20 min, and washed by ethanol once to obtain solid products. The solid products were dried at 80 °C in an oven to obtain IM-SDS-HTlc nanohybrid samples. The two IM-SDS-HTlc nanohybrid samples obtained with M1 and M2 are denoted as N1 and N2, respectively, seeing Table 1.

Characterizations The morphologies of the samples were observed by a JEM-100cxII model transmission electron microscope (TEM). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 model spectrometer in air at room temperature using KBr disc technique. Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D-5000 diffractometer, using a Cu $K\alpha$ irradiation source ($\lambda = 1.54050 \text{ \AA}$) at a scanning rate of $4 \text{ deg} \cdot \text{min}^{-1}$. Elemental chemical analyses for metals were carried out on an S/max3080E2 model X-ray fluorescent spectrometer, and for C, H, N, S on a Euro Elemental Analysis Eurovector instrument.

Loading amounts of SDS in modified HTlc and imidacloprid in IM-SDS-HTlc nanohybrids

The loading amounts of SDS in modified HTlc samples, A_{SDS} , were calculated according to the contents of C, H, S in modified HTlc.

The loading amounts of IM in IM-SDS-HTlc nanohybrids, A_{IM} , were measured by an HP-8453 model UV-Vis spectroscope using the following method.⁶ 0.05 g of the nanohybrid sample was added in 20 mL of methanol, and the suspension was ultrasonicated for 20 min and then centrifuged for 20 min under 3500 r/min. The IM concentration in supernatant was measured by monitoring the absorbance at 269 nm with UV-Vis spectroscopy to calculate the A_{IM} value. The concentration of imidacloprid was calculated by regression analysis according to the standard curve obtained from a series of standard solutions of imidacloprid in methanol.

Measurements of release amounts of imidacloprid from IM-SDS-HTlc nanohybrids

0.08 g of the nanohybrid sample was suspended in 2000 mL of deionized water or salt solution at desired temperature under magnetic stirring. The pH values of deionized water and salt solution were previously adjusted by using 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions. Aliquots (4 mL) of supernatant were taken at desired time intervals, and at the same time 4 mL of the solvent (deionized water or salt solution) were added in the system. The supernatants withdrawn were filtered through a 0.45 μm syringe filter, and the imidacloprid concentrations in supernatants were measured by monitoring the absorbance at 269 nm with UV-Vis spectroscope to obtain the release amounts (q_t) of IM from IM-SDS-HTlc nanohybrid sample, in turn to calculate

the accumulated percent releases (X_t) of IM from the nanohybrid sample. The tests were made in triplicate and the final values were an average of measurements. The X_t values of IM from the nanohybrid sample were plotted versus time (t) to examine the release rate of IM.

To compare the release rate of IM from the nanohybrids with that from the physical mixture of IM and modified HTlc, weighed IM and weighed modified HTlc were homogeneously ground, and replaced the nanohybrid samples to perform the same IM release experiments. The IM/modified HTlc ratios of physical mixtures were similar to those of IM-SDS-HTlc nanohybrids, and the two physical mixtures obtained with M1 and M2 were denoted as PM1 and PM2, respectively.

Results and discussion

Characterization of the products

Chemical composition and loading amounts of the products The chemical compositions of modified HTlc samples determined by chemical analysis are $[\text{Zn}_{0.64}\text{Al}_{0.36}(\text{OH})_2](\text{SDS})_{0.10}(\text{NO}_3)_{0.03}(\text{OH})_{0.21}$ for sample M1 and $[\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_2](\text{SDS})_{0.21}(\text{NO}_3)_{0.02}(\text{OH})_{0.12}$ for sample M2.

The A_{SDS} values of modified HTlc samples and A_{IM} values of AM-SDS-HTlc nanohybrids are listed in Table 1. As shown in Table 1, for the $R_{\text{SDS}/\text{Al}}$ values of 0.5 and 1, the A_{SDS} values of the resulting modified HTlc samples (M1 and M2) are 22.2% and 38.6%, and the A_{IM} values of the resulting IM-SDS-HTlc nanohybrid samples (N1 and N2) are 45.1% and 45.6%, respectively.

PXRD analysis Figure 2 shows the PXRD patterns of pristine HTlc, modified HTlc and IM-SDS-HTlc nanohybrids. The pristine HTlc exhibits all characteristic diffraction peaks of hydrotalcite (JCPDS card No.51-1528), showing the pristine HTlc sample is of a well-crystallized structure. The d_{003} value is the inter-layer distance (d -spacing) of the layered materials. It can be calculated from Figure 2 that the pristine HTlc has a d -spacing value of 0.89 nm. The PXRD patterns of modified HTlc are similar to those published previously.²⁸ The d -spacing values of modified HTlc samples M1 and M2 are 2.81 and 2.64 nm, respectively. The higher d -spacing values of modified HTlc samples than that of pristine HTlc indicate that SDS molecules were intercalated into the gallery of HTlc. Since the thickness of the HTlc basal layer is about 0.48 nm,²⁸ the gallery heights of modified HTlc samples M1 and M2 are about 2.33 and 2.16 nm, respectively. The length and height of SDS molecule calculated by the method of molecular mechanics²⁹ are about 2.08 and 0.42 nm, respectively. According to the gallery heights of modified HTlc samples and the size of SDS molecule, a probable morphology of SDS molecules in modified HTlc may be proposed,³⁰ as illustrated in Figure 3, where SDS molecules were intercalated into the gallery of HTlc with a

vertical-arranging monolayer. In addition, the d -spacing value of sample M1 with a lower A_{SDS} value is slightly higher than that of sample M2 with a higher A_{SDS} value, and similar result was reported previously.³¹

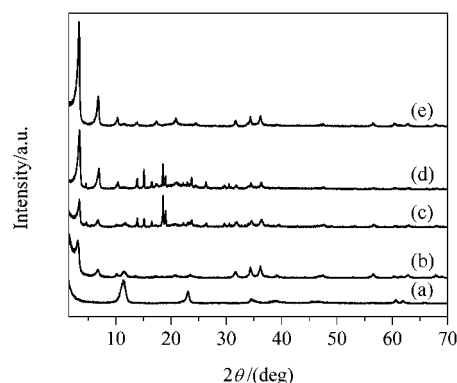


Figure 2 X-Ray diffraction patterns of (a) HTlc, (b) M1, (c) N1, (d) N2, and (e) M2.

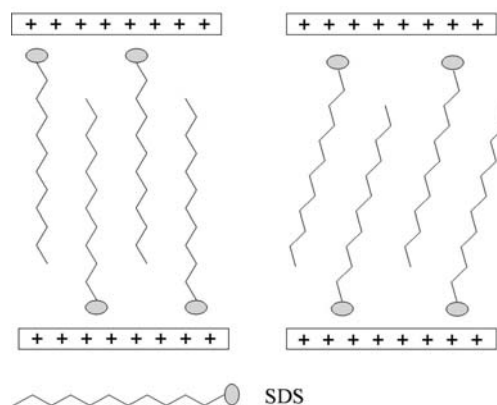


Figure 3 Schematic arrangement of SDS molecules within the HTlc interlayer.

The d -spacing values of IM-SDS-HTlc samples N1 and N2 are 2.60 and 2.58 nm, respectively. The d -spacing values of IM-SDS-HTlc nanohybrids are little lower than those of the corresponding modified HTlc samples, which is induced by the intercalation of IM molecules into the modified HTlc. The gallery heights of N1 and N2 are about 2.12 and 2.10 nm, respectively. The length, width and height of an IM molecule calculated by the method of molecular mechanics²⁹ are about 0.91, 0.65 and 0.53 nm. According to the size of an IM molecule and the gallery heights of IM-SDS-HTlc nanohybrids, it is possible that the IM molecule intercalated to the gallery of the modified HTlc.

It is needed to note that maybe not all IM molecules loaded in the nanohybrids were intercalated into the gallery of SDS-HTlc, only part of them were intercalated into the gallery of SDS-HTlc and other part of them were adsorbed on the surface of SDS-HTlc. However, we cannot yet distinguish the relative amount of the above two morphologies of IM molecules according to our available information.

FT-IR analysis The FT-IR spectra of pristine HTlc, modified HTlc, IM-SDS-HTlc nanohybrid and IM are shown in Figure 4, and the selected FT-IR data are summarized into Table 2, where it can be seen that the characteristic absorption peaks of SDS at 2956, 2919 and 2851 cm^{-1} for C—H stretch and at 1215 and 1065 cm^{-1} for S=O antisymmetry and symmetry stretches,³² respectively, appear in the spectrum of modified HTlc, indicating that SDS molecules were loaded into the pristine HTlc. The characteristic absorption peaks of IM at 1562 cm^{-1} for pyridine stretch, 1435 cm^{-1} for C=N stretch and 1102 cm^{-1} for C—Cl stretch appear in the spectrum of IM-SDS-HTlc nanohybrid,³³ indicating that IM molecules were loaded in modified HTlc.

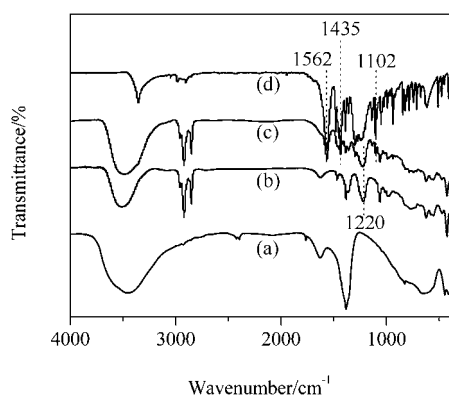


Figure 4 FT-IR spectra of (a) HTlc, (b) M1, (c) N1, and (d) technical imidacloprid.

TEM images Figure 5 shows the TEM images of pristine HTlc, modified HTlc and IM-SDS-HTlc nanohybrids. As can be seen, the pristine HTlc particles are of typical plate-like shape with the lateral size of 60–100 nm, while for modified HTlc particles and IM-SDS-HTlc nanohybrid particles, their sizes are in a range of 400–600 nm, much bigger than that of the pristine HTlc particles, indicating the modification of HTlc with

SDS and interaction with imidacloprid induced the obvious aggregations of the pristine HTlc particles.³⁴

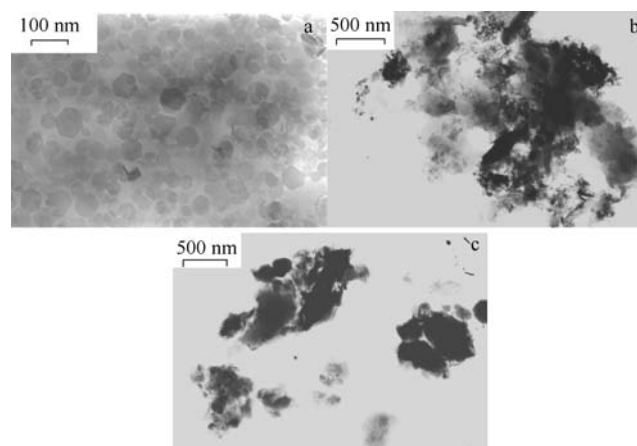


Figure 5 TEM images of (a) HTlc, (b) M1, and (c) N1.

Imidacloprid release from IM-SDS-HTlc nanohybrids

The release kinetic curves of imidacloprid from the IM-SDS-HTlc nanohybrids at pH 7.0 and 25 °C are shown in Figure 6, where it can be seen that a rapid release within the initial about 30 min is followed by a slow release of remaining pesticide, similar to the release results of other drugs from pillared HTlc described in literature.²³ Maybe the significant burst release at the beginning was induced by the release of pesticide molecules adsorbed on the surface of SDS-HTlc. The time taken for 80% (t_{80}) and total pesticide content (t_{100}) to be released from the nanohybrids, respectively, is listed in Table 3. It can be seen from Table 1 and Table 3 that the release rate of imidacloprid from the nanohybrids decreases with the increase of A_{SDS} value, which may be contributed to the interaction between imidacloprid and SDS molecules. For comparison, the release kinetics of imidacloprid from the physical mixtures was

Table 2 Summary of selected IR data (wavelength/ cm^{-1}) of pesticides and their complexes between 4000–1000 cm^{-1}

M1	N1	Imidacloprid	Assignment
<i>ca.</i> 3500	<i>ca.</i> 3500	—	OH stretch
2956, 2918, 2850	2955, 2918, 2850	2983, 2905	C—H stretch
1625	—	—	H ₂ O bend
1467	—	—	C—H bend
1383	1387	—	NO ₃ [−]
1365	1359	—	CO ₃ ^{2−}
1220	1226	—	S=O antisym.
1063	1062	—	S=O sym.
—	Very weak	3353	N—H stretch
—	—	3041	pyridine C—H stretch
—	1563	1562	pyridine
—	1435	1435	C=N stretch
—	1102	1102	pyridine C—Cl stretch

also shown in Figure 6 and Table 3. As can be seen, the release rates of imidacloprid from the nonahybrids are slower than those of imidacloprid from the physical mixtures, indicating that the nanohybrids are a potential pesticide controlled release formulation.

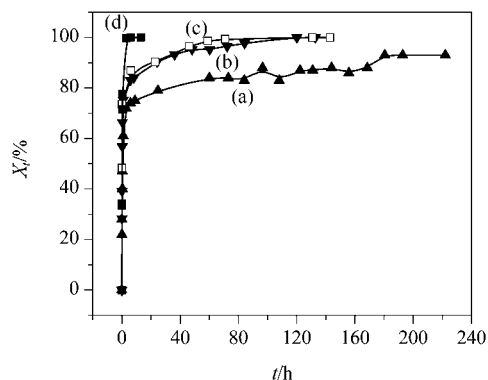


Figure 6 Release curves of nanohybrids and physical mixtures at 25 °C and pH 7.0: (a) N1, (b) N2, (c) PM1, and (d) PM2

Table 3 Release properties of nanohybrids and physical mixtures

Sample	pH	t_{80}/h	t_{100}/h	k_2/h^{-1}
Physical mixture				
PM1	7.0	3.9	131	2.2
PM2	7.0	1.1	6.1	12.6
IM-SDS-HTlc				
N1	7.0	54	385	0.72
N1	4.5	11.4	45.4	2.28
N1	9.1	11.7	101	2.16
N2	7.0	12.6	132	1.86

Effect of electrolyte on imidacloprid release

Figures 7 and 8 show the release profiles of IM from IM-SDS-HTlc nanohybrid sample N1 in the presence of electrolytes (NaCl and Na₂SO₄). As can be seen, the presence of electrolytes may slightly raise the release rate of IM from the nanohybrid, and the higher the electrolyte concentration, the higher the release rate of IM. Maybe this is because the anions of electrolytes exchange SDS out of gallery of HTlc,³⁵ inducing the higher release rate of IM.

Effect of pH on imidacloprid release

The release properties of IM from the IM-SDS-HTlc nanohybrid sample N1 at pH 4.5, 7.0 and 9.1, respectively, are shown in Figure 9, where it can be seen that the release rate of IM from the IM-SDS-HTlc nanohybrid at pH 4.5 is higher than those at pH 7.0 and 9.1, and the release rate at pH 7.0 is close to that at pH 9.1. The release rate in an acidic condition is higher than that in a basic condition, maybe this is because HTlc layers dissolve in the acidic condition.³⁶

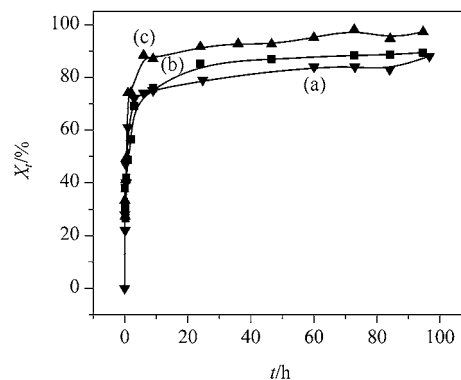


Figure 7 Release curves of N1 at 25 °C and pH 7.0 in the presence of Na₂SO₄ at (a) 0, (b) 100 and (c) 300 mg/L.

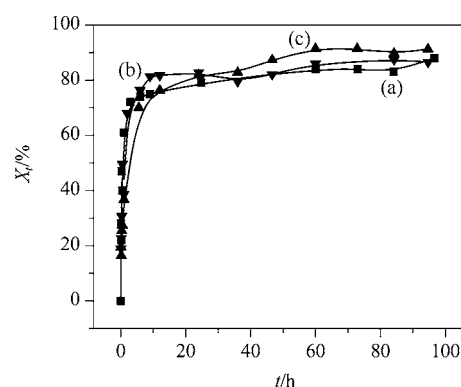


Figure 8 Release curves of N1 at 25 °C and pH 7.0 in the presence of NaCl at (a) 0, (b) 100 and (c) 300 mg/L.

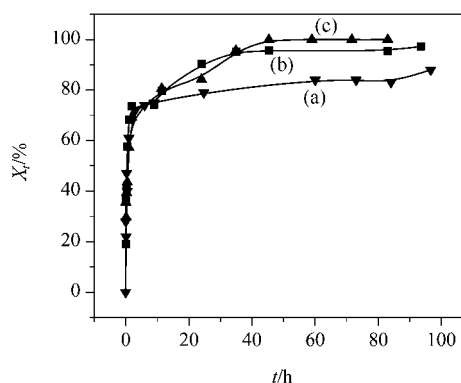


Figure 9 Release curves of nanohybrid N1 at 25 °C and different pH values: (a) 7.0, (b) 9.1, and (c) 4.5.

Release kinetics of IM from IM-SDS-HTlc nanohybrids

The kinetics of the release process can be studied by monitoring the release amount (q_t) with time (t) at constant temperature. Usually, the release process can be described with a pseudo-first-order kinetic equation or a pseudo-second-order kinetic equation.

The pseudo-first-order kinetic equation can be rep-

resented in the linear form,

$$-\ln(1-X_t)=k_1t$$

where, k_1 is the rate constant of pseudo-first-order release kinetics. If the pseudo-first-order kinetics is applicable, the plot of $-\ln(1-X_t)$ vs. t will give a linear relationship, and the k_1 value can be obtained from the slope of the linear plot.

The pseudo-second-order kinetic equation can be represented in the linear form,

$$t/X_t=1/k_2q_e+t$$

where, q_e is equilibrium release amount, and k_2 is the rate constant of pseudo-second-order release kinetics. If the pseudo-second-order kinetics is applicable, the plot of t/X_t vs. t will give a linear relationship, which allows computation of k_2 .

With the simulation of above two kinetic models for the release kinetic data, it was found that the pseudo-second-order model was satisfactory for describing the release kinetic processes of IM from the IM-SDS-HTlc nanohybrids. The typical plot of t/X_t vs. t for the release of IM from N1 sample at 20 °C and pH 7.0 is shown in Figure 10, where a fair straight line was obtained. The k_2 values obtained from straight lines are listed in Table 3. Similar results were obtained for physical mixtures and nanohybrids at other pH.

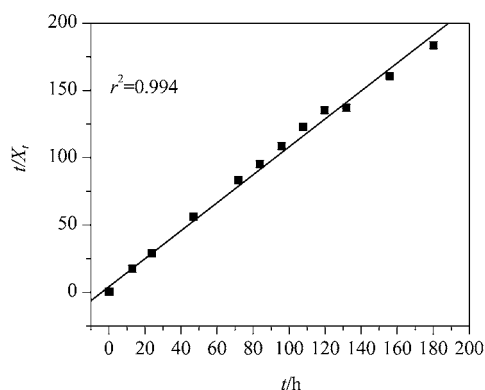


Figure 10 Linear regression curve of release data fitting with kinetic model for sample N1 at 25 °C and pH 7.0.

Conclusion

Imidacloprid molecules were successfully intercalated into the gallery of SDS modified HTlc in toluene/ethanol mixed solvent by an evaporating solvent enhanced intercalation method, forming IM-SDS-HTlc nanohybrids. The nanohybrids can better control the release of imidacloprid than the physical mixture, demonstrating the nanohybrids are a potential pesticide controlled-release formulation. Also it was found that the release rate of imidacloprid from the nanohybrids decreases with the increase of A_{SDS} value, which may be contributed to the interaction between imidacloprid and SDS molecules. The release of imidacloprid from IM-

SDS-HTlc nanohybrids is dependent on the pH and the presence of electrolyte in the release medium. Acidic medium and the presence of electrolyte may induce the higher release rate of imidacloprid. The release process of imidacloprid from IM-SDS-HTlc nanohybrids can be described by pseudo-second-order release kinetics.

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