

## Thermal-Degradation Kinetics of Neem-Alginate-Clay Based Controlled Pesticide Release Formulations

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**Abstract:** In the present study, neem-alginate-clay based controlled pesticide release formulations were characterized by thermogravimetric analysis and various kinetic and thermodynamic parameters for thermal degradation viz. Energy of activation ( $E_a$ ), Arrhenius pre-exponential factor ( $A$ ), activation entropy ( $\Delta S^*$ ), activation enthalpy ( $\Delta H^*$ ) and free activation energy ( $\Delta G^*$ ) were calculated by using integral Coats-Redfern method. Thermal degradation obeys the Jander model equation i.e.  $D_3$  (Three dimensional diffusion) solid state mechanism.

**Keywords:** Bentonite, Controlled release, Kaolin, Neem leaf, Thermal-degradation

### 1. INTRODUCTION

The pesticides have an important contribution in the modern agricultural practices and have become essential for the crop protection and pest management. These chemicals would continue to be indispensable in near future to meet the rapidly growing demand for food. Though we are fully convinced about the inevitability of these chemicals but at the same time we are also aware that these chemicals are extremely hazardous and potential pollutants of environment. Of the total applied pesticide, as little as 1% reaches the target pests and rest is lost to the environment leading to the loss of active ingredient as a consequence of various natural processes viz. degradation (photolytic, hydrolytic and microbial), volatilization, evaporation and leaching [1]. The net result is the decrease in the efficacy of pesticide chemical. This can be compensated by increasing the frequency and dose of application which again aggravate environmental, ecological and economical problems. In addition, these chemicals also enter into food chain which is of particular concern to human health. These chemicals are reported to cause carcinogenic, mutagenic, reproductive effects and also affect various developmental processes [2, 3]. This, therefore, calls to promote safe and effective use of pesticides with a view to maximize crop protection and production vis-à-vis minimizing environmental pollution and human health hazards.

The controlled pesticide release formulations are superior to conventional formulations in extending activity of active ingredient [4], preventing agro-environmental pollution by reducing leaching [5] and volatilization [6], minimizing residues on food stuffs, reducing health hazards and easing handling [7]. Polymers have attained special importance in the development of controlled pesticide release formulations by providing slow release profile of active ingredient [8, 9]. These formulations also increase the water holding capacity of soil and can act as water management materials for agricultural applications [10]. Alginate, a naturally occurring polysaccharide, has been used as controlled release formulations after ionotropic gelation with metal ions [11-13]. Neem is a wide spectrum pesticide and is reported to possess insecticidal, insect repellent, antifeedant, growth regulator, nematocidal and antifungal properties and is highly exploited tree among the present flora of pesticidal importance [14, 15]. The ionotropic gelation of alginate in the presence of neem leaf powder (NLP) will not only modify the formulation characteristics of controlled release system but also increase the potential of these systems due to its inherent pesticidal activity. At the same time clay minerals have large propensity for adsorbing and immobilizing these pesticidal chemicals and can be added to the

formulations to modify and enhancing the slow release of active ingredient [16]. In our earlier studies, the novel controlled pesticide release formulations were prepared by combining alginate with NLP and clays (kaolin and bentonite) [17, 18]. The release of thiram fungicide was studied from these beads and it has been observed to occur in very controlled and sustained manner, which is the primary requisite for the use of agrochemicals to control the environment, ecosystem and health hazards. Hence, these polymeric beads may be utilized for the safe handling of pesticide, to reduce their toxic effects, and to make their better delivery [17, 18].

Stability of polymer matrix in terms of mechanism(s) of pyrolysis reaction provides valuable information about the time and condition of storage and various applications at different temperatures. The knowledge of such parameters calculated from Arrhenius equation is essential not only in present case but also for energetic materials and for association of later with other component to elucidate miscibility/compatibility and its effects on thermal stability [19]. In the present work kinetics of thermal degradation has been discussed from the non-isothermal TG/DTG data which may be useful to the other workers for processing and other application. The various kinetic and thermodynamic parameters viz. Energy of activation ( $E^*$ ), Arrhenius pre-exponential factor ( $A$ ), activation entropy ( $\Delta S^*$ ), activation enthalpy ( $\Delta H^*$ ) and free activation energy ( $\Delta G^*$ ) were calculated by using integral Coats-Redfern method. The most probable mechanism for thermal degradation of each sample has also been evaluated.

## 2. MATERIALS AND METHOD

Bentonite, methanol and sodium hydroxide were obtained from Merck-Schuchardt, Germany. Kaolin, sodium alginate and 4-aminoacetophenone were obtained from Loba Chemie Pvt. Ltd., India. Neem leaf powder (NLP) was obtained by grinding dry neem leaves collected from Bilaspur District of Himachal Pradesh, India.

### *Synthesis of NLP-Alginate-clay beads*

The measured amount of NLP, alginate and clay (kaolin and bentonite) were dispersed in 25 mL hot water and stirred for 15 minutes to form homogenous solution. This homogeneous solution then was added drop wise, by using 50 mL syringe (needle size 1.2 mm) from 15 cm height, into 100 mL of  $CaCl_2$  solution (0.1M) under constant stirring. The beads thus formed were removed from  $CaCl_2$  solution after 30 minutes and washed with distilled water and were allowed to dry at room temperature. The reaction parameters for the synthesis of beads and the formulations characteristics such as bead diameter and amount of beads formed are presented in Table 1. Fifteen completely dried beads from each formulation were taken and their size was measured by using 12 Cm Vernier Calipers. The average bead size of each formulation is presented in Table 1.

**Table 1.** Reaction parameters and formulation characteristics of NLP-alginate-clay beads

Formulation code	NLP (% w/v)	Alginate (% w/v)	Kaolin (% w/v)	Bentonite (% w/v)	[ $CaCl_2$ ] (M)	Beads formed (g)	Bead diameter (mm)
A	-	2.5	-	-	0.1	0.93	0.65±0.14
NA	1.5	2.5	-	-	0.1	1.39	0.91±0.13
NAK	1.5	2.5	4	-	0.1	2.07	1.13±0.16
NAB	1.5	2.5	-	4	0.1	2.07	1.12±0.11

### *Thermal analysis*

Thermogravimetric analysis was carried out on a Perkin Elmer (Pyris Diamond) Thermal Analyzer in air at a heating rate of 20 °C/min to examine the thermal properties of the samples. The various kinetic and thermodynamic parameters viz. Energy of activation ( $E_a$ ), Arrhenius pre-exponential factor ( $A$ ), activation entropy ( $\Delta S^*$ ), activation enthalpy ( $\Delta H^*$ ) and free activation energy ( $\Delta G^*$ ) for the thermal decomposition of samples were obtained from the non-isothermal data of samples by using integral Coats-Redfern method [20].

### *Theoretical analysis*

In a decomposition reaction, the progress of reaction is defined by the degree of dissociation ( $\alpha$ ) which can be expressed in terms of mass loss as [21]

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (I)$$

Where  $W_0$  = initial weight,  $W$  = actual weight at each point of curve and  $W_\infty$  = final weight or weight of residue measured at the end of degradation process.

The rate of reaction in terms of degree of dissociation ( $\alpha$ ) is written as

$$\text{rate} = \frac{d\alpha}{dt}$$

According to Arrhenius equation, this rate of reaction i.e. degradation/conversion is given by

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (II)$$

Where  $t$  = time,  $A$  = Arrhenius pre-exponential factor,  $E_a$  = Energy of activation,  $T$  = absolute temperature,  $R$  = gas constant and  $f(\alpha)$  = differential conversion function.

The rate of degradation can be measured as a function of time 't' at constant temperature (isothermal method) or as a function of temperature 'T' at linear heating rate (non-isothermal method/ dynamic mode). The non-isothermal runs are more convenient to carry out as compared to isothermal TGA experiments because it is not necessary to perform a sudden jump of the sample at beginning [22].

For dynamic data obtained at constant heating rate,  $\beta = \frac{dT}{dt}$ , the equation (II) is given as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (III)$$

The temperature integral  $g(\alpha)$  is obtained by integrating the rate equation (III) under non-isothermal conditions and then reordering it as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-(E_a/RT)} dT \quad (IV)$$

Coats and Redfern used some approximations to solve equation (IV) as

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (V)$$

By considering that  $2RT/E_a \ll 1$ , the equation (V) can be written as

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E_a} \right] - \frac{E_a}{RT} \quad (VI)$$

The algebraic expressions of  $f(\alpha)$  and  $g(\alpha)$  corresponding to different degradation processes or mechanistic models of thermal decomposition is presented in Table 2 [21, 23]. The plot of  $\ln \frac{g(\alpha)}{T^2}$

Vs  $\frac{1}{T}$  for every  $g(\alpha)$  (given in Table 2) results into a straight line of slope  $\left( \frac{-E_a}{R} \right)$  and intercept

$\left( \ln \left[ \frac{AR}{\beta E_a} \right] \right)$ . From slope and intercept the kinetic parameters viz. Energy of activation ( $E_a$ ) and

Arrhenius pre-exponential factor ( $A$ ) can be calculated. The most probable kinetic model for the thermal degradation is the one which gives the best straight line through points i.e. with higher value of correlation coefficient. The thermodynamic parameters viz. activation entropy ( $\Delta S^*$ ), activation

enthalpy ( $\Delta H^*$ ) and free activation energy ( $\Delta G^*$ ) can be calculated by applying general thermodynamic equations [24] as

$$\Delta H^* = E_a - RT \tag{VII}$$

$$\Delta S^* = R \left\{ \ln \frac{hA}{kT} - 1 \right\} \tag{VIII}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{IX}$$

Where R is gas constant, h is Plank constant, T is DTA peak temperature and k is Boltzman constant.

**Table 2.** Algebraic expression for  $f(\alpha)$  and  $g(\alpha)$  for the most frequently used kinetic models of solid state process [21, 23].

Symbol	$f(\alpha)$	$g(\alpha)$	Solid-state process
D <sub>1</sub>	$1/2 \alpha$	$\alpha^2$	One dimensional diffusion (parabolic)
D <sub>2</sub>	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$	Two dimensional diffusion
D <sub>3</sub>	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$	Three dimensional diffusion (Jander equation)
D <sub>4</sub>	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	Three dimensional diffusion (Ginstling-Brounshtein)
F <sub>1</sub>	$(1-\alpha)$	$-\ln(1-\alpha)$	First order (Mampel)
R <sub>2</sub>	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$	Phase-boundary controlled reaction (contracting area i.e. bidimensional shape)
R <sub>3</sub>	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$	Phase-boundary controlled reaction (contracting volume i.e. tridimensional shape)

### 3. RESULTS AND DISCUSSION

The reaction parameters for the synthesis of various beads formulations and their characteristics (viz. bead diameter, amount of beads formed and entrapment efficiency (%)) are presented in Table 1. The yield and size of the beads increased with increase in clay contents in the NLP-alginate-clay beads. The beads were almost spherical in shape and their diameters varied from (0.65±0.14) mm to (1.13±0.16) mm in different formulations (Table 1).

The non-isothermal thermogravimetric (TG) and differential thermogravimetric (DTG) of NLP, sodium alginate, Ca<sup>2+</sup>-alginate beads, NLP-alginate beads, NLP-alginate-kaolin beads and NLP-alginate-bentonite beads have been discussed elsewhere [17-18]. The data on initial decomposition temperature (T<sub>0</sub>), final decomposition temperature (T<sub>f</sub>), final residues left at T<sub>f</sub> and temperatures of maximum rate of weight loss (T<sub>max</sub>) are shown in Table 3. Initial decomposition temperature (T<sub>0</sub>) is corresponding to the first detectable temperature at which the degradation of the material starts and has been considered after the initial loss of physically absorbed water and structural water (dehydration reactions) [25]. From non-isothermal TG/DTG data, the degradation mechanism and thermal kinetics were evaluated by applying seven kinetic degradation models and the results are presented in Table 4. The high values of the activation energies reflect the thermal stability of the beads. In general, more is the value of activation energy, greater is the thermal stability of sample [26-28]. From table it is clear that NLP-alginate-clay bead formulations have high activation energy among others and therefore incorporation of clay (kaolin and bentonite) in NLP-alginate beads resulted into higher thermal stability. This can be attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix [29]. The entropy of activation was found to have negative values for all the samples, which indicates that all the samples are more ordered in activated state and the decomposition reactions proceed at a lower rate [26, 27]. The positive value of free activation energy ( $\Delta G^*$ ) and activation enthalpy ( $\Delta H^*$ ) indicates the non-spontaneous and endothermic nature of reaction [28]. The analysis of the solid-state processes mechanism of all the samples with the Coats-Redfern method showed that the kinetic model function of thermal degradation obeys the Jander model equation i.e. D<sub>3</sub> (Three dimensional diffusion) solid state mechanism with  $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$ .

**Table 3.** Thermogravimetric analysis of NLP, sodium alginate, Ca<sup>2+</sup>-alginate beads, NLP-alginate beads, NLP-alginate-kaolin beads, NLP-alginate-bentonite beads.

Sample	T <sub>0</sub> (°C)	T <sub>max</sub> (°C)	T <sub>r</sub> (°C)	Residue (%)
NLP	227	430	489	10.75
Sodium alginate	217	265	578	23.28
Calcium alginate	198	290	787	29.34
NLP-alginate	217	293	791	20.91
NLP-alginate-kaolin	244	519	540	53.64
NLP-alginate-bentonite	232	502	548	51.37

**Table 4.** Kinetic and thermodynamic parameters from thermal degradation.

NLP								
Models	M	c	r	E <sub>a</sub> (KJ/mol)	A (s <sup>-1</sup> )	ΔH* (KJ/mol)	ΔS* (J/K/mol)	ΔG* (KJ/mol)
D <sub>1</sub>	-3824.11	-8.00	-0.944	31.79	6.243	25.95	-236.81	192.43
D <sub>2</sub>	-4414.03	-7.48	-0.959	36.70	12.148	30.85	-231.28	193.44
<b>D<sub>3</sub></b>	<b>-5147.08</b>	<b>-7.50</b>	<b>-0.972</b>	<b>42.79</b>	<b>13.919</b>	<b>36.95</b>	<b>-230.14</b>	<b>198.74</b>
D <sub>4</sub>	-4655.84	-8.49	-0.964	38.71	4.652	32.86	-239.26	201.06
F <sub>1</sub>	-2364.90	-9.27	-0.967	19.66	1.093	13.82	-251.30	190.48
R <sub>2</sub>	-1793.03	-11.11	-0.937	14.91	0.130	9.06	-268.98	198.15
R <sub>3</sub>	-1973.30	-11.15	-0.949	16.41	0.138	10.56	-268.51	199.32
Sodium alginate								
D <sub>1</sub>	-951.87	-12.17	-0.493	7.91	0.024	3.44	-280.82	154.52
D <sub>2</sub>	-1327.22	-11.92	-0.585	11.03	0.043	6.56	-275.93	155.01
<b>D<sub>3</sub></b>	<b>-1829.12</b>	<b>-12.20</b>	<b>-0.671</b>	<b>15.21</b>	<b>0.045</b>	<b>10.73</b>	<b>-275.63</b>	<b>159.02</b>
D <sub>4</sub>	-1491.76	-13.02	-0.617	12.40	0.016	7.93	-284.13	160.79
F <sub>1</sub>	-567.40	-11.79	-0.446	4.72	0.021	0.24	-281.92	151.92
R <sub>2</sub>	-169.59	-13.44	-0.167	1.41	0.001	-3.06	-305.70	161.40
R <sub>3</sub>	-292.70	-13.55	-0.269	2.43	0.002	-2.04	-302.04	160.46
Calcium alginate beads								
D <sub>1</sub>	-1414.50	-12.08	-0.782	11.76	0.039	7.08	-277.11	163.09
D <sub>2</sub>	-1846.14	-11.81	-0.857	15.35	0.067	10.67	-272.63	164.16
<b>D<sub>3</sub></b>	<b>-2448.21</b>	<b>-12.02</b>	<b>-0.921</b>	<b>20.35</b>	<b>0.072</b>	<b>15.67</b>	<b>-272.05</b>	<b>168.84</b>
D <sub>4</sub>	-2041.99	-12.89	-0.883	16.98	0.025	12.30	-280.79	170.38
F <sub>1</sub>	-895.28	-11.73	-0.857	7.44	0.035	2.76	-278.00	159.27
R <sub>2</sub>	-410.37	-13.45	-0.565	3.41	0.003	-1.27	-298.82	166.97
R <sub>3</sub>	-558.29	-13.54	-0.693	4.64	0.004	-0.39	-296.99	167.17
NLP-alginate beads								
D <sub>1</sub>	-736.60	-13.01	-0.676	6.12	0.008	1.42	-290.30	165.73
D <sub>2</sub>	-1111.76	-12.83	-0.810	9.24	0.014	4.54	-285.45	166.10
<b>D<sub>3</sub></b>	<b>-1625.58</b>	<b>-13.21</b>	<b>-0.902</b>	<b>13.52</b>	<b>0.015</b>	<b>8.81</b>	<b>-285.40</b>	<b>170.35</b>
D <sub>4</sub>	-1279.57	-13.97	-0.849	10.64	0.005	5.93	-293.70	172.17
F <sub>1</sub>	-414.68	-12.44	-0.691	3.45	0.008	-1.26	-290.39	163.10
R <sub>2</sub>	-4.11	-14.03	-0.009	0.34	0.000	-4.67	-341.95	188.87
R <sub>3</sub>	-130.21	-14.16	-0.279	1.08	0.001	-3.62	-314.28	174.26
NLP-alginate-kaolin beads								
D <sub>1</sub>	-1349.36	-11.85	-0.813	11.22	0.047	4.63	-278.44	225.16
D <sub>2</sub>	-1756.38	-11.62	-0.866	14.60	0.077	8.02	-274.36	225.31
<b>D<sub>3</sub></b>	<b>-2271.05</b>	<b>-12.00</b>	<b>-0.907</b>	<b>18.88</b>	<b>0.068</b>	<b>12.30</b>	<b>-275.35</b>	<b>230.38</b>
D <sub>4</sub>	-1926.11	-12.75	-0.882	16.01	0.027	9.43	-283.00	233.57
F <sub>1</sub>	-782.39	-11.75	-0.804	6.50	0.030	-0.80	-282.18	223.41
R <sub>2</sub>	-380.13	-13.32	-0.568	3.16	0.003	-3.42	-301.23	235.15
R <sub>3</sub>	-506.50	-13.45	-0.670	4.21	0.004	-2.37	-299.91	235.16
NLP-alginate-bentonite beads								
D <sub>1</sub>	-1709.98	-11.34	-0.918	14.22	0.099	7.77	-272.03	218.60
D <sub>2</sub>	-2170.49	-11.03	-0.946	18.05	0.172	11.60	-267.47	218.89
<b>D<sub>3</sub></b>	<b>-2764.97</b>	<b>-11.27</b>	<b>-0.965</b>	<b>22.99</b>	<b>0.172</b>	<b>16.54</b>	<b>-267.51</b>	<b>223.86</b>
D <sub>4</sub>	-2366.00	-12.12	-0.954	19.67	0.063	13.23	-275.81	226.98
F <sub>1</sub>	-1080.85	-11.31	-0.932	8.99	0.065	2.54	-275.61	216.14
R <sub>2</sub>	-613.32	-12.99	-0.838	5.10	0.007	-1.34	-294.26	226.71
R <sub>3</sub>	-759.29	-13.08	-0.884	6.31	0.008	-1.31	-293.29	227.17

Where m= slope; c=intercept and r=correlation coefficient

#### 4. CONCLUSION

The various kinetic and thermodynamic parameters for thermal degradation of bead formulations have been evaluated by using integral Coats-Redfern method. The values activation energy ( $E_a$ ) for NLP-alginate-clay beads were found to be higher than other bead formulations suggesting that incorporation of clays in NLP-alginate beads has increased the thermal stability of formulations. The thermal degradation for all samples obey the Jander model equation i.e.  $D_3$  (Three dimensional diffusion) solid state mechanism with  $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$ . The values of thermodynamic parameters  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  showed the endothermic and non spontaneous nature of the process.

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