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Adsorption of amitraz on the clay

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Abstract : Amitraz (AZ) that is used as acaridies was tried to extract with a clay. The experimental data were modelled as using Langmuir and Freundlich isotherms. The adsorption data fit well with Langmuir isotherm that indicated the AZ adsorption is homogeneous and monolayer. The monolayer adsorption capacity was found to be 35.02 mg/g at 20 ºC temperature. Effect of the phases contact time, the initial solution pH and the initial pesticide concentration were investigated from the point of adsorption equilibrium and yield. The adsorption kinetics were investigated by applying pseudo first order, pseudo second order and intra particle diffusion laws. Adsorption of AZ was found to be best fitted by the pseudo second order model. The intra particle diffusion also plays an important role in adsorption phenomenon.

Key words: Adsorption, amitraz, clay, pesticide

I. INTRODUCT□ON

Pesticides have advantage from the point of controlling insects, disease and weeds in crops and postures and also disadvantage of causing serious problems in water quality. Once a pesticide is applied to crops, several processes may be observed. It may be taken up by plants and/or ingested by animals, insects, worms or microorganisms in the soil; it may downward in the soil and adhere to soil particles, or it may dissolve, it may volatilize; it may be broken down into less toxic compounds; it may be leached or moved out of the plants' root zone by rain or irrigation water; or it may be carried away by run off water or erosion (Amin and Jayson, 1996, Chen et al., 2004).

Pesticides are detected world wide in surface and ground water in agricultural areas, especially in North America and Europe (Pickon et al., 1998); http;//comwinchen...2013; Senseman et al., 1997).

Amitraz is the most used acaricide as commercial formulation. The molecular formula and weight of Amitraz is $C_{19}H_{23}N_3$ and 293.41 gram per mole. The chemical name of it is 1,5-Di (2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene; Methyl-bis(2,4xylyliminomethyl) amine. It is a white to buff crystalline powder

Clays are the main components of the mineral fraction of soils. They are effective natural adsorbents due to their small particle sizes, lamellar structures and negatively charged surfaces, with make them good cation adsorbents with large reactive surface areas for ion exchange or electrostatic attraction (Tsai et al., 2003).

Anionic clays also called layered double hydroxides (LDH) or hydrotalcites (HT) are natural or synthetic materials containing magnesium (II) hydroxide by Al(III). The net positive charge is compensated with hydrated inorganic or organic anions in the interlayer (De Roy et al., 1992; Rives and Ulibarri, 1999). These anionic clays can be represented by the general firmula.:
$[M_{1-x}^{II} M_x^{III}(OH)_2]^{x+}[X^{m-}_{x/m}nH_2O]^{x-}$, abbreviated as $[M_{II}M_{III}\text{-}X]$ where M_{II}: Mg^{2+}, Mn^{2+}, Zn^{2+}..., $M_{III}=Al^{3+}$, Fe^{3+}, Cr^{3+}... and $X=CO_3^{2-}$, Cl^-, NO_3^-...

Anionic clay structure (Chibue and Jones, 1989); Meyn et al., 1990) results in their ability to be used as suitable materails for adsorption of anionic contaminants from water. They can be used for removal of inorganic anions (Nethravathi et al., 2011), phenolic compounds (Liotta et al., 2009), surfactants (Lin et al., 2009) or pesticides (Inacio et al., 2001, Gülen et al., 2012).

The aim of this study was to use clay for removal of amitraz. Several factors that effecting the adsorption ability of clay were also tested.

II. MATER□ALS AND METHODS

II.1 Adsorbate Characterization

The amitraz (AZ) used in this study was supplied by Hektaş AŞ, in Turkey. Amitraz is a non-systemic acaricide and insecticide. Amitraz has been found to have an insect repellent effect, works as an insecticide and also as a pesticide synergist. It's effectiveness is traced back on alpha-adrenergic agonist activity, interaction with octopamine receptors of the central nervous system and inhibition of monoamine oxidases and prostaglandin synthesis. Therefore it leads to overexcitation and consequently paralysis and death in insects. Because amitraz is less harmful to mammals, amitraz is among many other purposes best known as insecticide against mite- or tick-infestation of dogs. Pestiside stock solution was prepared by dissolving 0.01 g amitraz in 100 ml distilled water. The chemical formula is given in Fig 1. Its characteristics are listed in Table 1 (http://en.wikipedia.org 2013).

II.2 Adsorbent Characterization

The clay belongs to Bartın area of Black Sea region of Turkey. The chemical characteristics are given in Table 2.

II.3 Adsorption Experiment

The adsorption experiments were carried out in batch system and the adsorbent amount was kept constant as 0.1 g in the experiments. Amitraz solutions with the amount of 20 ml each were prepared at several concentrations of 1, 2, 3, 4 and 5 mg/L in an erlenmeyer flask. The adsorption test was conducted by adding 0.1 g clay in each of the flasks. Initial solution pH was adjusted to desired pH. 0.1 M HCl and 0.1 M NaOH were used to adjust the AZ-Clay system to the desired pH. The flasks were then inserted in a thermostath shaker (Nüve ST402) set at 250 rpm with temperature of 20 ºC. At the end of the predetermined time intervals, the samples were centrifuged at 4000 rpm for 5 min. Changes in the concentration readings of the mixture were analyzed every 30 minutes using ATI UNICAM UV/VIS Spectrophotometer. The adsorption wavelength of the AZ was obtained at 245 nm from the first derivetive absorption spectra. The absorbance-concentration relationship was y = 0.5171x+0.024 (R^2=0.9884).

II.4 Equilibrium studies

For the adsorption experiments, a 5 ml stock solution was diluted to 40 ml with distilled water. An 3 ml aqueous solution was diluted to 20 ml again. The concentration of the pesticide solution was 2 mgL^{-1} (2 ppm). The amount of adsorption at equilibrium, q_e(mg/g) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where,

C_o (mg/L) and C_e (mg/L) are liquid phase pesticide concentrations at initially and at equilibrium, respectively.

V is the volume of the pesticide solution (L) and

W is the mass of adsorbent (g)

II.5 Kinetic studies

The amount of adsorption at time t, q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where,

C_o (mg/L) and C_t (mg/L) are pesticide concentrations (mg/L) at the beginning and at t time

V is the volume of the pesticide solution (L)

W is the mass of adsorbent (g).

II.6 Effect of initial solution pH

The pH value of the initial experimental solution was 5. The effect of pH on removal of amitraz was studied by varying the pH of the medium from 2.5 to 11 (pH values are 2.5, 3.5, 5, 7, 9, 11). The measurements were performed using WTW series inolab meter. An adsorbent (0.1 g) was added to each samples. After 3 hours, the adsorbance equilibrium values were measured by UV spectrometer. The experiments were performed at temperatures of 20 ºC.

II.7 Effect of initial pesticide concentration

Initial pesticide concentration is one of the important factors that affect adsorption kinetics. The effect of initial AZ concentration on clay was studied at different initial concentrations (5, 10, 15, 20 mgL^{-1}) at 20 ºC. The experiments were performed at fixed adsorbent dose (0.1 g), initial solution pH (pH=4) (due to the maximum adsorption yield) and phases contact time (3 h).

II.8 Adsorption isotherms

Experimental data were modelled using some isotherms such as Langmuir, Freundlich. The Langmuir equation (Kadirvelu et al., 2003; İmamoğlu and Tekir, 2008) is in the linear form,

$$\frac{C_e}{x/m} = \frac{1}{K.X_m} + \left(\frac{1}{X_m}\right)C_e$$

where x/m represents the amount of pesticide ions adsorbed at equilibrium, C_e is the equilibrium concentrations, X_m and K are Langmuir constants related to maximum adsorption capacity (mono layer capacity) and energy of adsorption, respectively (Machido et al., 2005).

The Langmuir isotherm can be defined as dimensionless constant separation factor R_L by

$$R_L = \frac{1}{1+K.Co}$$

K= the Langmuir constant
C_o=the highest pesticide concentration (mg/L)
The values of R_L

$R_L>1$	The adsorption is unfavorable
$R_L=1$	The adsorption is linear
$0<R_L<1$	Adsorption is favorable
$R_L=0$	Adsorption is irreversible

The Freundlich equation (Kalavathy et al., 2005; Liang et al., 2006) is in the linearised form,

$$\log\frac{x}{m} = \log k + n.\log C_e$$

where x/m is the amount of pesticide ions adsorbed at equilibrium, C_e is the equilibrium concentrations, k and n are Freundlich constants concerning the multilayer adsorption capacity and adsorption intensity, respectively (Rao et al., 2006; Machido et al., 2005).

II.9 Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of amitraz adsorption on the clay were analyzed using pseudo first order (Lagergren, 1898), pseudo second order (Ho et al., 2000) and intra particle diffusion (Yue et al., 2007) kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close to or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of amitraz adsorption.

The pseudo first order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where
q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g)
k_1 is the rate constant of pseudo first order adsorption (l/min^{-1})
After integration and applying boundary conditions t=0 to t=t and q_1=0 to q_t=q_e, the integrated form of Eq becomes

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$

The values of log (q_e-q_0) were linearly correlated with t. The plot of log (q_e-q_0) vs t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The pseudosecond order adsorption kinetic rate equation is expressed as (Ho et al., 2000)

$$\frac{dq_t}{dt} = k_2(q_e - q_1)^2$$

where

k_2 is the rate constant of pseudo second order adsorption (g/mg.min)

For the boundary conditions t=0 to t=t and q_1=0 to q_t=q_e, the integrated form of Eq becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt$$

which is the integrated rate law for a pseudo second order reaction. Equation can be rearranged to obtain Eq which has a linear form.

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$$

The intra particle diffusion model is expressed (Yue et al., 2007)

$$R = k_{id}(t)^2$$

A linearised form of the equation is followed by

log R=log k_{id} +alog(t)

where

R is the percent of pesticide adsorbed

t is the contact time (h)

a is the gradient of linear plots

k_{id} is the intra particle diffusion rate constant (h^{-1})

A depicts the adsorption mechanism, k_{id} may be taken as a rate factor, ie percent pesticide adsorbed per unit time.

III. RESULTS AND DISCUSSION

III.1 Effect of contact time

For the adsorption process, the experiments were carried out for different contact times with a fixed adsorbent dose of 0.1 g with the 2 mg/L concentration at 20 ºC. Fig 2 shows the relationships between equilibrium concentration and time at 20 ºC temperature and Fig 3 shows the adsorption capacity as a function of time. As it can be seen from Fig 2, the experiment became constant in 3 hours. q_t was determined from the formula given before. 58 % adsorption capacity was established in 1 hour of contact, 82 % of pesticide removal was achieved at the end of adsorption in 3 hours (Fig 3).

III.2 Effect of pH

The effect of pH is shown in Figure 4 in term of uptake % - pH.

Uptake % was determined from the formula given below.

$$Uptake\% = \frac{C_0 - C_e}{C_0} x100$$

C_0 = initial concentration (mg/L)

C_e = equilibrium concentration (mg/L)

The adsorption percent were 17 and 23 % at 2.5 pH value increased to 37.5 % at 3.5 pH value. The acidic region (2.5-5) gave approximately about 29 and 45 % absorbance. This high values can be affected by the acidic character of pesticide and anionic structure of clay. The uptake values were found as 14 % at pH 11 for 20 ºC.

III.3 Effect of pesticide concentration

The results of pesticide concentration effect are shown on Fig.5. The increase in the pesticide concentration over 20 ppm did not affect the adsorption capacity significantly.

III.4 Adsorption isotherms

The graphics and the constants of Langmuir and Freundlich isotherm models are given in Fig. 6, 7 and Table 3, respectively. The experimental values conform to the Langmuir equation with respect to the low correlation value of the Freundlich equation as seen in Table 3. The process is a monolayer process based on the Langmuir isotherm model. The amount of R_L was calculated to as 0.24. That shows us Langmuir adsorption was favorable.

III.5 Adsorption dynamics

The kinetic graphics are given in Fig. 8, 9 and 10. The pseudo fisrst order, second order and intra particle rate coefficients were calculated. The values of k_{id} were calculated from the slope of such plots and the R^2 values led to the conclusion that the intra particle dissusion is the rate limiting step. Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger k_{id} values illustrate a better adsorption mechanism, which is related to an improved bonding between pesticide ions and the adsorbent particles (Table 4).

IV. CONCLUSIONS

The amitraz, a kind of acaricide was extracted with a clay adsorbent. Adsorption tests were carried out as a function of contact time, pH, pesticide concentration at fixed adsorbent dose. The adsorption completed in 3 hours. Removal of pesticide % was almost 40 % in the first hour and at the end of process the yield increased to 60 %. pH was effective for amitraz removal. The percentage of removal increased with the increasing concentration of pesticide in the solution. The fitness of the adsorption data onto Langmuir isotherm confirmed the monolayer adsorption due to the high correlation coefficient. The monolayer capacity was found as 35 mg/g. The results show us that pseudo second order kinetics was managed the process. Intra particle diffusion played an important role in the whole process. Given the facts that clay is ecofriendly and low cost, and it has a satisfying adsorption efficiency.

V. ACKNOWLEDGEMENTS

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Table 1. Chemical characteristics of Amitraz

Chemical name	[N-di-(2,4-ksiliminometil)metilamin]
Molecular formula	$C_{19}H_{23}N_3$
Molecular weight	293.4 g/mol
Melting point	86–87 ºC

Table 2. Chemical composition of clay

Compo.	B_2O_3	SO_4^{2-}	CaO	Na_2O	SiO_2	MgO	SrO	Al_2O_3	Fe_2O_3	Heatloss
Weight%	14	2	13.53	6.87	13.8	11.8	1.15	0.94	0.35	35.75

Table 3. Langmuir ve Freundlich isoterm constants at 20 ºC.

İsoterm tipi	Constants		R^2	Q_{max}(mg/g)
Freundlich isotherm	n = -1.2558	k = 3.9343	0.936	3.93
Langmuir isotherm	X_M = 0.029	K = -4.656	0.956	35.02

Table 4. Kinetic rate constants of adsorption dynamics

		R^2	q_e mg/g
k_1 (min^{-1})	**0.89**	**0.94**	**724.44**
k_2 ($g.mg^{-1}min^{-1}$)	**17.01**	**0,98**	**0.096**
k □d	**1.06**	**0.97**	

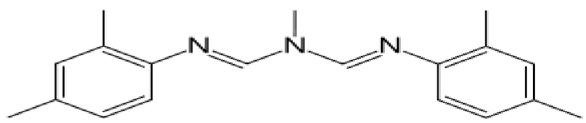

Fig.1 **Chemical structure of** Amitraz molecule

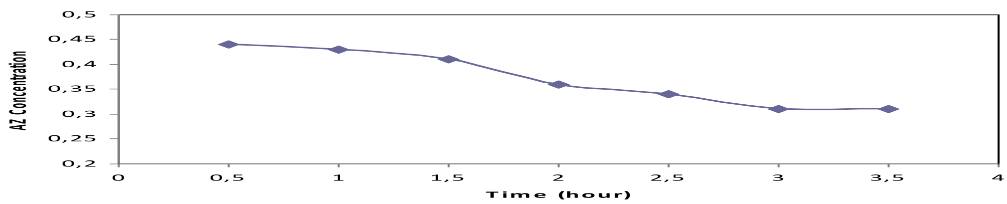

Fig 2. AZ Concentation vs time relationship T=20 ºC (clay dose= 0.1 g, C_{AZ}=2 mg/L, pH=5)

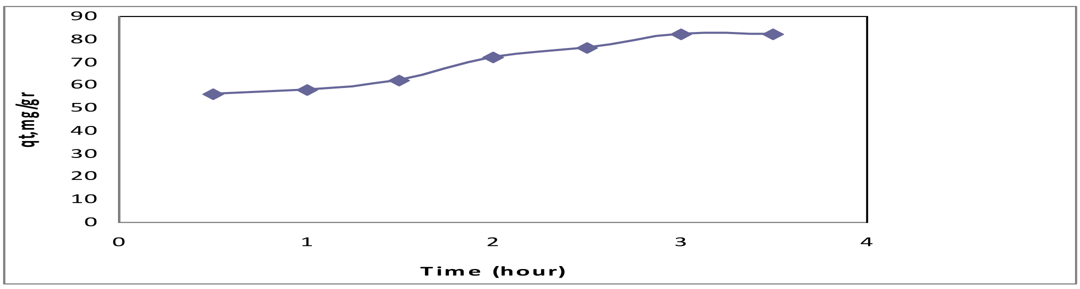

Fig 3. q_t(mg/g) vs time relationship (clay dose 0.1 g, C_{AZ}= 2mg/L, pH=5, T=20 °C)

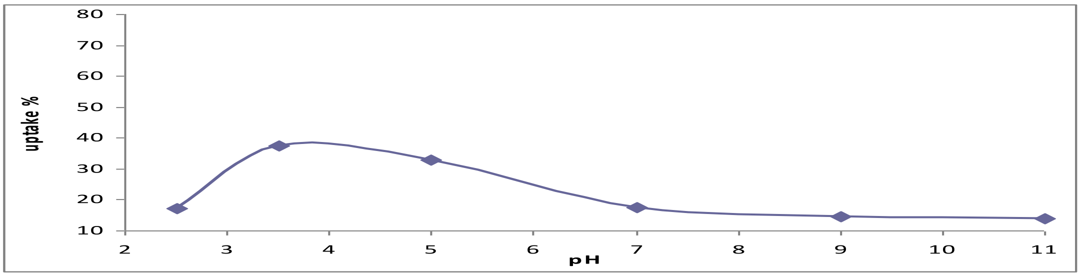

Fig 4. Effect of initial solution pH on adsorption of AZ on clay (C_{AZ}=2 mg/L, T=20 °C, clay dose=0.1 g, pH=4

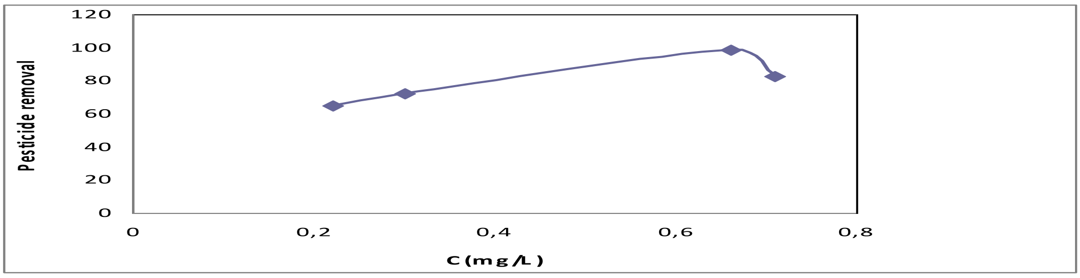

Fig 5. Effect of AZ concentration on the adsorption of amitraz by clay (phase contact time 3 hours, clay dose 0.1 g, pH=4, T=20 °C)

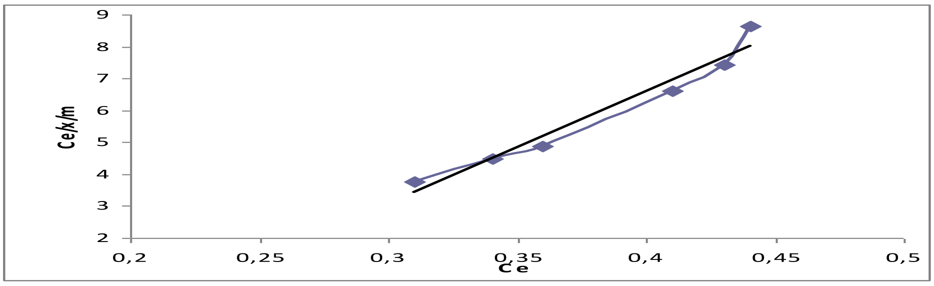

Fig 6.Linearized Langmuir isotherm

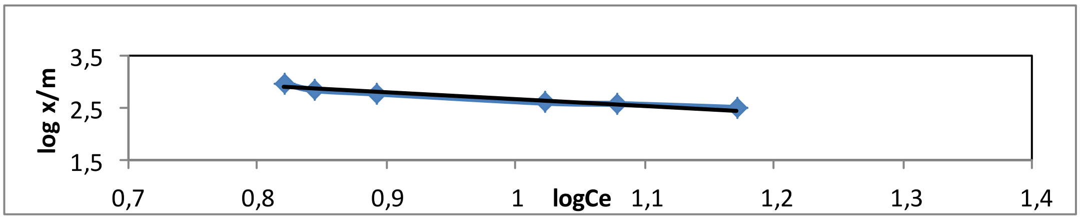

Fig 7. Linearized Freundlich isotherm

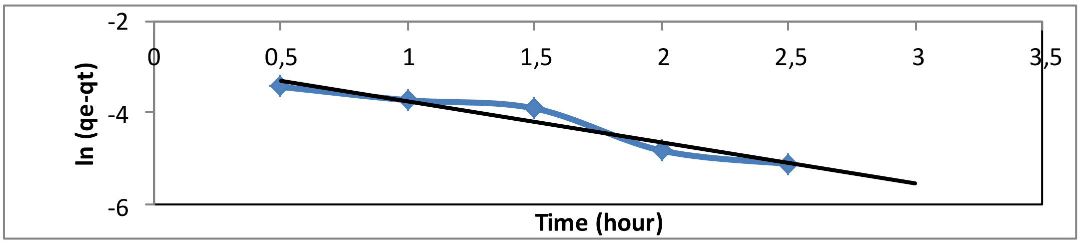

Fig.8. Pseudofirst order kinetics

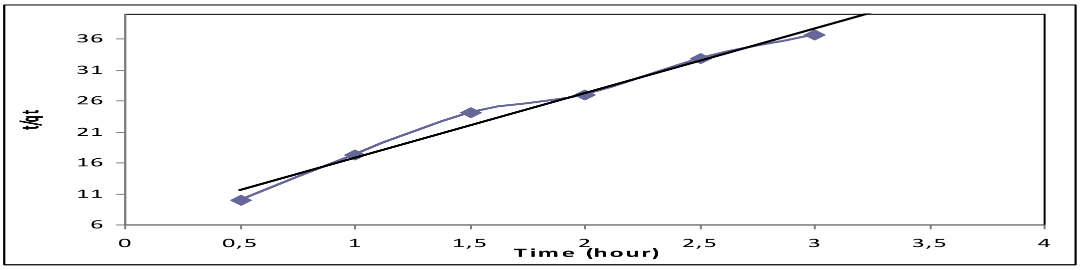

Fig 9. Pseudosecond order kinetics

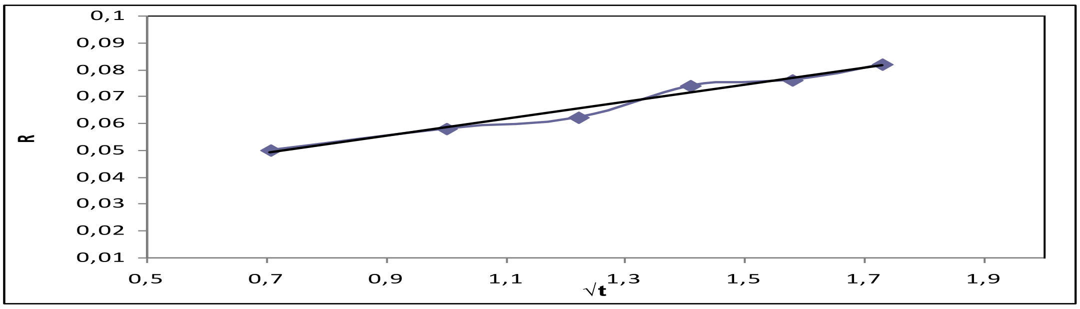

Fig 10. Intra particle kinetics