Kinetics of Nano-zinc Oxide in Desert Calcareous Soils

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Abstract

A laboratory experiment was carried out to study the kinetics reaction of zinc added to calcareous soils from different fertilizer sources and extracted by DTPA solution. Where two types of fertilizers were added, the first, nano-zinc fertilizers in the form of nano-metallic zinc oxide (Zn_nO), nano-chelated zinc (Zn_nDTPA), and nano-zinc humate (Zn_nHA), while the second type was the same fertilizer sources, but in their regular form (ZnO, ZnDTPA and ZnHA). All of them were added at a concentration of 100 mg kg^{-1} and the nano and regular zinc sources were incubated after they were added to the soil to know their physical and chemical behavior during different incubation periods of 0, 5, 10, 20, 40, 80, 120 and 160 days, with two replications for each incubation period. After the end of each period, zinc was extracted by DTPA, and the data of extracted zinc were subjected to five kinetic equations to reach the best equation describing the behavior of zinc release. The results showed a rapid decrease in the concentration of zinc extracted at the incubation period of 0 days for all fertilizer sources and the continuation of the decrease in concentration with the length of the incubation period gradually until the end of the period after 160 days. The percentage of decrease in nano-zinc fertilizer was less than that of regular fertilizers. The Zn_nDTPA chelated zinc source was superior among the regular and nano fertilizer in giving the highest concentration of zinc throughout the incubation period. The second-order equation was the most efficient in describing the behavior and reaction of zinc kinetics in soil from its different sources. The behavior and kinetics reaction of zinc in soil from its different sources.

Key Words: Kinetics Reaction, Nano-zinc Oxide, Calcareous Soil, Kinetic Equations, Zn-DTPA.

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Introduction

The lack of micro-nutrients is a widespread problem in many countries, and the reason for this is that most of those countries have calcareous soils and have a high soil reaction and low organic matter content, which makes the ability of those soils to process nutrients weak, especially the smaller ones. This makes the ability of those soils to nutrient availability is weak, especially the micro-nutrients. The availability of zinc in soil depends on the physical, chemical, and biological properties of the soil and in a complex system such as soil. These different properties determine the type, bioavailability, and kinetics of micronutrients in the soil, including zinc (Covelo *et al.*, 2004). In a study comparing nano-fertilizers and regular fertilizers, Jassim *et al.*, (2020) found that zinc nano-fertilizers added to the soil outperformed in increasing the availability of zinc in the soil compared to regular fertilizers. The amount of carbonate and its distribution in the soil is one of the most important factors affecting the physical, chemical, and biological properties of the soil, it affects the soil pH and the reactions of adsorption, release, dissolution, sedimentation, and fixation due to its effectiveness and its alkaline form.

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The study of the release of nutrients from the soil is carried out by applying the laws of speed, and the kinetic equations that are adopted in the calculations of the coefficient of the speed of release of nutrients from the soil are all based on the laws of speed depending on the time factor to predict the speed of the interaction of the element in the soil and its mechanics (Sparks, 1992), and the use of the kinetics approach to study the availability of the element for absorption and its ability to release is done by using several solutions such as dilute organic acids such as citric, lactic and dilute salts since such solutions have a similar effect to the effect of radical and biological secretions in the root area. The best equations are the equation that gives a good relationship with plant growth indicators according to statistical indicators such as correlation coefficient r, coefficient of determination r^2, t value (variance between values) and SEe (Standard Error estimate). Al-Obaidi, (2010) found that when studying the physicochemical behavior of three fertilizer sources of zinc, the second-order equation (the exponential decreasing equation) with the time in determining the availability of zinc. Al-Hadithi and Al-Obaidi (2011) also found that the second-order equation (exponential decreasing) was the best in determining the amount of availability of zinc with time. In another study, Alolo, (2016) found in her study of zinc release in 9 different locations of Syrian soils that the second-order equation was superior among all the kinetic equations used in the study by giving the best description of the kinetics of zinc in all studied soils.

The study of the kinetics of nutrients is very necessary to determine the behavior of the continuous reaction between different ions in the soil solution and the solid phase with time. Because of the low availability of zinc in Iraqi soils and the increase in their content of calcium carbonate, and the absence of a study on the behavior and reaction of zinc nanoparticles in desert soils, this study was conducted with aims to study the kinetics of nano-zinc from different fertilizer sources and compare it with the kinetics of regular zinc oxide.

Materials and Methods

The kinetics experiment was carried out in the soil and water research laboratories - Desert Studies Center - University of Anbar, to study the reaction of zinc added from different fertilizer sources, namely, the nano-metal source (Zn_nO), the nano-chelated source (Zn_nDTPA), the nano-organic source (Zn_nHA), the regular mineral source (ZnO), the regular chelated source (ZnDTPA) and the regular organic source (ZnHA). Samples were taken from the soil surface with a depth of 0-0.3 m belonging to Al-Dawwar Research Station - Agricultural Research Department - Ministry of Agriculture (35 km west of Ramadi) as a representative site for desert soils. The soil was air-dried, then crushed, and sieved with a sieve of 2 mm. Table 1 shows some chemical properties of the soil used. Nano and regular fertilizer sources were prepared using nano-zinc oxide (Zn_nO) as a nano-metallic zinc fertilizer, and the chelating substance Diethylene Triamine pentaacetic acid (DTPA) was used as an artificial chelating material with nano-zinc oxide (Zn_nO) at a ratio of 1:6 respectively on the weight basis to prepare zinc nano chelate fertilizer (Zn_nDTPA). Humic acid was used in dry powder form as a natural chelating organic source with nano zinc oxide in a ratio of 1:6 respectively on the weight basis to prepare nano zinc humate fertilizer (Zn_nHA).

Regular zinc oxide (ZnO) was used as a fertilizer for regular metallic zinc, and the chelated substance DTPA was used as a chelating substance with regular zinc oxide (ZnO) at a ratio of 1:6, respectively on the weight basis, to prepare the usual chelated zinc fertilizer (ZnDTPA). Humic acid was used in dry powder form as a natural chelated organic source with regular zinc oxide in a ratio of 1:6 respectively on the weight basis to prepare zinc humate fertilizer (ZnHA).

After preparing the fertilizers, polyethylene containers were used to carry out the experiment, which was filled with 50 gm of air-dry soil and sieved with a sieve of 2 mm, with two replicates. Then zinc was added from the nano and regular fertilizers at a concentration of 100 mg kg^{-1} soil, as 10 ml of each fertilizer source was added in each container and completed the addition to 12 ml with distilled water. Where this quantity represents the moisture percentage at the field capacity of the study soil. The containers were incubated and the incubation periods were eight periods of time, namely 0, 5, 10, 20, 40, 80, 120, and 160 days. The number of containers used in the experiment was 6 (fertilizer source) x 2 (replicates) x 8 (incubation periods) = 96 containers. At the end of each incubation period, zinc was extracted with DTPA solution.

Table 1. Chemical properties of soil

saturated soil paste pH		7.51	
saturated soil paste EC		7.56	dS m^{-1}
O.M		3.3	gm kg^{-1}
$CaCO_3$		330	gm kg^{-1}
$CaSO_4.2H_2O$		5.20	
Cations	Ca^{+2}	21.7	mmole^{-1}
	Mg^{+2}	5.9	
	Na^{+}	22.9	
Anions	Cl^{-}	26.2	
	$SO_4^{=}$	22.5	
	HCO_3^{-}	4.6	
	CO_3^{-}	Nill	
P		15.68	mg kg^{-1}
K		152	
Soil Separators	Sand	502	gm kg^{-1}
	Silt	178	
	Clay	320	
soil texture		Sandy Loam	

To study the speed of zinc release from the soil with the time factor and its concentration in the soil solution. Kinetic equations used, some of which depend on the foundations of kinetic chemistry, such as:

1. Zero-order equation $Ct = C0 - Kt$
2. The first order equation $\ln Ct = \ln C0 - Kt$
3. The second-order equation $1/Ct = 1/C0 + Kt$
4. Parabolic diffusion equation $Ct = C0 - Kt^{1/2}$

And other equations that depend on experimental physical foundations, such as:

5. Elovich equation $Ct = C0 - K \ln t$

Where:
C0 = the concentration of zinc present in the soil solution at time zero
Ct = the concentration of zinc in the solution at the specified time,
K = the zinc release constant,
t = time.

Where the statistical indicators adopted, the coefficient of determination r^2, the value of the variance between the t-values and the SEe (Standard Error estimate) in determining the most efficient equation in describing the release of added zinc from different fertilizer sources in the study soil.

Results and Discussion

Effect of Incubation Time on Available Zinc Concentration

It is clear from Figure 1 that the concentration of extracted zinc in soil extracted with DTPA solution decreases with increasing incubation time for zinc added from its nano sources Zn_nO, Zn_nDTPA and Zn_nHA. Whereas, the highest concentration of available zinc was at the incubation period (0 days) of 4.52, 6.92, and 6.02 µg/gm^{-1} for the above sources, respectively, that is, a decrease of 95.48, 93.08, and 93.98%, respectively. It is noticeable that the available concentration continued to decrease with the increase in the period until reaching the end after 160 days, reaching 2.11, 2.91, and 2.74 µg g^{-1}, i.e., a decrease of 97.89, 97.09, and 97.26% for the above nano sources respectively, as the highest percentage of decrease among the nano sources was when using the nano zinc oxide Zn_nO it reached 97.89%.

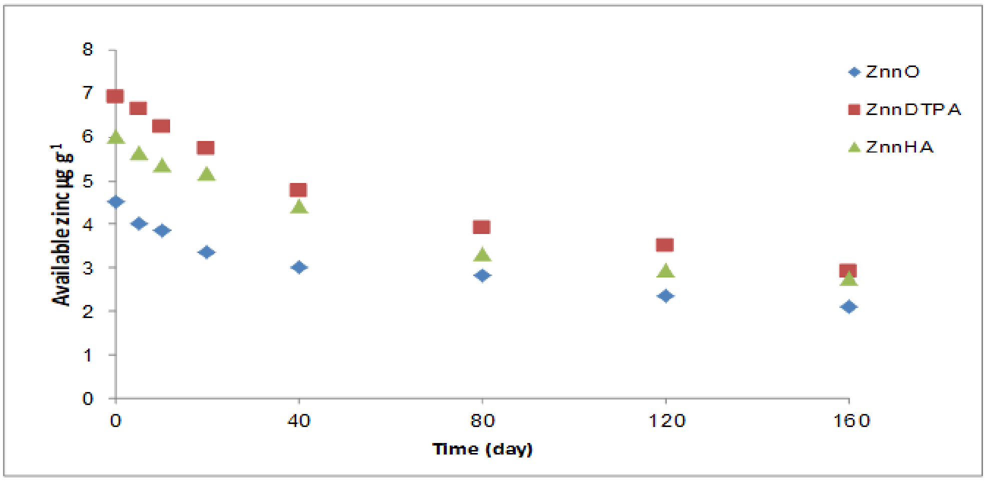

Figure 1. The relationship between available zinc (µg g^{-1}) from different nano sources in the study soil with time (day)

Whereas, for the regular zinc fertilizers, it is noted from Figure 2 that the concentration of available soil zinc extracted with DTPA solution also decreases with the increase in the incubation period when it is added from the usual zinc fertilizers ZnO, ZnDTPA, and ZnHA. The highest concentration was at the incubation period (0 days) amounting to 4.05, 6.81, and 5.70 μg g^{-1} with a decrease of 95.95, 93.19, and 94.30% for the regular sources, respectively. The decrease continued with an increase in the incubation period until reaching the end after 160 days, where the concentration of available zinc reached 0.83, 1.43, and 1.10 μg g^{-1}, which means a decrease of 99.17, 98.57, and 98.90% for the regular sources, respectively. The highest percentage of decrease in the concentration of available zinc was 99.17%, and this decrease in the concentration of zinc was after 160 days, which is the entire incubation period. This may be due to the role of calcium carbonate under the conditions of calcareous soils in the precipitation and fixation of zinc, as zinc can easily exchange with calcium ions if it is abundant in the soil solution (Van Bladel *et al.,* 1988).In addition to the high degree of soil reaction, which has an important and influential role on the solubility of zinc, as the availability of zinc decreases with its height, and this is consistent with what was found by Marschner, (1993) that increasing the degree of soil reaction from 5.5 to 7 reduced the availability of zinc by about 30 to 45 times, and with what was found by Al-Obaidi (2010). The rapid drop rate at the beginning of the incubation period is due to the speed of reactions that occur after adding the fertilizer to the soil directly, as the concentration of zinc added is large and the lack of sufficient time for the reactions to occur and the formation of complexes and the occurrence of sedimentation reactions that preserve the element in the available form if the appropriate conditions are available for its release. These reactions are followed by slow reactions that last for long periods that may be months or years and are responsible for the slow decline in the availability of zinc in the soil this is consistent with what was found by El-Obaidi, (2010) and Montaluo *et al*., (2016).

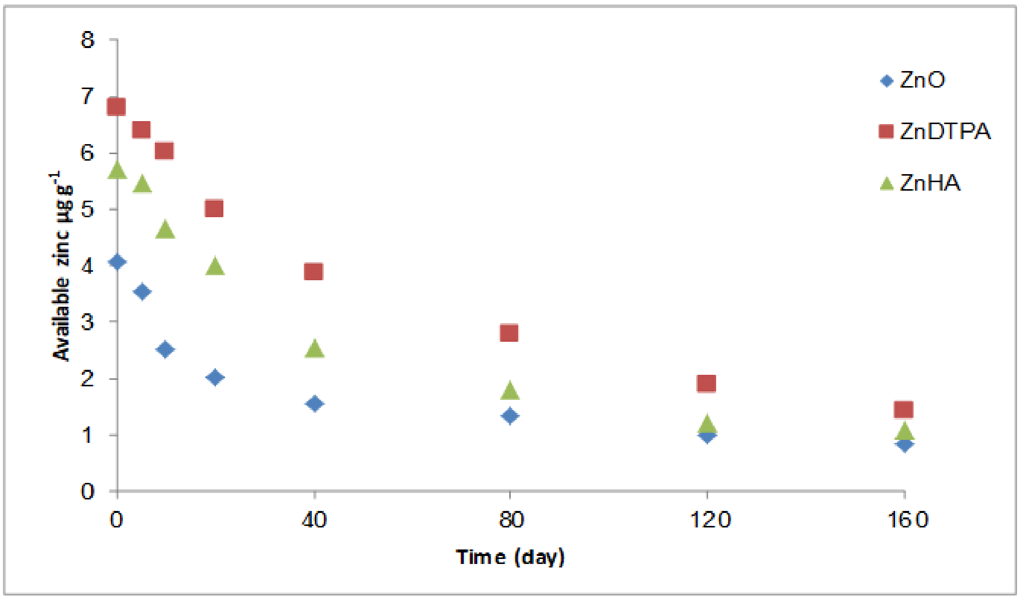

Figure 2. The relationship between available zinc (μg g^{-1}) from the regular sources of zinc in the study soil with time (day)

It is also noted from the same figures that the concentration of available zinc added from the nano-chelated fertilizer was the highest among the other nano-sources throughout the incubation period. When comparing the regular sources, it was also clear that the concentration of available zinc added from the usual chelated fertilizer was the highest among the regular sources throughout the incubation period. The reason may be due to the role of DTPA in the chelation of micro-nutrients, including zinc, and the formation of stable complexes for a wide range of the degree of soil interaction, as it works to chelate zinc by the effective aggregates it contains, forming complexes that can dissolve in the soil solution slowly and with high resistance to hydrolysis so that it cannot be replaced The zinc in it is easily retained, so it retains a larger amount of zinc for a longer period, and this is consistent with what was observed by Kanwal *et al.,* (2009).DTPA is the most stable artificial chelate in alkaline reaction conditions. As for the effect of the type of nano and regular fertilizer on the extracted zinc, it is clear from the same figures that the nano fertilizer with its three sources maintained the concentration of available zinc during the different incubation periods in greater quantities than if the regular fertilizers were used. Where the initial concentration of zinc immediately after adding the nano-fertilizers at a time (0 days) reached 4.52, 6.92, and 6.02 µg mg-1 for sources Zn_nO, Zn_nDTPA, and Zn_nHA respectively. While the concentration of zinc extracted from the regular sources was 4.05, 6.81, and 5.70 µg g^{-1} ZnO, ZnDTPA, and ZnHA, respectively. The superiority of nano-fertilizers continued to increase zinc availability throughout the incubation period until completion after 160 days, the reason may be due to the role of nano-fertilizers and their important characteristics in terms of the small size of the nano particles and the large surface area that increases the reactive activity of zinc with soil and other sources, in addition to the important role of nano-fertilizers in making the process of releasing zinc slower than it compared to regular fertilizers, and this is consistent with what Adhikary *et.al*, (2020) observed.

Zinc Kinetics Release

It is clear from Table 2 that the second-order equation 1/Ct=1/C0+Kt is the most efficient equation among the equations used to describe the nature of the relationship between zinc release from the soil during the reaction time. It gave the highest coefficient of determination (r^2) of 0.968 and the lowest standard error (SEe) of 0.045, which makes it the most appropriate among the kinetics equations in describing the behavior of zinc and its reactions from its nano and regular sources during different incubation periods.

Table 2. Indicators of different kinetic equations to describe the kinetic reaction of zinc in the study soil treated with different sources of zinc

Treatment	Indicators	Zero- Order	1St- Orde	2nd- Order	Diffusion	Elovich
ZnO	R^2	0.686	0.855	0.960	0.876	0.968
	SEe	0.707	0.228	0.070	0.443	0.222
	T	-3.621	-5.971	12.125	-6.526	-13.693
ZnDTPA	R^2	0.923	0.985	0.969	0.982	0.897
	SEe	0.615	0.076	0.038	0.297	0.710
	T	-8.490	-19.862	13.772	-18.140	-7.245
ZnHA	R^2	0.882	0.978	0.950	0.969	0.912
	SEe	0.745	0.133	0.125	0.380	0.643
	T	-6.715	-16.680	10.717	-13.795	-7.903
Zn_nO	R^2	0.859	0.922	0.963	0.976	0.962
	SEe	0.338	0.079	0.018	0.139	0.175
	T	-6.050	-8.433	12.552	-15.664	-12.398
Zn_nDTPA	R^2	0.918	0.964	0.989	0.983	0.902
	SEe	0.470	0.065	0.008	0.210	0.513
	T	-8.199	-12.781	23.664	-18.992	-7.453
Zn_nHA	R^2	0.920	0.954	0.977	0.978	0.885
	SEe	0.394	0.071	0.012	0.203	0.471
	T	-8.308	-11.186	16.155	-16.633	-6.811
Mean	R^2	0.864	0.943	0.968	0.960	0.921
	SEe	0.544	0.108	0.045	0.278	0.455
	T	-6.897	-12.485	14.830	-14.958	-9.250

As some previous studies indicated the superiority of the second-order equation in describing the kinetics of zinc release from the soil, Al-Obaidi (2010) found that the second-order equation was the most efficient among six equations used to describe the speed of release of available zinc added from three mineral, chelated and organic fertilizer sources to two calcareous soils. As well as what Mhamdi et al. (2013) found in the superiority of the second-order equation in describing the kinetics of zinc release associated with elemental cations in smectite soil in Tunisia. This is consistent with what was found by Aloulou, (2016) in her study of zinc release in 9 different locations of Syrian soils.

Figures 3 and 4 show the relationship between each of the reciprocal of the concentration of the available zinc and the incubation period (day) according to the second-order equation, which is $1/Ct=1/Co+Kt$ for nano and regular sources respectively. It was found by applying the equation in Figure 3 for the nano fertilizers Zn_nO, Zn_nDTPA, and Zn_nHA after an incubation period of 50 days that the concentration of extracted zinc was 3.09, 4.77, and 4.20 µg g^{-1}, respectively. Whereas, when applying the same equation in Figure 4 for the regular zinc fertilizers ZnO, ZnDTPA, and ZnHA, the amount of zinc extracted after the same incubation period is 1.68, 3.42, and 1.90 µg g^{-1}, respectively. It is noted that the nano-zinc fertilizers are superior in giving a higher concentration of available zinc after any incubation period, and that difference in the amount of zinc extracted between the nano- and regular sources may be due to the properties of the nano-material by preserving the element by reducing the speed of its release and increasing the reactive chemical activity of the material and that by increasing its surface area. This is consistent with what was found by Mandal *et al.*, (2018) that nano-fertilizers release nutrients at a slower speed compared to regular fertilizers due to their large surface area, which helps them to retain a larger amount of the nutrient, in addition to their high stability and slow solubility, which contributes to the availability of nutrients for longer periods, as well as the high reactive activity of nano-fertilizers due to its large surface area, which may help it to link with other sources in the soil after it is liberated from the fertilizer. This is in agreement with Adhikary *et al.*, (2020), who observed the superiority of nano-zinc sulfate fertilizer and nanopolymer in giving the highest concentration of zinc after an incubation period of 45 and 60 days for both sources, respectively, compared to regular zinc sulfate. 254

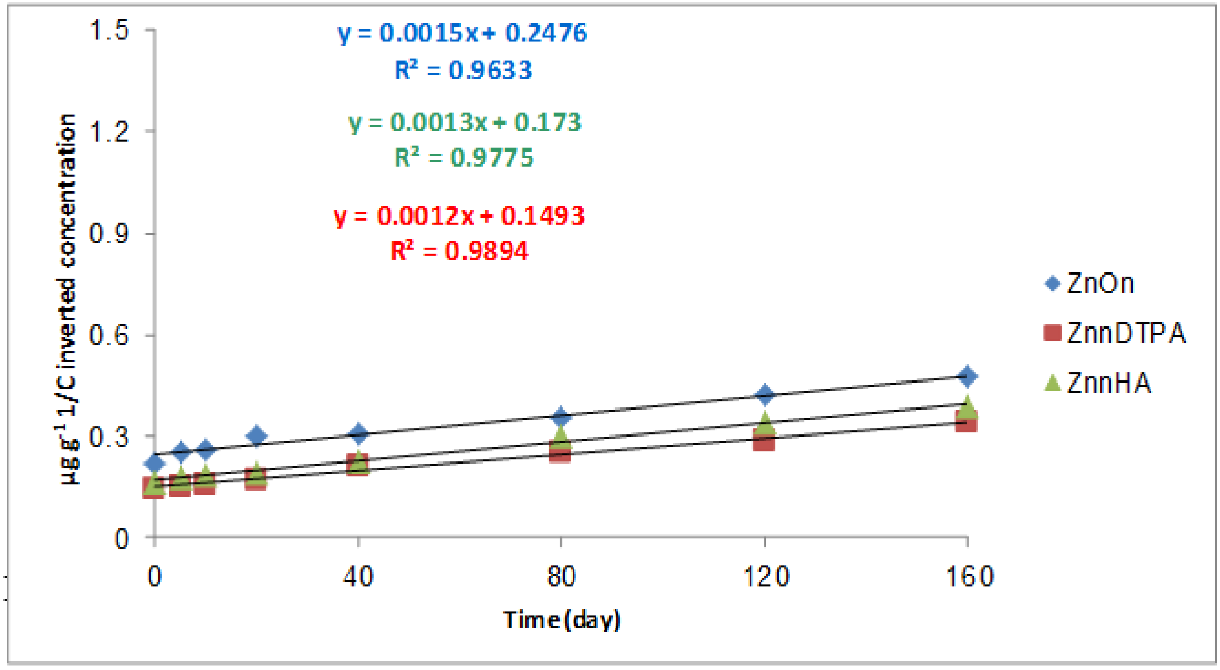

Fig. 3. The relationship between inverted zinc extracted (µg-1/Ct) and the incubation time (day) for the nano-fertilizers

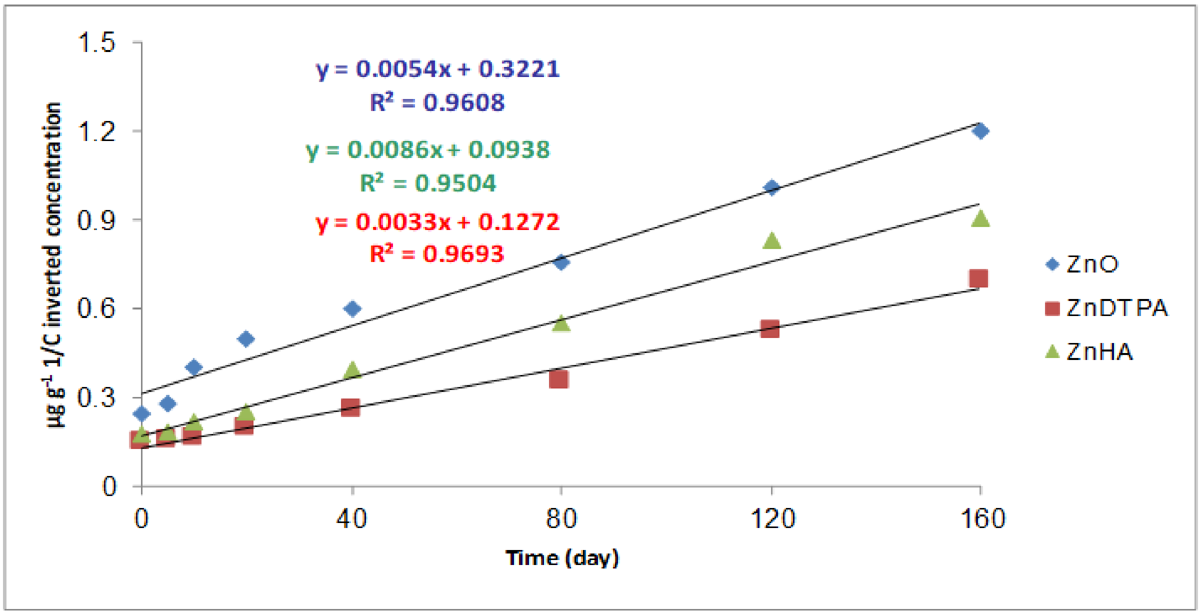

Fig. 4. The relationship between inverted of extracted zinc (μg-1/Ct) and the incubation time (day) for regular fertilizers

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