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MODELING AND CFD SIMULATION OF ZINC SULPHATE FERTILIZER GRANULE DISSOLUTION IN SOIL SOLUTION

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ABSTRACT

Improving the use efficiency of fertilizers and controlling the rate of fertilizers dissolution has been an important mater in fertilizers manufacturing. In this study, an unsteady two dimensional model has been considered to predict release time of zinc sulphate fertilizer granules. Note that zinc sulphate is a strong electrolyte. The spherical granule modelling has been coupled to the soil solution. This coupling model has been used to remove reaction rate term in the spherical granule governing equation. It is assumed that the surface reaction is existed on solid-liquid surface. The computational fluid dynamic (CFD) calculation with the finite element method (FEM) has been carried out to simulate the governing equation. The effects of some important parameters such as the height of soil solution (h) and the radius (R) of fertilizer granule have been investigated. The complete release time has been achieved for different value of ratio of h and R.

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Keywords: *Computational fluid dynamic, finite element method, Zinc sulphate*

1. INTRODUCTION

Poor soil needs enough fertilizers and water to reach high quality of the soil solution. The release time of fertilizer nutrients depends on several parameters as the aqueous solution diffusivity in the solid fertilizers, shape and size (diameter) of fertilizers and the amount of contact surface. These parameters are important to improve the nutrients use efficiency by plant. The Application technology of controlled-release fertilizers retains the nutrients concentration at a good level in the aqueous solution. The study of nutrients release and control of water diffusion in the granule have been known for several years. Ortil and Lunt [1] have first practice about use of controlled-release fertilizers by the encapsulating membranes. A recent practice was used controlled-release fertilizers to increase efficiency and to decrease pollutant of environmental [2]. Another study was estimating amount of fertilizers nutrients that are dissolved in the soil solution [3]. The nitrogen (N) - containing fertilizers with slow release of N have been investigated by [4, 5]. Robert L. Mikkelsen [6] has offered the use of hydrophilic polymers to control nutrient release. Shavit et al. [7] have demonstrated a rather

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new technology of controlled release fertilizers. The release rate of fertilizer from polymeric membrane has been estimated by Al-Zahrani [8].

Most fertilizers nutrients are Zn, N, K, P, Pb, Mg and etcetera. These nutrients are the main components of the high- quality soil. The zinc sulphate is a salt and a strong electrolyte. When a strong electrolyte dissolves in water, it will be completely ionized. Ions are divided into cation and anion. The diffusion coefficient of the strong electrolyte is dependent on the diffusion coefficient and the charge of cation and anion. This function is used to simulation. The solid fertilizers are produced at different form, granule or powder. Note that spherical granule is used in the model. These CFD results benefit all farmers about optimum use of the zinc sulphate fertilizers and water.

2. MATHEMATICAL EQUATIONS

The fertilizer is taken as a spherical granular with radius R and center O in Fig.1.a. According to this figure, h describes the height of the soil solution around the fertilizers granules. In this research, the mass transfer of fertilizer components will be studied into liquid phase in which all nutrients dissolve. The surface reaction occurs in the interfaces between liquid- solid phases. As the nutrients continue to be consumed from the non-porous granule surface, the soil solution must diffuse farther into the solid to reach the unreacted solid phase. The fertilizer components have to overcome two mass transfer resistant on their way from the solid to the liquid phase: the first resistant on the solid surface, in which surface reaction exists, and the second resistant within the liquid phase. According to these resistances, two mass transfer equations are required to achieve the concentration equation for the fertilizer granules. The general formula of mass transfer is:

$$\begin{Bmatrix}\text{Mass}\\ \text{input}\end{Bmatrix}-\begin{Bmatrix}\text{Mass}\\ \text{output}\end{Bmatrix}+\begin{Bmatrix}\text{Rate of}\\ \text{surface reaction}\end{Bmatrix}=\begin{Bmatrix}\text{Mass}\\ \text{accumulation}\end{Bmatrix} \quad \textbf{Eq. (1)}$$

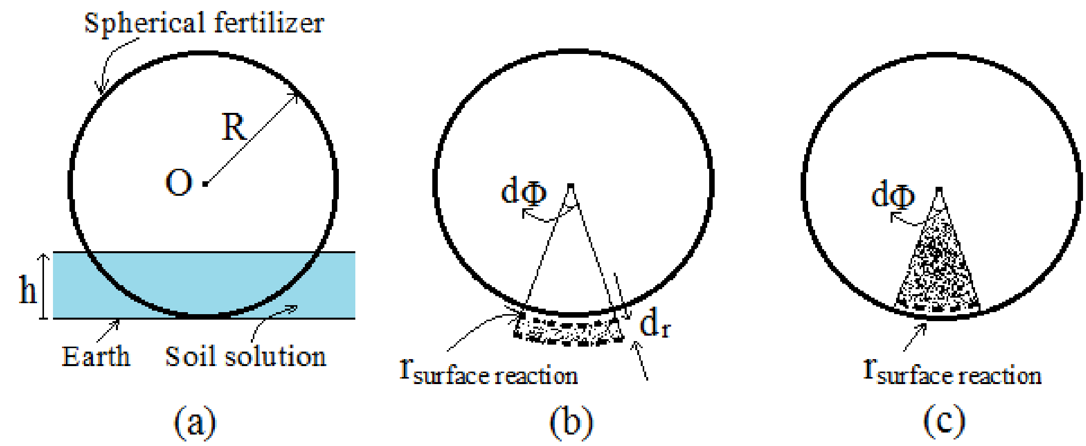


Fig.1. (a). The spherical granule in contact with the soil solution (b) Liquid element (c) Solid element.

The initial and important step is to create an element in the modelling. Note that two elements are required, one for the liquid phase and another for the solid phase. The mass transfer equation is developed for both elements and then these equations are coupled to reach an equation for concentration of fertilizer components. According to **Eq. (1)**, the mass transfer is derived for both phases as below:

2.1. Liquid phase

The liquid diffuses from the soil solution to the solid surface where it reacts with the solid fertilizer, Fig.1.a. The reaction on the solid surface is

$$\text{nutrients}_{\text{(solid)}} + \text{water} \rightarrow \text{nutrients}_{\text{(aqueous)}} \qquad \textbf{Eq. (2)}$$

As regards the fertilizers are spherical granular, a good element is selected and indicated in Fig.1.b. A theoretical model is derived on the assumption that steady state profile is valid. This assumption is referred to the quasi-steady state approximation [9]. According to the element of liquid phase and Eq. (1), the Mass balance on the liquid phase yields

$$(W_{in}\ A_W) - (W_{out}\ A_W) + (r_W\ V_W) = 0 \qquad \textbf{Eq. (3)}$$

Where W_{in} and W_{out} are input and output flux of water, respectively. A_w is the perpendicular cross-sectional area to the flux motion and V_w is the volume of element. r_w is the rate of surface reaction. Dividing Eq. (3) through by V_w and taking the limit gives

$$\nabla(A_W\ W_W) = -\ r_W \qquad \textbf{Eq. (4)}$$

The left side of this equation is the flux gradient and the right side is the rate of surface reaction. Note that, the amount of reaction rate inside the liquid element is negligible compared with the surface reaction.

2.2. Solid phase

A theoretical model is derived on the assumption that the solid is non porous and the reaction is only on the solid surface. For this phase, the best element is considered and indicated in Fig.1.c. This element doesn't inter or leave the nutrients. According to this element and Eq.(1), mass balance on the solid granule yields

$$0 - 0 + (-r_s) = \frac{\partial C_S}{\partial t} \qquad \textbf{Eq. (5)}$$

In this equation, r_s is the rate of reaction, V_s is the volume of element and C_s is the solid concentration. The right side of this equation is amount of solid mass accumulation. If 1 mole of water dissolved 1 mole of solid granule, then $(-r_s) = (-r_w)$. After rearrangement we obtain

$$-\nabla(A_w W_w) = \frac{\partial C_s}{\partial t} \quad \textbf{Eq. (6)}$$

For the case of dilute solution or non-convection, value of mass flux of solid is equal to the mass flux of water as:

$$W_s = -W_w \quad \textbf{Eq. (7)}$$

Substituting Eq. (7) into Eq. (6) and rearranging yields

$$-\nabla(A_w W_s) = \frac{\partial C_s}{\partial t} \quad \textbf{Eq. (8)}$$

The total mass flux of solid to the solid- water interface is

$$\text{total mass flux} = \text{diffusion} + \text{bulk motion}$$

$$W_s = J_s + B_s \quad \textbf{Eq. (9)}$$

Where J_s is diffusion flux and B_s is the bulk flow term for species. The bulk flow term is the multiplication of the species concentration and the mass average velocity of species. At this case B_s is zero because the mass average velocity of species is zero.

The constitutive equation for term diffusion flux of release of nutrient is related to the concentration gradient by Fick's first law [*]:

$$J_s = -\nabla(D_s C_s) \quad \textbf{Eq. (10)}$$

Where C_s is total concentration of solid and D_s is diffusivity. Combining **Eq. (8)**, **Eq. (9)** and **Eq. (10)**, we obtain expression for the solid concentration

$$\nabla(A_w \nabla(D_s C_s)) = \frac{\partial C_s}{\partial t} \quad \textbf{Eq. (11)}$$

According to **Eq. (11)** the partial differential equation (PDE) which describes the unsteady transport of mass concentration, due to diffusion, in a three-dimensional spherical space is:

$$\frac{\partial(D_r r^2 \frac{\partial C}{\partial r})}{r^2 \partial r} + \frac{\partial(D_\theta \sin\theta \frac{\partial C}{\partial \theta})}{r^2 \sin\theta \partial\theta} + \frac{\partial(D_\varphi \frac{\partial C}{\partial \varphi})}{r^2 \sin^2\theta \partial\varphi} = \frac{\partial C}{\partial t} \quad \textbf{Eq. (12)}$$

Where D_r, D_θ and D_φ are the components of the diffusion coefficient along the three spherical directions, respectively. If the diffusion coefficient were not function of the spherical coordinate we can assume that $D_r = D_\theta = D_\varphi = D_s$, then the diffusion equation will be equal to:

$$D_s\left(\frac{\partial(r^2\frac{\partial C}{\partial r})}{r^2\partial r}+\frac{\partial(\sin\theta\frac{\partial C}{\partial \theta})}{r^2\sin\theta\partial\theta}+\frac{\partial(\frac{\partial C}{\partial \varphi})}{r^2\sin^2\theta\partial\varphi}\right)=\frac{\partial C}{\partial t} \qquad \textbf{Eq. (13)}$$

According to Fig1.c, it is predicted that the profile of concentration exist at the r and φ directions. Simplifying gives

$$D_s\left(\frac{\partial(r^2\frac{\partial C}{\partial r})}{r^2\partial r}+\frac{\partial(\frac{\partial C}{\partial \varphi})}{r^2\sin^2\theta\partial\varphi}\right)=\frac{\partial C}{\partial t} \qquad \textbf{Eq. (14)}$$

This equation describes the variation of zinc sulphate concentration. The spherical granules contain with zinc sulphate (ZnSo4) that it is a salt and a strong electrolyte. The diffusion coefficient of strong electrolytes can be a function of diffusion coefficient of anion and cation. This function has been investigated in [*] as bellow:

2.3. Diffusion coefficient of strong electrolyte

If an electrolyte contact with water, it will be ionized. The electrolytes are divided to the strong electrolyte and the weak electrolyte. The diffusion coefficient pattern is difference for two types of electrolytes. The diffusion coefficient of the strong electrolytes is function of charge and the diffusion coefficients of cation and anion.

$$D_{\text{zinc sulphate (s)}} = F(D_{\text{cation}}, D_{\text{anion}}) = \frac{|Z_c|+|Z_a|}{\frac{|Z_c|}{D_a}+\frac{|Z_a|}{D_c}} \qquad \textbf{Eq. (15)}$$

Where D_s is the diffusion coefficient of the strong electrolyte. D_c , D_a are the diffusion coefficients and Z_c , Z_a are the charges of cation and anion, respectively.

3. NUMERICAL SIMULATION

The spherical granule is simulated with use of computational fluid dynamic (CFD). The base of CFD is computational numerical analysis [10]. CFD develops numerical codes to solve the partial differential equation (PDE). At this study, the finite element method (FEM) [11] has been applied. Note that FEM is one of CFD techniques. For CFD simulation the important case is best choice of mesh (element) because the mesh size influences the accuracy of the simulation. In this study, the fine mesh has been used. The mesh size parameters have been shown in table.1. The information of this table is for a mesh with minimum error in the results.

Table.1. The element size parameters.

Maximum element size (mm)	0.106
Minimum element size (mm)	6e-4
Resolution of curvature	0.3
Resolution of narrow regions	1

3.1. Boundary and initial conditions

For solve PDE equation, the boundary conditions and an initial condition are required. The spherical granules are surrounded by the soil solution in down and the air in up. Note that fertilizers according to Fig1.a aren't suspended in the soil solution. The maximum height of the soil solution is assumed less than the spherical granules diameter. So they are divided into two regions. A region is contact between liquid and solid phase in which the surface reaction exists. It is assumed that the rapid surface reaction is existed so the equilibrium state can be used at the interface. The equivalent role for strong electrolyte can be expressed with Hückel-Onsage [12] equation.

$$A = A_0 - (\alpha + \beta A_0)C^{0.5} \qquad \textbf{Eq. (16)}$$

A_0 is ionic conductivity in the infinite dilution, α and β are constant and C is the concentration of electrolyte on the liquid-solid contact surface. This concentration is selected as a boundary condition. At another region (contact between air and solid), no-flux boundary condition is used. The mass of salt per unit volume at t equal zero is considered as the initial condition (C_0). Also the constants values indicated in table.2.

Table.2. The constants values for CFD simulation.

Charges of cation (zinc)	+2
Charges of anion (sulphate)	-2
Diffusion coefficients of cation(zinc) at 25 ^oC, $cm^2.s^{-1}$	0.703e-5
Diffusion coefficients of anion (sulphate) at 25 ^oC, $cm^2.s^{-1}$	1.065e-5
Ionic conductivity A of zinc sulphate at25 ^oC, $cm^2.s.mol^{-1}$	85

Ionic conductivity of zinc sulphate in the infinite dilution A_0 at 25 °C, $cm^2.s.mol^{-1}$	132.7
Density of zinc sulphate, kg. L^{-1}	1.957
Constants of Hückel-Onsage equation, α and β	60.2, 0.229

4. RESULTS AND DISCUSSION

It mentioned that h shows the amount of fertilizers in the soil solution or the height of soil solution around the fertilizers. This paper investigates the variation of release time and zinc sulphate fertilizer concentration with change of h and granule radius (R). These results will be useful for farmers with better control of the soil solution level; also these are useful results for the fertilizers manufacturing to produce fertilizers with the optimum size. The two dimension contour graph of the zinc sulphate concentration has been indicated in Fig.2.a and Fig.2.b. These figures show the effect of h on the release of nutrients from the spherical granule so that increase of h is a good influence on the permeation and the rate of diffusion.

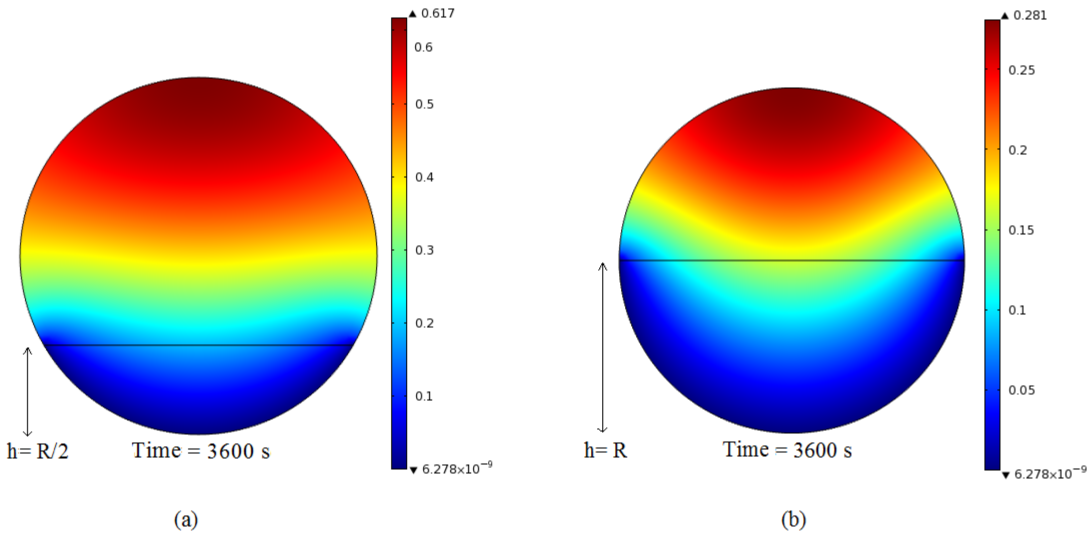


Fig.2. The contour of zinc sulphate concentration at 3600s for (a) h=R/2 (b) h=R.

The dimensionless concentration versus the dimensionless radius at different time is been shown in Fig.3. Three values of t are selected as 500s, 1500s, and 3500s. The heights of soil solution (h) are 0.5R and R for Fig.3.a and Fig.3.b, respectively. The slope of lines describes how the release of nutrients varies during the radius. The steepness of the slope at the same time and the different h shows the resistance is high. In other words, a lower h value indicates a steeper incline and a small diffusion. For example, the slope of the line with t=500 s, for h=0.5R is more than h=R, so the distribution of nutrients is small for h=0.5R.

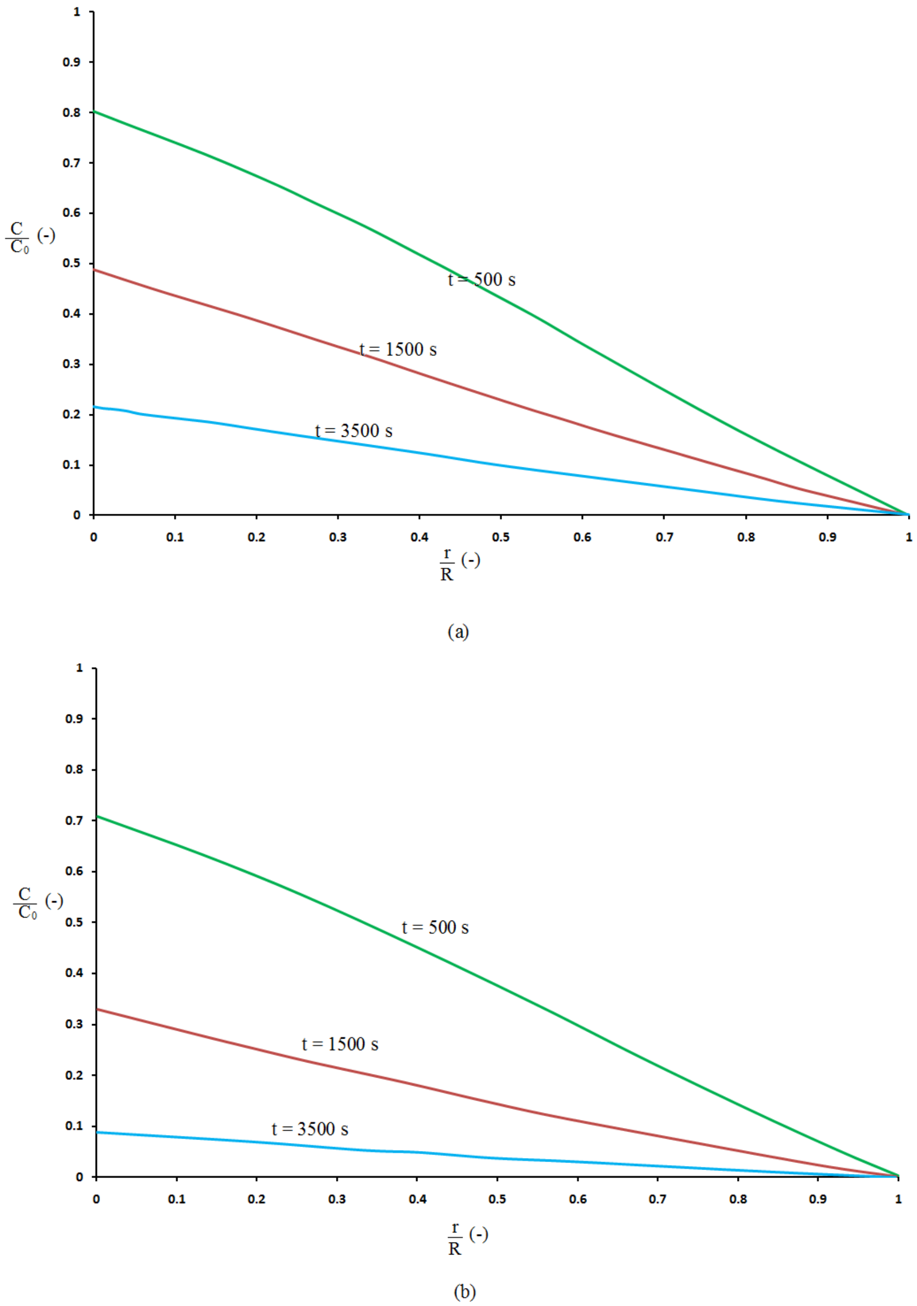
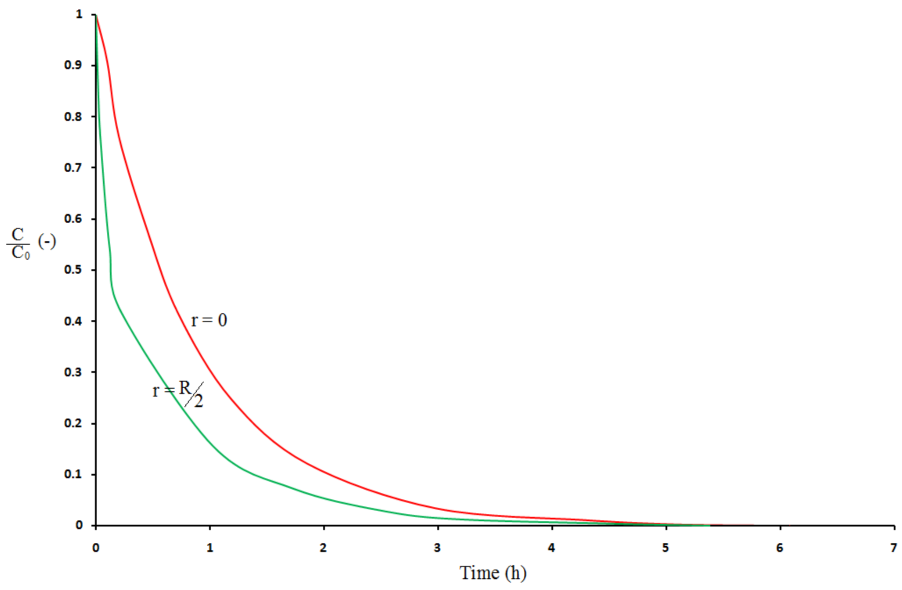
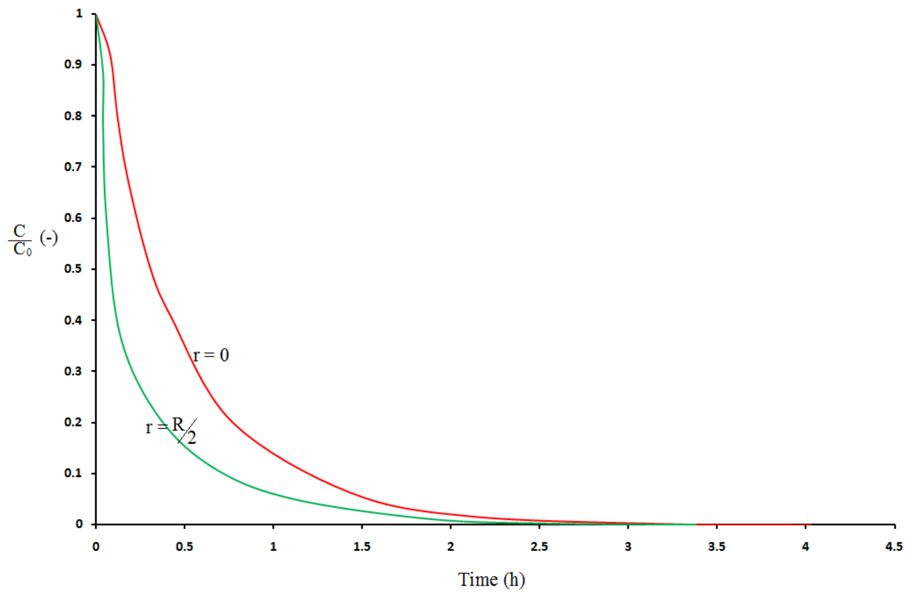


Fig.3. The dimensionless concentration versus the dimensionless radius at 500s, 1500s, 3500s for (a) h= 0.5R (b) h= R.

Fig.4 describes the release time for the different points of granule. The Fig.4.a and Fig.4.b compare the release time for two values of h. According to this compression, the release time decreases with increase of h. Also Fig.4 estimates the complete time consumption of the zinc sulphate fertilizer.



(a)



(b)

Fig.4. The dimensionless concentration versus the release time at the center of granule(r=0) and r= R/2 for (a) h= 0.25R (b) h= 0.75R.

Fig.5.shows the linear variation of complete release time (t_c) of zinc sulphate fertilizer with ratio of h and R. The below equation describes this variation

$$t_c = -3.99(\frac{h}{R}) + 6.29$$

According to this figure at the constant h, the increase of R influences on the release time as the complete release time increases. Also at the constant R, the full release time increases with the decrease of h.

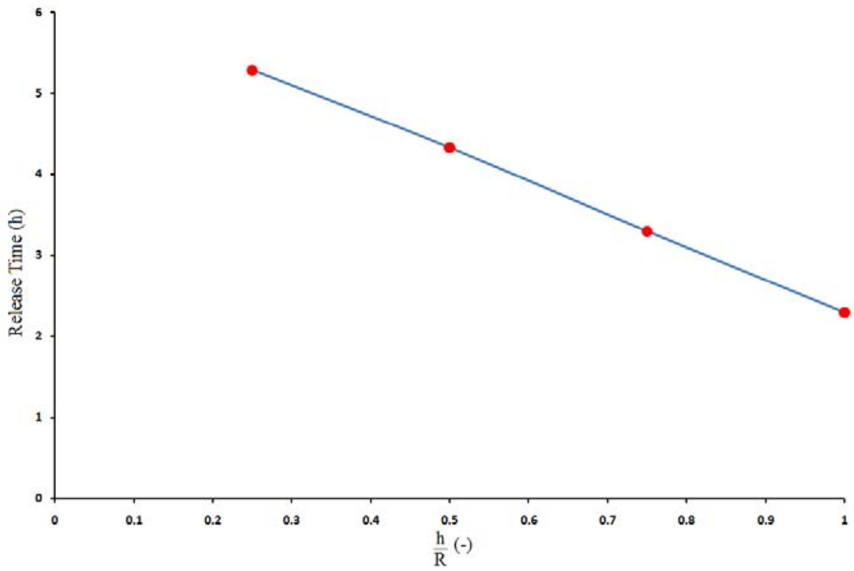


Fig.5. The variation of complete release time of zinc sulphate with ratio of h and R (h/R).

5. CONCLUSION

In this study, the dissolution of zinc sulphate fertilizers into soil solution has been investigated. A parameter (h) has been defined to show the level of soil solution. It is assumed that the surface reaction is existed on solid-liquid surface. Both the soil solution and the spherical granule are modelled to reach concentration equation of fertilizer. These models are solved together to remove the surface reaction term in the solid mass equation. Finally, an unsteady two dimensional equation is considered for zinc sulphate concentration. The model has been simulated by the computational fluid dynamic (CFD) code and the finite element method (FEM). Influence of h and R on the release time and the amount of fertilizers consumption has been discussed. It is shown that the release time depends on h and radius of spherical granule.

6. REFERENCES

[1] J. Ortli, J. Lunt, Controlled release of fertilizer minerals by encapsulating membranes: I. Factors influencing the rate of release, Soil Science Society of America Proceedings 26 (6) (1962) 579.

[2] R.G.S. Bidwell, Plant Physiology, Macmillan Publishing Co., New York, 1979.

[3] R. Prasad, G. Rajale, B. Lacakhdive, Nitrification retards and slow-release nitrogen fertilizers, Advances in Agronomy 23 (1971) 337.

[4] R.D. Hauck, Slow release and bio-inhibitor-amended nitrogen fertilizers, in: O.P. Engelstaed (Ed.), Fertilizer Technology and Use, SSSA Publication, Madison, WI, 1985, pp. 293–322.
[5] A. Shaviv, R.L. Mikkelsen, Slow release fertilizers for a safer environment maintain high agronomic use efficiency, Fertilizers Research 35 (1993) 1–12.
[6] R.L. Mikkelsen, Using hydrophilic polymers to control nutrient release, Fertilizers Research 38 (1994) 53–59.
[7] Uri Shavit, Avi Shaviv, Gil Shalit, Dan Zaslavsky, Release characteristics of a new controlled release fertilizer, Journal of Controlled Release 43 (1997) 131–138.
[8] S.M. Al-Zahrani, Controlled-release of fertilizers: modeling and simulation, International Journal of Engineering Science 137 (1999) 1299–1307.
[9] L. A. Segel and M. Slemrod, The quasi–steady–state assumption: a case study in perturbation, SIAM Rev., 31 (1989), 446-477.
[10] P. Wesseling, Principles of Computational Fluid Dynamics. Springer, 2001
[11] Giuseppe Pelosi (2007). "The finite-element method, Part I: R. L. Courant: Historical Corner
[12] P. Debye and E. Hückel (1923). "The theory of electrolytes. I. Lowering of freezing point and related phenomena.
[13] J. BOWEN, A. ACRIVOS and A. OPPENHEIM, Singular perturbation refinement to quasi steady state approximation in chemical kinetics, Chem. Engrg. Sci., 18 (1963), pp. 177-188.
[14] 1859-1927, Svante August Arrhenius - Swedish physicist and chemist; originated the modern theory of ionization of electrolytes; received the Nobel Prize for chemistry (1903).