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ORIGINAL ARTICLES

Nitrogen Slow Release Biodegradable Polymer Based on Oxidized Starch Prepared via Electrogenerated Mixed Oxidants

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ABSTRACT

Controlled slow release nitrogen compound based on biodegradable plastic was prepared. It is expected that this compound may be useful as nitrogen slow release fertilizer. Oxidized starch prepared using the electrogenerated mixed oxidants was the raw material for the preparation of the biodegradable plastic polymer. Optimum nitrogen slow release biodegradable plastic was obtained at the synthesis conditions of 350gm/1kg starch of glycerine, urea concentration 300 gm/1kg oxidized starch, pH 7, curing temperature 120°C, and curing time of 4hrs. The synthesis conditions of the slow release biodegradable plastic were studied systematically. The slow release properties of prepared biodegradable plastic also investigated. The results showed that the product had high degradation time of 450 days. The kinetic study shows that the nitrogen release rate from the obtained biodegradable plastic polymer could be represented by pseudo second order equation.

Key words: Biodegradable plastic, slow release, fertilizer, electrolytic, oxidized starch.

Introduction

Nowadays, Fertilizer specially NPK is the vital material for the development of crop production and plays an important role in food security. These NPK fertilizers are added into soil to save the necessary nutrients for plant growth. However, various environmental and economic drawbacks associated with the use of conventional fertilizers have become a focus of worldwide concern. Also the main problem facing the agrochemical industry is the huge loss of fertilizers added to the soil, (Maria Tomaszewska, 2003). One method for overcoming these shortcomings involves the use of slow-release fertilizers, which has demonstrated many advantages over the conventional types, such as decreasing fertilizer loss rate, supplying nutrient sustainably, lowering application frequency, and minimizing potential negative effects associated with overdosage. Coated fertilizers are the major category of slow-release fertilizers (Salman 1989, and Pipko 1988), due to the reduction in dissolution rate (Tomaszewska and Jarosiewicz 2002, Tomaszewska *et al.*, 2002, Kakoulides and Valkanas 1994). Depending on the method of fertilizer application and the soil type and properties, the lost percentage of fertilizers to the surrounding environment varied to reach about 50% of the applied fertilizers. Many environmental negative impacts are obtained due to this lose such as contamination of surface and ground water. Also the use of traditional fertilizers may lead to over concentration reaching the levels that are too high for effective action which may produce undesirable side effects on the target and the environment. On the other hand the lost percentage of these fertilizers causes economical negative impact which leads to the price increment of the food products.

Currently the most cost effective method to reduce losses of nutrients is the application of slow and controlled-release fertilizers (SCRF). These fertilizers may be prepared from granular conventional agrochemicals by coating them with the materials, which reduce their dissolution rate. The general idea is to provide granules of water-soluble fertilizer with an insoluble coating. The main advantages of SCRF are sustained supply of nutrients for a prolonged time, lower frequency of applications in accordance with normal crop requirements and minimization of the potential for negative effects associated with over dosage. Although of the above mentioned advantages still one disadvantage has to be overcome. This disadvantage is that the most of the used coating polymers are non biodegradable and accumulated in the soil causing many environmental problems. There are three types of these fertilizers: matrix-type formulations constitute the first major category of slow or controlled release fertilizers due to their simple production process. The active matter is dispersed in the matrix and diffuses through the matrix continuum or inter-granular openings, that is, through pores or channels in the carrier phase. Another way of regulating the release of fertilizer is coated fertilizer, i.e. a fertilizer core is coated by inert materials. The release of the fertilizer is controlled by diffusion through the shell (Jarosiewicz and Tomaszewska 2003). The third major category of such fertilizers is accomplished by means of chemically controlled releasing products, such as urea-formaldehyde (Prasad *et al.*,1971, polyphosphates Ray

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et al.,1993). The release of such kind of slow release fertilizer is controlled by the degradation rate, which in turn is affected by various factors, such as molecular weight of the polymer, and pH, temperature, ions and microorganisms in soil, etc. Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining huge volumes of water in the swollen state. Recently, research on the use of superabsorbents as water management materials for agricultural and horticultural applications has attracted great attention and test of superabsorbents for agricultural applications has shown encouraging results as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in soil, and increase plant growth rate (Bouranis *et al.*,1995). However, its applications in this field have met some problems because most of these superabsorbents are based on pure poly(sodium acrylate), and then they are too expensive and not suitable for saline-containing water and soils Y.M. Mohan et al.,2005. Recently, there have been many reports on introducing inorganic clays, such as kaolin, bentonite, montmorillonite(Wu *et al.*,2003, Attapulgite Zhang *et al.*,2006, and Mica Lee and Chen2005). into pure polymeric superabsorbents in order to improve swelling property, hydrogel strengths, and reduce production costs. (Borzacchiello *et al.*, 2001) show that the soluble fertilizer coated by chitosan would be an ideal slow release formulation (Borzacchiello, *et al.*,2001) Double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention (DSFSW), whose inner coating was chitosan (CTS), and the outer coating was cross linked poly(acrylic acid)/diatomite-containing urea (PAADU) was prepared by (Chen *et al.*, 2005; Ma *et al.*, 2004 and Liu *et al.*, 2004; Guo *et al.*, 2005; Liang and Liu, 2006). The product prepared not only has slow-release property but also could absorb a large amount of water and preserve the soil moisture at the same time. In the present work the so called biodegradable plastic (polymer) is used as a holding polymer for the NPK nutrients SCRF formulations. Biodegradable plastic is a biologically degradable product obtained by the reaction of modified starch and glycerine.

Chemical modification of starch with a view of improving its properties has been the subject of several studies (Rutenberg & Solarek, 1984). It can be effected via oxidation (Ali & Kempf, 1986; Daris Kuakpetoon & Ya-Jane Wang, 2006; Kawaljit, Maninder, Narpinder, & Seung-Taik, 2007; Li & Vasanthan, 2003; Muhrbeck, Eliasson, & Salomonsson, 1990; Salomonsson, Anderson, Torneport, & Theander, 1991; Salomonsson & Theander, 1992; Sa´nchez-Rivera, Garcı´a-Sua´rez, del Valle, Gutierrez- Meraz, & Bello-Pe´rez, 2005), hydrolysis (Abraham, Krishnaswamy, & Ramakrishna, 1988; Pessa, Suorit, Auto, & Poutanen, 1992; Singh & Ali, 1987), esterification (Agboola, Akingbala, & Oguntimein, 1991; Jarowenko, 1987; Maroza & Tomasik, 1991; Muhrbeck, Svensoon, & Eliasson, 1991; Muhrbeck & Tellier, 1991), etherification (Forrest, 1992; Hellwlg, Bishoff, & Rubo, 1992; Nachergaele, 1989), crosslinking (Chaudhari, Kamath, Bhide, & Kale, 1989; Hahn & hood, 1980; Kulicke, Aggour, & Elsabee, 1990), dextrinization (Jones, Morgan, Robert, & Todd, 1955), and grafting (Chinnaswamy & Hanna, 1991; El-Rafie, Zahran, El- Tahlawy, & Hebeish, 1995; Fanta, Burr,&Doane, 1984; Hebeish, El-Rafie, Higazy, & Ramadan, 1992; Hebeish, Zahran, El- Rafie, & El-Tahlawy, 1996; Hong & Carr, 1992).

Such reaction process cause significant changes in the physical as well as chemical structure of starch which, in turn, are reflected in solubility, viscosity performance and resistance to ageing of native starch and solution or pastes prepared thereof. Oxidation of starch is one of the most promising techniques for modification of starch to achieve suitable sizing agent for textile industry. Oxidation of starch could be achieved via chemical oxidation in several mediums such as hypochlorite, chlorates, hydrogen peroxide,. . ..etc (Qin, Rainer, Kari, & Eric, 1998; Ya-Jane & Linfeng, 2003) and Air oxidation (Anna & Piotr, 1999). On the industrial production of oxidized starch by chemical means acquire that the law reaction temperature is needed to inhibit cooking during the oxidation process. The chemical oxidation of starch has several disadvantages such as loss of catalytic activity, unstable concentration due to storage, unused residual oxidant at the end of the reaction and difficulty of handling and some of them are environmentally and healthy unsafe. Electrocatalytic oxidation is a new trend for oxidation of starch due to the ease of control of the electrochemical oxidation process, the high catalytic and chemical activity of the Electrogenerated species and Starch oxidation represents the most important and the cheapest technique of starch modification, as presented in (Shaarawy *et al.*,2009).

Several parameters are controlling the properties of the biodegradable plastic properties such as pH, starch to glycerol ratio, curing temperature, reaction time …etc. The effect of the biodegradable plastic structure on the release rate of active nutrients from the granule core into solution was investigated.

Materials and Methods

Experimental:

Materials:

Rice starch was kindly provided by the Egyptian starch and glucose Manufacturing Company, urea was supplied by Abu-Quir Company for fertilizer production, Food grade glycerine was also provided by Gamra Company for oil and soap production. Sodium hydroxide and sulfuric acid were used for pH adjustment.

Preparation of modified or oxidized starch:

Rice starch supplied by the Egyptian starch and glucose Manufacturing Company was subjected to electrocatalytic oxidation process as described in Shaarawy et al.,2009 using Titanium/Rhodium thermally activated modified electrode which is prepared via electrodepositing of rhodium metal over titanium pretreated and pre-anodized titanium substrate as described elsewhere Baraka et al., 2002. Figure (1) represents the electrochemical setup used for the electrocatalytic oxidation of Rice starch. Unless otherwise stated, the oxidation process was carried out as follows: The electrocatalytic oxidation reaction was carried out in the electrolytic cell placed in a thermostatic water bath. A known concentration of supporting electrolyte was added to 1000ml water and the desired pH was adjusted, 100gm rice starch was added to the reaction medium and the reactants were kept at the desired temperature under continuous stirring. The electric current is switched on at the desired current density. Once the desired electrolysis time is finished the current is switched off and filtration of the slurry is carried out followed by washing with 50% ethyl alcohol solution. After complete filtration oxidized starch is dried at 50-55^{O}C for 3hrs in an oven.

Table 1 represents the relation between current density applied during starch oxidation and the properties of the obtained oxidized starch.

Preparation of biodegradable polymer containing Nitrogen source:

The obtained electrocatalytic oxidized starch is mixed with glycerine, and urea according to the desired ratio with water, then mixed for about 30 min. the obtained slurry then subjected to the curing temperature for the required time. After completion of the curing reaction the solid obtained material is subjected to cooling then grounded to the desired particle size.

Table 1: Relation between current density and oxidized starch properties.

Variable current Density (mA/cm^2)	Apparent Viscosity (mpas^{-1}/ 516)	Carbonyl content (meq/100gm starch)	Carboxyl content (meq/100gm starch)
Untreated Starch	350	1.77	5.91
7.5	151	6.02	19.34
8.4	72	4.8	28.36
12	20	20.52	32.7

Analysis of the nitrogen slow release biodegradable polymer:

One gram of the obtained biodegradable polymer containing nitrogen was poured in 250ml distilled water. Periodically water samples was taken with interval time 24hr to determine the concentration of the released nitrogen from the solid biodegradable polymer and for monitoring the required time for complete degradation of the solid sample.

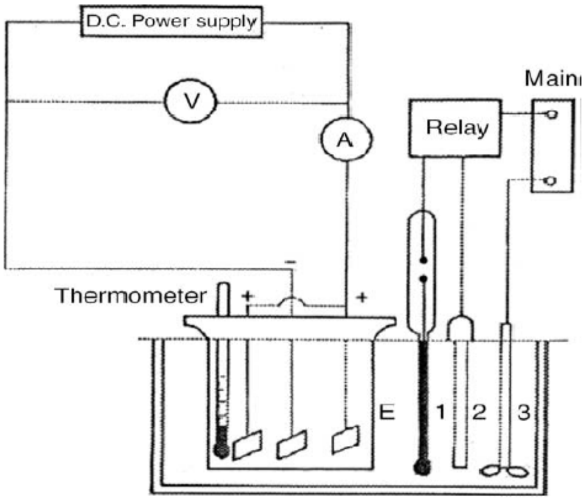

Fig. 1: Electrolytic oxidized starch preparation setup.

3. Results:

This study dealing with the investigation of the optimum conditions for the preparation of starch base biodegradable polymer as a holding polymer for urea to be used as nitrogen slow release compound. The success in this study will lead to the use of this biodegradable polymer as a slow release fertilizer of the main agriculture elements such as NPK. The influence of glycerine concentration, urea concentration, pH of reaction, curing time and curing temperature on both the polymer degradation time and released nitrogen concentration are studied.

Effect of Glycerine concentration:

Based on 1 kg electro-oxidized starch the preparation experiment of starch based biodegradable plastic was carried out. The experiment conditions were as follows: urea concentration 50gm/kg electro-oxidized starch, pH was 7, curing time 2hrs, and curing temperature 100^{O}C. Figure (2a) represents the effect glycerin concentration on the degradation time of the obtained of the electro-oxidized starch base biodegradable plastic, while fig. 2b shows the nitrogen release due to change in glycerine concentration. The results shows that the as the glycerine concentration increases the time required for the degradation of the starch base biodegradable plastic increases too while the rate of nitrogen release decreases. At glycerin concentration 350gm/1 kg starch the degradation time reaches to about 16 months. More increment of glycerine concentration the obtained polymer not solid enough, paste like and easily soluble in water, so glycerine concentration of 350gm/1kg starch was chosen as the optimum concentration for the preparation of the biodegradable starch base polymer.

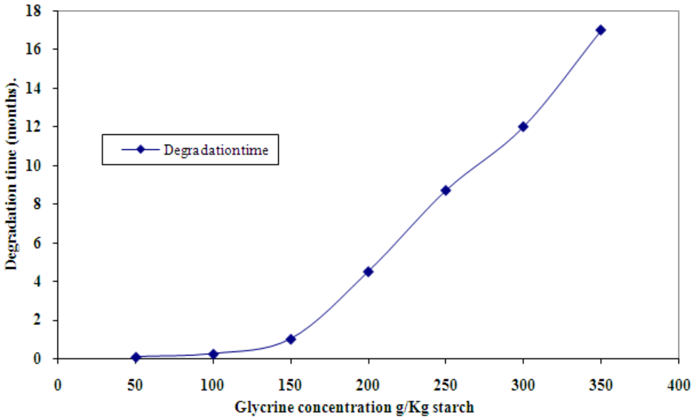

Fig. 2a: Effect of glycerine concentration on the dgradation time of the nitrogen slow release biodgradable plastic.

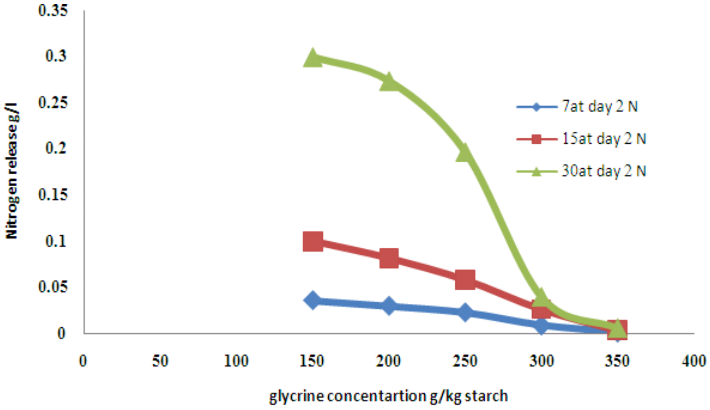

Fig. 2b: Nitrogen release due to change of glycrine concntration with respect to electro-oxidized starch.

Effect of Urea Concentration:

Biodegradable plastic based on 1 kg electro-oxidized starch was prepared using the optimum glycerine concentration obtained before (350gm/1kg starch) at experimental conditions: pH was 7, curing time 2hrs, and curing temperature 100^{O}C. Figure (3) represents the effect of varying urea concentration as nitrogen source on the degradation time of the electro-oxidized starch based biodegradable plastic. The results reveal that, as the urea concentration increases the required time for complete degradation of the obtained biodegradable plastic decreases reaching its minimum period 10 days at urea concentration 1000gm/1kg electro-oxidized starch.

At low urea concentration the life time or the degradation time of the obtained polymer increases reaching to its maximum period at 50gm urea for each 1kg of electro-oxidized starch where they obtained degradation time is about 20months. Although 50gm urea per 1kg electro-oxidized starch was represent the maximum degradation time but 300gm urea per 1kg electro-oxidized starch was taken as optimum urea concentration in the formulation of biodegradable plastic to increase nitrogen content per formulation due to industrial concept.

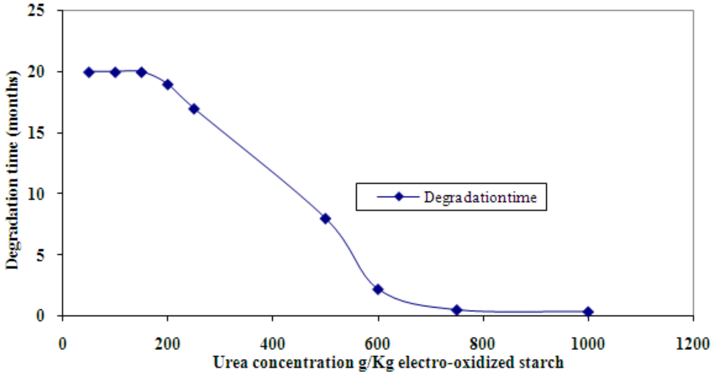

Fig. 3: Effect of urea concentration on the degradation time of the nitrogen slow release biodegradable plastic.

Effect of pH variation:

It is clear from figure 4a that as the pH increases the required time for complete degradation of the obtained biodegradable plastic increases to reach its maximum period 16months at pH 7, where the degradation time was 15 days then start to decrease as the pH increases reaching its minimum degradation period at pH 9. Also fig. 4b shows as the pH increases from 2 to 4 the rate of nitrogen release increases then start to decrease with increment of pH. Based on the above pH 7 was taken as the optimum pH for the preparation of the nitrogen slow release biodegradable plastic.

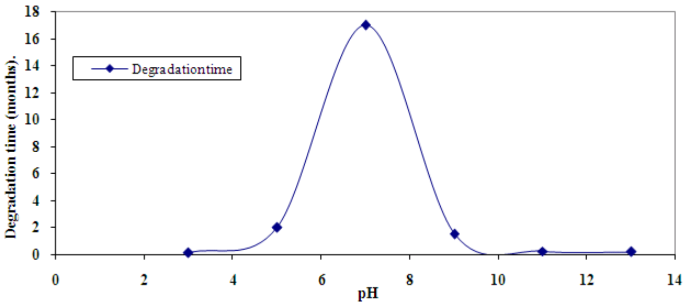

Fig. 4a: Effect of pH on the degradation time of the nitrogen slow release biodegradable plastic.

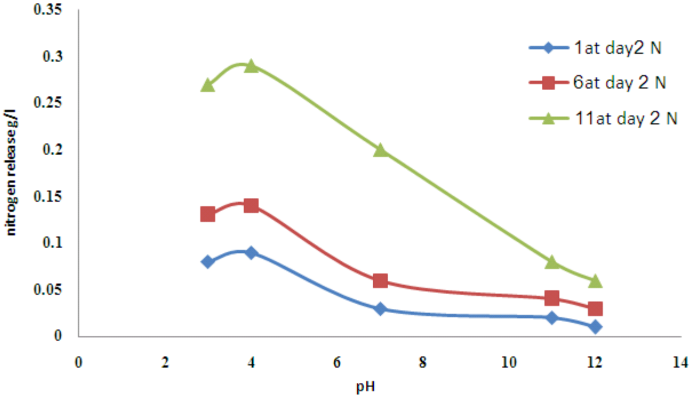

Fig. 4b: Effect of pH on nitrogen release.

Effect of curing temperature:

Figure 5, represents the effect of curing temperature on the degradation time of the obtained nitrogen slow release biodegradable plastic. The results shows as the curing temperature increases, the degradation time increases to reach to its maximum at curing temperature 120°C where the degradation time was 17months. Then as the curing temperature increases the degradation time decreases, so curing temperature of 120°C was selected as optimum for preparation of nitrogen slow release biodegradable plastic.

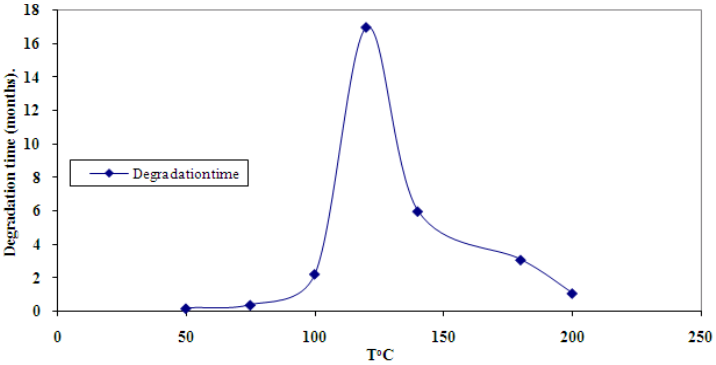

Fig. 5: Effect of reaction temperature on the degradation time of the nitrogen slow release biodegradable plastic.

Effect of curing time:

Fig. (6) Represents the effect of curing time on the degradation of the obtained nitrogen slow release biodegradable plastic. The results shows as the curing time increases, the degradation time increases too reaching to its maximum at curing time 4hrs, then any increment in curing time no change in degradation time was obtained, so curing time of 4hrs was selected as optimum for preparation of nitrogen slow release biodegradable plastic.

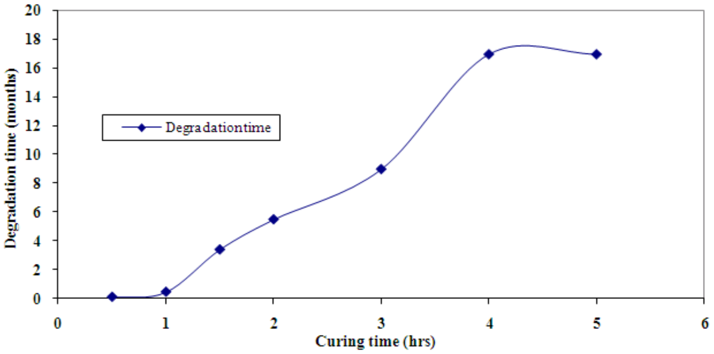

Fig. 6: Effect of curing time on the degradation time of thenitrogen slow release biodegradable plastic.

Based on the above obtained results the following conditions were selected as the optimum conditions for the preparation of nitrogen slow release biodegradable plastic. These conditions were glycerine concentration was 350g/kg electro-oxidized starch, urea concentration of 300g/kg electro-oxidized starch, pH of 7, curing temperature of 120°C, and curing time of 4hrs. The nitrogen slow release biodegradable plastic prepared at the above selected conditions was soaked in water and nitrogen concentration was measured with soaking time as presented in fig. 7. The results shows that as the soaking time increases nitrogen concentration also increases reaching its maximum at 450 day where the nitrogen concentration was 0.09g/l. the nitrogen concentration in the obtained product was 10% by weight.

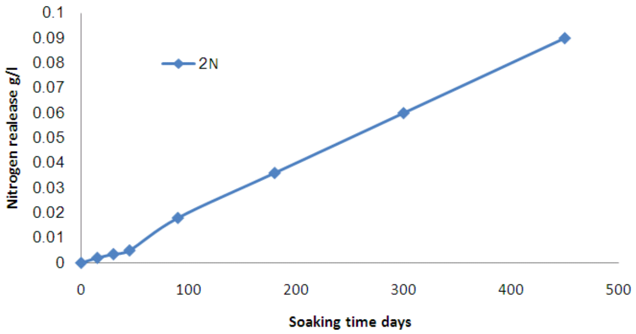

Fig. 7: Nitrogen release with respect to soaking time for the nitrogen slow release biodegradable plastic prepared at the selected optmium conditions.

Nitrogen release kinetic study:

The obtained biodegradable plastic slow release fertilizer was subjected for kinetic study. The cumulative released nitrogen was plotted against time and different kinetic equations were fitted to the data. The kinetic equations used to describe the rate of nitrogen release from the biodegradable plastic fertilizer are presented in Table 2. The goodness of fit of each kinetic equation was evaluated according to its coefficient of determination (R^2). With respect to Pseudo- first order reaction to describe the releasing process of nitrogen in water as a model for real soil nutrient (nitrogen), the following equation could be used.

$-dC_N /dt = k (C_{n\ eq.} - C_n)$
$Ln(C_{n\ eq.} - C_n) = -kt - \ln(C_{n\ eq.} - C_{ni})$
Where:
C_n = Concentration of nitrogen in mg/ Kg of water at time, t
$C_{n\ eq}$= Equilibrium concentration of nitrogen in mg/ Kg of water.
C_{ni} = Concentration of nitrogen in mg/ Kg of water at initial time, t=0
With respect to pseudo second order regression model between cumulative nitrogen release the following equation could be obtained
$\mathbf{-dC_n /dt = k (C_{n\ eq.} - C_n)^2}$
By integrating both sides, the following equation will be formed
$\mathbf{1/ (C_{n\ eq.} - C_n) = k\ t + 1/ (C_{n\ eq.} - C_{ni})}$

Reaction Order	Kinetic equation	Rate constant	R^2
Zero-order	C_n = 7E-06t + 0.002	$7*10^{-6}$	0.955
First-order	$Ln(C_{n\ eq.} - C_n) = -0.00001t - 2.133$	0.00001 hr^{-1}	0.915
Second-order	$1/ (C_{n\ eq.} - C_n) = 0.002\ t + 9.569$	0.002 g l^{-1} hr^{-1}	0.962

Table 2 shows the kinetic equations, rate constants and R^2 of the proposed reaction orders. It appears that the zero-order equation, first order equation, and the second order equation can all very well describe the experimental data with slight difference in fitting data, indicated by comparable correlation coefficients. But table 2 shows the best fit for data with rate constant of 0.002 g l-1 hr-1 for pseudo second order reaction kinetics which can be attributed to the slow dissolution rate of nitrogen from urea coated biodegradable plastics due to its dependence on square the concentration of cumulative nitrogen released from biodegradable plastics. It is illogical to believe the independence of dissolution rate of nitrogen on nitrogen concentration present in biodegradable coatings.

Conclusion:

Controlled slow release nitrogen compound based on biodegradable plastic which could be used as slow release fertilizer was prepared via the reaction of glycerine, urea, and oxidized starch prepared using the electrogenerated mixed oxidants. The Optimum synthesis conditions were glycerine concentration 350gm/1kg starch, urea concentration 300 gm/1kg oxidized starch, pH 7, curing temperature 120°C, and curing time of 4hrs. The synthesis conditions of inversion suspension polymerization were studied systematically. The water absorbency of the product was 91 g/g in tap water. The slow release properties of prepared biodegradable plastic also investigated. The results showed that the product had high degradation time of 450 days. The kinetic study shows that the nitrogen release rate from the obtained biodegradable plastic polymer could be represented by pseudo second order equation.

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