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Review

Role of inhibitors and biodegradable material in mitigation of nitrogen losses from fertilized lands

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Loss of N, occurring mainly through NH_3 volatilization, biological denitrification, and NO_3^- leaching, has both economic and environmental implications. Therefore, the economic benefits of reduced environmental pollution and future damage to our environment as a result of the use of urease inhibitors are of higher significance to the production of gains over the long-term. The literature review discussed the role, effectiveness and mechanism of urease inhibitors as well as coating of urea to reduce ammonia volatilization loss from urea fertilizer. Coating with urease inhibitors can improve the bioavailability of N, resulting in increased dry matter yield and N uptake. Such increases result from delayed urea hydrolysis by urease inhibitors and coating materials. The value of inhibitors in mitigating N loss would depend on their rate of biodegradation and persistence in soils. Previous studies has proven that micronutrients could be competent urease inhibitors, but the information about their effects on soil, nutrient uptake of plants and dry matter yield is poorly documented. Some nutrients such as Cu and Zn as urease inhibitors and natural biodegradable material such as agar, gelatin and palm stearin were found effective in reduction of nitrogen losses from nitrogen fertilizer especially from urea fertilizer. The article deals with the importance of use of above mentioned materials and micronutrient.

Key words: Nitrogen, urea, fertilizer, inhibitors, biodegradation, land, nitrogen loss.

INTRODUCTION

Nitrogen is a mobile nutrient, thus, it easily moves and losses quickly from soils. Agricultural soils need a continuous supply of N from various sources to maintain productivity. Most agricultural land is deficient in nitrogen (N) for the growth of crops.

There are a variety of nitrogenous fertilizers available in the market; however, urea consumption is 38%, which is higher than other nitrogenous fertilizers due to the relatively low manufacturing cost and high concentration of N (Bouwman et al., 1997). Urea is a widespread, major form of N produced and used by agricultural world. Urea consumption ranged from about 67,146,000 tons during 2008 and 2009 (IFA, 2008) (Figure 1); however, there is concern about the efficiency of using urea-N for agricultural crops because farmers' practices in Asia commonly result in recoveries of <40% of the applied N (Malhi et al., 2001).

The addition of urea to soil not only increases plant productivity but also results in increased nitrate (NO_3^-) leaching as well as the release of gaseous N, such as ammonia (NH_3) and nitrous oxide (N_2O), which are detrimental to the environment. Urea volatilization is a function of several factors which includes:

1. Hydrolysis rate
2. Equilibrium reactions
3. NH_3 exchange between the soil and the atmosphere
4. Exchange between NH_4 in solution and exchange sites in the soil.

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Abbreviations: N, Nitrogen; **NIs,** nitrification inhibitors; **UIs,** urease inhibitors; **CRF,** controlled release fertilizers; **SRF,** slow release fertilizers.

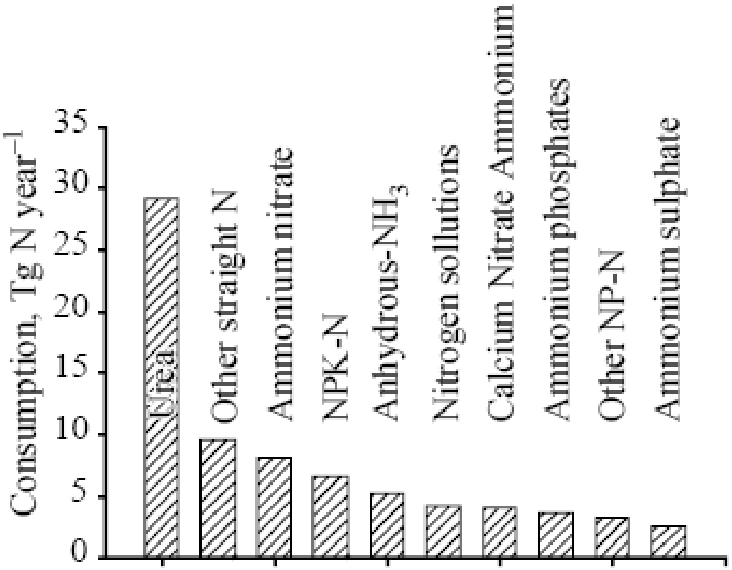

Figure 1. Global consumption of mineral fertilizers (IFA, statistics 2008 to 2009).

Gaseous emissions of N, via ammonia (NH_3) volatilization and denitrification, have been identified as the dominant mechanisms of fertilizer N loss in many different agricultural systems (Peoples et al., 1995). There has been a concern to improve the effectiveness of urea fertilizers via the use of coatings or modifications using various urease inhibitors and synthetic materials to mitigate N loss.

NITROGEN DYNAMICS IN SOIL

It is important to understand the process of N transformation in soil and the biochemical mechanism involved in alleviating N loss through the use of inhibitors (Singh et al., 2004).

Nitrogen mineralization

In nitrogen mineralization, plant in unavailable organic forms is converted into plant-available inorganic forms through the activity of soil micro-organisms. The process includes two reactions, which include the following: ammonization and ammonification (Figure 3).

Ammonization is a microbial process, in which micro-organisms first hydrolyze macromolecules of organic N compounds. In ammonification, micro-organisms convert amines and amino acids into NH_4^+ ions. For example, urea ($CO(NH_2)_2$) in fertilizer undergoes an ammonification reaction, releasing NH_4^+ ions. This process is also known as ‘urea hydrolysis’ and is carried out in the presence of urease enzymes in soil. Urease is an enzyme produced by some microbial and plant species. The ammonification process also releases hydroxyl (OH^-) ions and increases soil pH around urea granules, resulting in alkaline conditions. The high NH_4^+ ion concentration and the elevated pH during the ammonification reaction provide ideal conditions for ammonia volatilization to occur (Singh et al., 2008).

$$CO\,(NH_2)_2 \rightarrow 2NH_4{+} + 2OH^- + CO_2 \quad (1)$$

Ammonia volatilization loss

The total ammonical N in a soil solution comprises of two principle forms of N (NH_4 and NH_3). When NH_3 is present in a soil solution, the physical process of NH_3 transfer across a water surface (in contact with the atmosphere) is described by the simple reaction:

$$NH_3\ (aq) \rightarrow NH_3\ (gas\ air)$$

Some of the most important factors regulating NH_3 loss are the concentration of ammonical N, the temperature and the pH of the soil solution or irrigation water; moreover, all three variables markedly affect the partial pressure of NH_3 (Singh et al., 2008).

The pH in particular, affects the equilibrium between ammonium and NH_3 so that the relative concentration of NH_3 increases from 0.1 to 1, 10 and 50% as the pH changes from 6 to 7, 8 and 9, respectively (Freney et al., 1983). The high soil pH (> 7) favors ammonia volatilezation. In the case of urea application, the initial increase

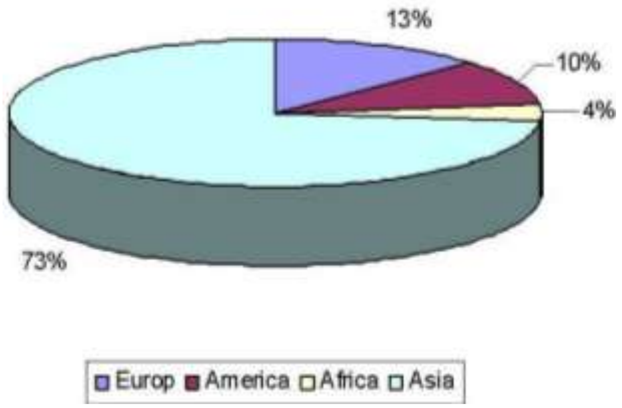

Figure 2. World production of urea (IFA, statistics 2008 to 2009).

in soil pH through the ammonification process results in NH_3 volatilization (Figure 2).

$$NH_4{+} + OH^- \rightarrow NH_3 \uparrow + H_2O \text{ (pKa 7.6)}$$

The lost NH_3 is consequently deposited on land or in water, which causes eutrophication and acidification of natural ecosystems on a regional scale (Sommer and Hutchings, 2001).

As temperatures rises, the relative proportions of NH_3 to ammonium present at a given pH increases, while the solubility of NH_3 in water decreases (Figure 4), which increases the diffusion of NH_3 through the soil solution and affects the rate of microbial transformations. The rate of urea hydrolysis in soil and NH_3 volatilization are greatly affected by soil temperature (Vlek and Carter, 1983; Carmona et al., 1990). Wind speed is another major factor that controls volatilization (via its effect on mixing in the liquid phase) as well as the rate of transport of NH_3 away from the air-water or air-soil interface (Freney et al., 1981; Denmead et al., 1982; Fillery et al., 1984).

Other variables that influence NH_3 volatilization include the pH-buffer capacity, cation exchange capacity of the soil, levels of urease activity, and the availability of moisture, soil texture, nitrification rate, and the presence of plants or plant residues (Freney and Black, 1988).

Large losses of NH_3 from applied fertilizer have been detected from soil, floodwater and irrigation water in many agro ecosystems (Freney and Black, 1988; Peoples et al., 1995). Losses of NH_3 measured from different upland and lowland cropping systems have ranged from negligible amounts to > 50% of the fertilizer N applied, depending upon fertilizer practices and environmental conditions (Bacon et al., 1986; Keller and Mengel, 1986; Black et al., 1989; Freney et al., 1992). In flooded rice, NH_3 volatilization can account for 20 to > 80% of the total N lost from fertilizer sources (Simpson et al., 1984; De Datta et al., 1989; Freney et al., 1990; Mosier et al., 1989; Zhu, 1992). Ammonia emission can be reduced by reduction of ammonical N in soil solutions through microbial processes, such as leaching, cation exchange complex, immobilization and nitrification.

Immobilization

Immobilization is a microbial process, in which the plant-available in NH_4^+ and NO_3^- ions are converted to plant unavailable organic N. For instance, the addition of carbon (C)-rich substances in arable soils promotes immobilization and reduces N availability to plants. When the N content of the decomposing organic matter is small, a reduction in N availability occurs because microbes become deprived of N and compete with plants for available N in soil. Thus, the addition of organic matter with high C:N ratios causes immobilization of soil N by micro-organisms, thereby decreasing the amount of plant-available soil N (Singh et al., 2008).

Nitrification and denitrification

Nitrification is the oxidation of ammonium to nitrate. In soil, the process is mediated by some bacteria. The effect of soil water content on N transformations can be observed by its effect on oxygen diffusion.

The nitrification process is dependent upon the movement of ammonium into the oxidized zone to be processed by nitrifying organisms. The transport of NH_4 by diffusion is affected by both the organic matter status and the cation exchange capacity of the soil as well as the presence of reduced iron and manganese, the bulk density and the rate of nitrification in the oxidized soil layer (Peoples et al., 1995).

The mechanism of denitrification involves the transformation of nitrate and nitrite to NO, N_2O and N_2. Soil factors that significantly influence denitrification are oxygen (which is controlled primarily by soil water content), nitrate concentration, pH, temperature and organic carbon (Peoples et al., 1995). Soil water tends to moderate oxygen diffusion in soil, and denitrification occurs only when the soil water content is > 60% of the air-filled pore space in flooded rice fields (Linn and Doran, 1984). Soil organic matter provides energy for denitrified growth as well as supplies of protons and electrons for the reduction process. In crops, the effect of application timing of fertilizer on N loss by denitrification may be more related to precipitation rate.

Ammonia fixation

The influence of the NH_4 fixation capacity of soil on gains and losses has not been fully ascertained; however, there is some evidence that the quantities of fixed NH_4 do not change greatly over long periods of time when concurrent

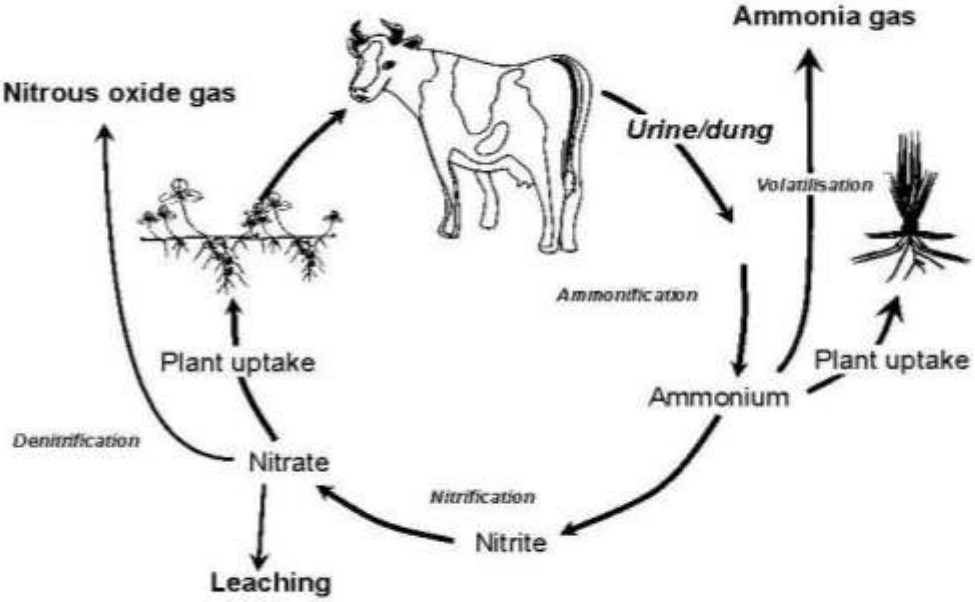

Figure 3. Schematic representation of nitrogen transformation (Singh et al., 2008).

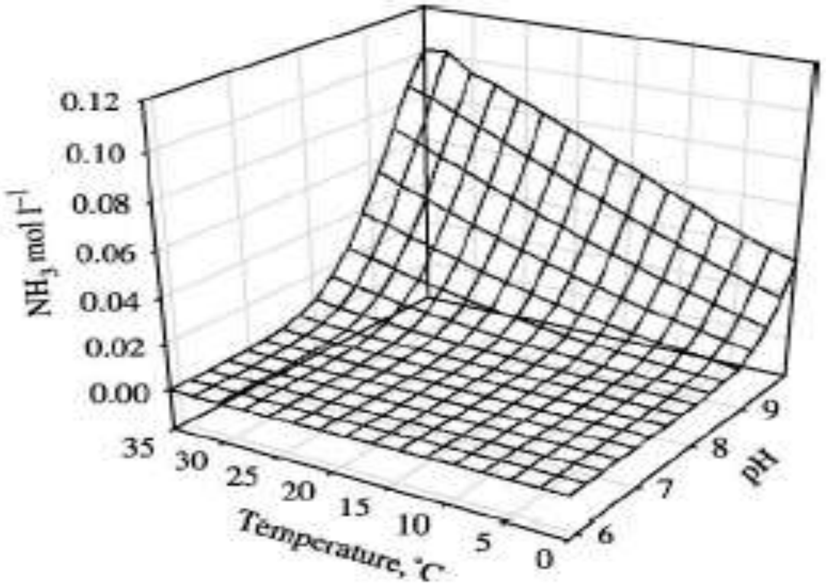

Figure 4. Effect of pH and temperature in a soil solution of total ammonical N (Sommer et al., 2002).

changes on soil organic N have occurred (Jaiyebo and Bouldin, 1997). Fixation can influence NH_4-N transformation by reducing NH_3 loss and nitrification rates. In a ^{15}N balance study, Kowalenko (1998) found that 59% of the $^{15}NH_4$ applied to the 0 to 15 cm layer of an ammonium-fixed clay loam soil was immediately fixed by clay minerals.

Leaching losses

Leaching is very common in Malaysian soils due to the high annual rate of rainfall. Losses occur mainly as NO_3, the movement of which is closely related to water movement. Major losses of N occur when soil NO_3 content is high and water movement is large.

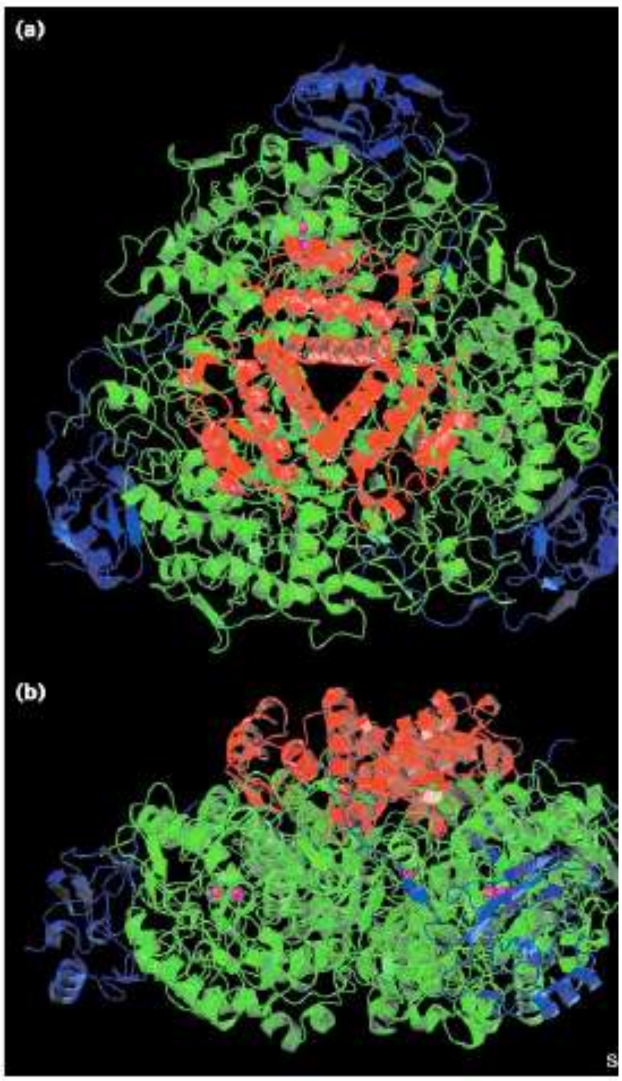

Figure 5. Ribbon diagram, Urease enzyme, the blue green and red presenting the sub units (Stefano et al., 1998).

Leaching losses are also strongly influenced by seasonal effects, such as water and temperature. In humid regions, mineralization rates are low in water, but leaching of residual NO_3 from the previous season often occurs. In the spring, NO_3 accumulates as nitrification rates increases, and N fertilizers are applied. Nitrate leaching is least likely to take place during the summer. Leaching not only depletes NO_3^-N but also takes away clay, soil and organic matter, which leads to low chemical and low plant available water reserves (Allison, 1993).

Temporal ammonia loss pattern from urea fertilizer

When urea is applied on the soil, it absorbs water and is hydrolyzed, producing ammonical nitrogen and bicarbonate (HCO_3). The rate of hydrolysis is related to the amount of soil moisture and temperature. The NH_3 loss rate decreases after 5 to 10 days due to a reduction in NH_3 concentration through various processes, such as volatilization, leaching, denitrification and immobilization (Black et al., 1985; Haynes and Williams, 1992). The maximum NH_3 volatilization loss rates may occur within 1 to 10 days after application, depending on the soil and environmental conditions (Stevens et al., 1989). The pattern of NH_3 volatilization from urea is affected by applied forms of urea despite whether it is applied in pellets, in solution, or crushed to a fine powder because the release and hydrolysis of urea into the soil solution is different. From urea applied in different forms, such as powder or in solution, the ammonia volatilization occurs earlier than after application of urea. This delay in emission from urea is related to hydrolysis of the applied urea.

UREA HYDROLYSIS

Urea, an odorless, white, crystalline water- soluble solid, is a diamide of carbonic acid. In soil, urea decomposes enzymatically to CO_2 and NH_4. The urease enzyme (Figure 5) present in soil, plants and plant litter is responsible for the urea hydrolysis process (Freney and Black, 1988)

The urease active site consists of two nickel (II) atoms linked by a carbamate bridge. Two imidazole N atoms bind to each Ni atom, with a carboxylate group and water molecule filling the remaining coordination sites of the metal ion. The capacity to hydrolyse urea varies from 17 to 70% for soil bacteria and from 78 to 98% for soil fungi (Lloyd and Sheaffe, 1973). However, soil urease is considered to be of microbial origin, and there is indication that some soil urease activity may be derived from plants (Frankenberg and Tabatabai, 1982).

Factors affecting urea hydrolysis

Urease activity of soils is associated with organic matter, soil pH, temperature, moisture and urea concentrations (O'Toole et al., 1982; Reynolds et al., 1985; Kissel and Cabrera, 1988). Urease activity decreases when the organic matter content of soil decreases with depth (Bremner and Mulvaney, 1978; Mulvaney and Bremner, 1981).

Effect of pH on urea hydrolysis

Urease enzymes are responsible for the hydrolysis of urea fertilizer (into NH_3 and CO_2) applied to the soil, with the concomitant rise in soil pH (Byrnes and Amberger, 1989) resulting in rapid N loss to the atmosphere through NH_3 volatilization (Filleryand Freney, 1988).

The rate of urea hydrolysis was measured under laboratory conditions using soils with a range of pH values (from 2.2 to 8.0). It has been reported that soil pH

Table 1. Fatty acid content of Palm stearin.

Type of fatty acid	Colour	Content (%)
Lauric saturated C12		48.2
Myristic saturated C14		16.2
Palmitic saturated C16		8.4
Capric saturated C10		3.4
Caprylic saturated C8		3.3
Stearic saturated C18		2.5
Oleic monounsaturated C18		15.3
Linoleic polyunsaturated C18		2.3
Other/Unknown		0.4

Red, saturated; orange, monounsaturated; blue, polyunsaturated (Hyes and Khosla, 1992).

increases as the rate of urea hydrolysis increases, and the highest rate of hydrolysis was observed at pH 8.0 (Ahmed et al., 2006) Table 1.

Effect of temperature on urea hydrolysis

Hydrolysis of urea is temperature dependent and increases with increasing soil temperature over the range from 0 to 40°C (Vlek and Carter, 1983); however, slight hydrolysis has been detected at sub-zero temperatures as well (Bremner and Mulvaney, 1978). It was found that as temperature increases, the rate of dissolution of urea in water increases. Urea hydrolysis is accelerated by increasing temperatures in part because the rate of urea diffusion is positively correlated with temperature.

Moreover, urease is an extra cellular enzyme produced by microorganisms, and high temperatures can increase both microorganism growth and urease production. Moyo et al. (1989) found that increasing temperature (from 5 to 45°C) greatly increases urease activity. Urease activity reaches a maximum between 60 and 70°C.

Effect of urea concentration on urea hydrolysis

Urea hydrolysis is also influenced by urea concentration, soil water and soil pH. The optimum pH for urea hydrolysis is between 6.0 to 7.0 (Kissel and Cabrera, 1988). When urea is applied to the soil, the concentration may range from 0.01 to 10 M. There is a possible existence of two reactions, one with high affinity and one with low affinity for urea. The high affinity reaction is responsible for most of the urea hydrolysis at urea concentrations lower than 0.1 M. In general, the urea N concentration, at which both affinity enzyme reactions contribute equally, is 0.5 M. Cabrera et al. (1991) found that when urea concentration is > 6 M, the rate of urea hydrolysis decreases, which is possibly due to enzyme denaturizing (Kistiakowsky and Rosenberg, 1952).

Effect of moisture on urea hydrolysis

Soil moisture content is one of the important factors affecting urea hydrolysis because urea is a hygroscopic material and absorbs water through contact with liquid water as well as from water –vapor in the air (Wahl et al., 2006). After application of urea to soil, the process of dissolution of urea initiates immediately because urea is a compound that is highly soluble in water (about 1080 gL^{-1} can be dissolved at 20°C) (Wahl et al., 2006).

Strategies to reduce ammonia volatilization loss from urea fertilizer

There are several strategies that have been adopted to reduce ammonia volatilization loss, such as fertilizer placement and time of applications as well as amendment of acidic materials and the use of polymers and other chemicals as coatings.

Modification in placement, rate and method of fertilizer application

Placement of urea in the lower zone is related to soil properties, and this strategy is not very useful for sandy and peat soils because in sandy soil, urea diffuses to the surface very fast and is lost (Blaise et al., 1996), and in peat soils, it may cause toxicity to plant roots due to high concentrations of NH_4.

The placement of urea is directly related to the rate of application in calcareous soils. High application rates should be placed at a greater depth than low application rates of fertilizer due to heavy N losses in theses soils (Fenn and Miyamoto, 1981; Ismail et al., 1991).

In contrast on acidic soils, NH_3 emission has increased due to the high rate of fertilizer applications because the addition of high rates of fertilizer increases the fertilizer micro site pH, which results in a high accumulation of NH_4 on soil surface (Rachhpal and Nye, 1984).

Methods of fertilizer application have also been considered to reduce ammonia loss. It has been suggested that application of urea in split doses with band applications instead of broadcasting could be helpful in reducing ammonia loss (Rachhpal and Nye, 1984).

Amendment and coating of urea with chemicals

Amendments or applications of urea mixed with inorganic salts and acidic materials, such as humic acid, $CaCl_2$ and KCl, may reduce NH_3 emission significantly (Fenn et al., 1982; Ahmed, 2008).

Controlled/Slow release fertilizers (CRF/SRF)

Controlled release fertilizers (CRF) have been shown to increase plant yields in some but not all studies (Shoji et al., 2001; Chen et al., 2008), and in some studies, reduced N_2O emissions have been observed (Shoji and Kanno, 1994). Controlled release fertilizers are used only to a small extent in agriculture which is mainly due to their high cost (Chen et al., 2008).

CRFs, in which a physical barrier is used to reduce dissolution rate, are commonly prepared by coating (or matrix formation) of water soluble, granular plant nutrients with low permeability and hydrophobic membranes (Shaviv and Mikkelson, 1993). The nutrient in CRF is made to release its contents gradually and to coincide with the requirements of the plant. This fertilizer can be physically prepared from granules of the soluble fertilizers by coating them with materials, which reduce their dissolution rate, and it also causes an increase in the fertilizer efficiency, reduces soil toxicity, minimizes the potential negative effects associated with over dosage and reduces the frequency of application (Tomaszewska et al., 2002).

The control of fertilizer release keeps its' concentration at effective levels in soil and releases nutrients when they are most needed by the plant. As a result, maximum utilization of the fertilizer from the plant system reduces nutrient loss, decreases fertilizer rate and applications, prevents seedling damage, and provides full protection of the environment.

By adopting specific fertilizer formulations and techniques to improve fertilizer efficiency, it should be possible to provide sufficient N in a single application to satisfy plants' needs. If this could be done, any N loss event would be small because of the limited amount of N in the substrate.

Various slow-release forms of N have been suggested, including the following: coated fertilizers (Shoji et al., 1991), complex organic N compounds that are much less soluble in water than urea (Oertli, 1980; Allen, 1984) and urea super granules (Youngdahl et al., 1986).

The effect of slow-release forms on levels of soil mineral N as well as the recovery of fertilizer N have been assessed, and the use of these products has generally decreased total loss of fertilizer N (Chauhan and Mishra, 1989; Malhi and Nyborg, 1992). Sulfur coated urea has the potential to reduce ammonia emission, but it may not be very significant in all environments. For example, in a study by Black et al. (1985), NH_3 emission from sulfur-coated urea was lower than from untreated urea (10.1% as compared with 12.6%). Sediments of pyrite (FeS) have been shown to reduce emission from urea by 54% (Blaise et al., 1996), and a 10% reduction in hydrolysis rates was reported by amending urea with thiosulfate under drying conditions (Black et al., 1985).

USE OF INHIBITORS

Urea N use efficiency could be enhanced if the hydrolysis of urea to ammonium by soil urease could be retarded by the use of urease inhibitors. UIs (Urease Inhibitors) slow the conversion of urea to NH_4^+ by inhibiting the urease enzyme, which reduces the NH_4^+ concentration in the soil solution and hence, lowers the potential for NH_3 volatilization and seedling damage; slow urea hydrolysis allows more time for it to release nitrogen from the fertilizer micro site.

Mechanism of Inhibition of Urease

A number of chemicals have been tested as potential inhibitors of soil urease activity for use with urea fertilizers. These chemicals can be divided into three groups according to their structures and binding modes with urease, including the following; (1) reactive organic or inorganic compounds, (2) chelating compounds that cause inhibition due to complex formation with one of the Ni atoms at the active site of urease, and (3) competitive inhibitors that resemble urea molecules and bind to the active site of the urease enzyme (Amtul et al., 2002).

Bioavailability of N with inhibitors

Plants take N both as NH_4^+ and NO_3^-. Synchronization of plant N uptake with released NH_4^+ or NO_3^- by controlling the rate at which urea (in applied urea) is hydrolyzed to NH_4^+ and its subsequent oxidation to NO_3^- as well as the temporary rise in soil pH is critical to minimize gaseous and leaching losses of N. Most plants prefer NO_3^- over NH_4^+; however, the rate of uptake of NH_4^+ is often found to be greater than that of NO_3^-, especially at low temperatures. Since plant roots can absorb both NH_4^+ and NO_3^- ions, ammonification and nitrification processes markedly influence N absorption efficiency by plants, mainly by controlling the concentrations of these ions in soil solution. It has often been observed that while UIs decrease the concentration of NH_4^+ ions, Nis (nitrification inhibitors) increase the concentration of NH_4^+ ions and decrease NO_3^- ions. Urease inhibitors slow down urea hydrolysis and, thus, keep N in urea form (Bremner et al., 1991; Wang et al., 1991; Watson et al., 1994b).

In the presence of sufficient sun light as a source of energy, N assimilatory enzymes (NO_3^- reductase) in plants rapidly reduce NO_3^- to NH_3, which is then assimilated into glutamine and glutamate. Glutamine, glutamate and organic acids produced from carbohydrate metabolism then serve as N donors in the biosynthesis of amines, amides and essentially all amino acids and nucleic acids. The amino acids serve as building blocks for the synthesis of proteins; thus, NO_3^- reduction occurs both in aerial portions (shoots and leaves) as well as in the roots of plants, with most reduction occurring in shoots. The relative importance of these two sites of NO_3^- conversion is considered most important.

It is obvious that the rate of NH_4^+ assimilation is faster than that of NO_3^- because the former is directly incorporated into organic compounds. To maintain a charge balance, plant uptake of NH_4^+ and NO_3^- affects the pH of rhizosphere by releasing either hydrogen (H^+) or hydroxyl (OH^-) ions. The release of such ions by plants also affects the uptake of other anions and cations. For example, NH_4^+ absorption reduces the uptake of cations such as calcium (Ca^{++}), magnesium (Mg^{++}) and potassium (K^+) and increases the uptake of anions, such as phosphate and sulphate. NO_3^- uptake reduces the absorption of anions.

Many studies have been carried out in different agricultural systems that have stated that the application of N fertilizer with UIs or NIs improves the bioavailability of N, resulting in increased plant production and N uptake (Watson et al., 1998; Xu et al., 2002; Zaman et al., 2005). Such increases are always attributed to slow urea hydrolysis by UIs. Increase of 20, 17 and 15% in pasture production have been reported from urea applied with UI, NI and UI+NI, respectively (Zaman et al., 2005). Increase in dry matter production have been obtained from urea applied with UIs. This high, dry matter yield and N uptake with inhibitors can be attributed to the retention of applied N as mineral N or organic N in the soil profile, which consequently becomes available for plants.

Effect of inhibitors on N loss

Many research studies have confirmed that inhibitors are effective in delaying the conversion of either urea to NH_4^+ (UIs) or NH_4^+ to NO_3^- (NIs). Most research has shown that the application of UIs to soil with urea reduces NH_3 volatilization, while the application of NIs reduces NO_3^- leaching as well as N_2O emissions. Some studies also have shown that NIs increases NH_3 volatilization (Davies and Williams, 1995; Nastri et al., 2000).

Treating urea with urease inhibitors reduces NH_3 loss from surface applications (Bremner et al., 1991; Clay et al., 1990; Carmona et al., 1990). Laboratory (Carmona et al., 1990; Vittori-Antisari et al., 1996) and field studies (Rawluk et al., 2001; Watson et al., 1994a) have reported increased inhibition of urease activity with an increasing rate of UI, which followed the law of diminishing returns (Watson et al., 1994b).

The environmental concern over the use of toxic and hazardous chemicals is increasing worldwide. There are many such chemicals polluting the environment, with their damage depending on their exposure and persistence in the ecosystem as well as the characteristics of the affected organisms (Hashim et al., 1992).

In general, soil microorganisms readily degrade natural polymers because they contain chemical bonds that may be broken down through enzymatic hydrolysis in soil. Synthetic polymers are not degradable and are more resistant to biological breakdown; however recently, there have been some degradable synthetic polymers introduced (Devassine et al., 2002).

Use of micronutrients as urease inhibitors

Some micronutrients (Cu and Zn) were investigated as competent urease inhibitors. These micronutrients have a crucial value in the growth of plant. Before describing their inhibitory effects, it is important to understand their role in plant production and status in soil. Copper is an essential element for all crops, and it influences both carbohydrate and nitrogen metabolism in plants (Mengle and Kirby, 1987). Cu is present in soils as oxides, carbonates, silicates and sulfides. Copper availability decreases in soil solutions due to adsorption of Cu in soil exchange complexes, as well as due to chemical fixation of Cu as sulfides (Lea et al., 1993). Soil Cu availability depends on soil pH; it is lower in the alkaline range and higher in the acidic range. Most Cu deficiencies occur in sandy soils, which have a high pH, or on soils with a 5% higher organic matter content (Johne, 1983).

Zinc is an essential nutrient that plays an important role in plant growth. It is an important part of protein that works as a synthesizer of sugars and starch (Marschner, 1995; Sharma, 2006). Zinc is the most common crop micronutrient deficiency, particularly in high-pH soils. Notably, 50% of cultivated soils in the world are classed as Zn-deficient (Graham et al., 1992; White and Zasoski, 1999; Cakmak, 2002, 2004; Alloway, 2004).

Cu and Zn were firstly tested as urease inhibitors in 1971 by Bremner and Douglas. The authors observed that NH_3 volatilization loss from urea, that is surface applied to soil can be mitigated by 30.3 and 24.6%, and N-use efficiency improved by 28.3 and 23.9% if urea was amended with $CuSO_4$ (Reddy and Sharma, 2000). In their study, copper amended urea was applied to reduce urea volatilization loss and to provide Cu as a micronutrient. This approach has been shown to be effective (Leong, 2002). The amendment of urea with $ZnSO_4$ can improve the agronomic efficiency of fertilizer by 11% (Purakayastha and Katyal, 1998).

FATTY ACIDS

Natural materials, such as natural oils and fatty acids, have been used to reduce nitrification loss and avoid environmental pollution. Some natural products, such as karanjin, neem, tea waste and mint oil, can reduce nitrification significantly (Sahrawat, 1987; Patra et al., 2009). It was observed that the constituents of fatty acid are linolenic acid, and lanoleic acid, which have 98% inhibitory effects on nitrosamine successfully reduce nitrification loss (Subbarao, 2008).

Palm stearin is one of the preferred natural and cost effective fatty acids used by many manufacturers in formulations of consistent fats, such as margarines, bakery fats and frying fats. It was also found that different dementholized oils and terpenes are potential retardants of urease activity and nitrification (Patra et al., 2009); palm stearin could be one of them. In addition, the coating by palm stearin enables Cu and urea to come together at the micro site.

Use of agar and gelatin as biodegradable polymers

Agar, the sea weed well known in commerce, is derived from several species of aquatic plants and is made principally from algae. The algae grow on rocks along the coast and are collected by divers between May and October, with the best months for collection being July and August. The weed is dried on the shore, and during the process, it is partially bleached and is then ready to be manufactured into the commercial product. The chemical formula of agar is $C_{11}H_{16}$ O_{10}, which is composed of crude protein, carbohydrates and crude fiber (Whittaker, 1910). Gelatin is the secondary product of collagen and is subjected to degradative processes. The properties of gelatin are similar to rigid-chain synthetic polymers.

Gelatin macromolecules assume, at high temperatures, the conformation of a statistical coil. Under specific conditions (temperature, solvent and pH), gelatin macromolecules can display flexibility sufficient to realize a wide variety of conformations (Kozlov, 1983). Gelatin mostly is a constituent of the shells of pharmaceutical capsules to make them easy to swallow.

These materials (agar and gelatin) were considered to be natural polymers (Ward and Courts, 1977) but were never used as a coating for fertilizer.

In the presented study, these materials have been used as adhesive agents of urease inhibitors, and a source of coating to release urea–N slowly from fertilizer.

CONCLUSION

Loss of N, occurring mainly through NH_3 volatilization, biological denitrification and NO_3^- leaching has both economic and environmental implications. Therefore, the economic benefits of reduced environmental pollution and future damage to our environment as a result of the use of urease inhibitors are of higher significance to the production of gains over the long-term.

The literature review discussed the role, effectiveness and mechanism of urease inhibitors as well as coating of urea to reduce ammonia volatilization loss from urea fertilizer. Coating with urease inhibitors can improve the bioavailability of N, resulting in increased dry matter yield and N uptake. Such increases result from delayed urea hydrolysis by urease inhibitors and coating materials.

The value of inhibitors in mitigating N loss would depend on their rate of biodegradation and persistence in soils. Previous studies has proven that micronutrients could be competent urease inhibitors, but the information about their effects on soil, nutrient uptake of plants and dry matter yield is poorly documented

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