International Journal of Applied Research 2017; 3(6): 323-325

International Journal of Applied Research

ISSN Print: 2394-7500
ISSN Online: 2394-5869
Impact Factor: 5.2
IJAR 2017; 3(6): 323-325
www.allresearchjournal.com
Received: 13-04-2017
Accepted: 16-05-2017

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Metal dialkyldithiocarbamates as soil nitrification inhibitors

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Abstract
Dimethyldithiocarbamate (DMDTC) and diethyldithiocarbamate (DEDTC) complexes of molybdenum (Mo), tungsten (W) and platinum (Pt) along with sodium diethyldithiocarbamate were screened for retarding nitrification in soil at three different concentrations i.e. 10 µg g^{-1} soil, 50 µg g^{-1} soil, and 100 µg g^{-1} under laboratory conditions. After 21 days, soil samples were treated with solutions / suspensions of metal complexes and analyzed for KCl-extractable ammonium-N and nitrate-N to estimate the extent of nitrification and then per cent nitrification inhibition was calculated. Molybdenum dimethyldithiocarbamate proved to be most effective in inhibiting nitrification in soil at 100 µg g^{-1} soil

Keywords: Metal dialkyldithiocarbamates, soil nitrification, environmental issues

Introduction

One of the most important environmental issues confronting agriculture is the loss of soil N derived either from fertilizer N or symbiotic N fixation by legumes, to the atmosphere as gases such as ammonia (NH_3) by direct volatilization, dinitrogen (N_2) and nitrous oxide (N_2O) by denitrification, or to groundwater via leaching as nitrate (NO_3^-). The losses of nitrogen lead to reduced N-use efficiency, and hence have economic implications as well.

Nitrogen is an important element for plant growth and reproduction. Although soil application of fertilizer nitrogen leads to increase in crop yields, portion of fertilizer nitrogen not utilized by plants can leach as nitrate below the root zone of plants and reach ground water bodies making it unfit for drinking purposes. Some attention has been given to the level of nitrate in drinking water and ground water bodies in India (Singh *et al.* 1995) [9]. Fertilizer N applied as urea or ammonium is converted to nitrate through a microbiologically controlled process called nitrification. Retarding nitrification in the soil can lead to high fertilizer N use efficiency and reduced production of nitrate-N which in turn leads to reduced losses of nitrate-N to ground water as well as production of N_2O, a gas known for enhancing greenhouse effect. One way to retard nitrification is the use of chemicals known as nitrification inhibitors.

Nitrification inhibitors restrict the microbiological conversion of ammonium (NH_4^+) to nitrate (NO_3^-). A large variety of chemicals can retard nitrification. These include: 2-chloro-6-(trichloromethyl)-pyridine (N-serve), 5-ethoxy-3-trichloromethyl-1, 2, 4-thiadiazol (Dwell), Dicyandiamide (DCD), 2-amino-4-chloro-6-methyl-pyrimidine (AM), 2-mercapto-benzothiazole (MBT), 2-sulfanilamidothiazole (ST), and Thiourea (TU). Metal dithiocarbamates are well known for their pesticidal properties (Malik, 1999) [4]. There also exist a few references in the literature highlighting soil nitrification inhibition capacity in these compounds. A well-known soil fumigant, Vapam, inhibits both ammonia and nitrate oxidation (Nishihara, 1962) [6]. Sodium diethyldithiocarbamate inhibited soil nitrification inhibition up to 12 per cent at 10 mg kg^{-1} concentration after 14 days of incubation (Bundy, 1973). Ammonium dithiocarbamate has also been identified as a potential nitrification inhibitor, although its commercial production has not yet started (Nelson and Huber, 2001) [5]. Benomyl, Mancozeb, Captan and Thiram are also known to be associated with inhibition of nitrification in soil either by affecting nitrifying bacteria or by impacting bacteria related to N and C cycling in soils (Yang *et al.* 2011) [11]. We have attempted to investigate the role of some transition metal dialkyldithiocarbamates as nitrification retardants in soils.

Materials and Methods

Synthesis of Metal dialkyldithiocarbamates

Metal dialkyldithiocarbamates, [{M $(R_2NCS_2)_n$}, M = Mo, W or Pt; alkyl = R_2 = $(-CH_3)_2$ or $(-C_2H_5)_2$], were synthesized by the reaction of sodium dialkyldithiocarbamate with corresponding metal halide in dichloromethane/water mixture (Arora *et al.* 2003) [1].

Soil

The soil was sieved through 2mm screen, mixed thoroughly, air dried and used for the experiment. A representative sample was drawn for the determination of organic carbon, pH and electrical conductivity (EC). The organic carbon content was determined by wet digestion method of Walkley and Black (1934) [10]. The characteristics of the soil under study were: organic carbon content (0.35%), pH 7.8 (1:2 soil: water) and EC 0.25 Sm^{-1} (1:2 soil: water).

Experimental setup

The experiment was conducted with 10g air-dried soil portions in 250 mL plastic bottles and treated with 1 mL of solution containing 2 mg nitrifiable nitrogen as ammonium sulphate. The stock solutions/suspensions (500 mg kg^{-1}) of metal complexes were prepared and these were serially diluted to obtain 250 mg kg^{-1} and 50 mg kg^{-1}. Two milliliter solution/suspension of the metal complex was applied to 10 g soil sample. The treatments were tested at field capacity moisture regime. The bottles, made in triplicate, were covered with parafilms having holes for aeration, were weighed and kept in incubator at 25±1ºC. The experiment was conducted for 21 days. Moisture loss during incubation was replenished every two days after weighing the bottles. Control was kept along with the treatments.

After 21 days, soil samples were analyzed for KCl-extractable ammonium-N and nitrate-N to estimate the extent of nitrification. The contents in bottles were shaken with known volume of 2N KCl for one hour. The suspensions were filtered and the filtrates were analyzed for NH_4^+ and NO_3^- forms of nitrogen following microkjeldahl method (Keeney and Bremner, 1966) [3]. A blank without soil was also carried out. The amount of ammonium and nitrate nitrogen was calculated using following formula:

$$14/1000 * a * b/c * 1/d * e * 10^6$$

Where

a = Normality of H_2SO_4 used (N)

b = Volume of KCl used for extraction + Moisture content of soil (ml)

c = Weight of soil taken (g)

d = Volume of KCl extract used for estimation of nitrogen (ml)

e = Volume of H_2SO_4 used for NH_4^+- N or NO_3^-- N (ml)

The per cent nitrification inhibition was calculated using the formula:

$$(C - S) / C * 100$$

Where C is the nitrification in control And S is the nitrification in treatment.

The results were analyzed statistically.

Results and Discussion

Metal dialkyldithiocarbamates, [{M $(R_2NCS_2)_n$}, M = Mo, W or Pt; alkyl = R_2 = $(-CH_3)_2$ or $(-C_2H_5)_2$], were synthesized by displacement reaction of sodium dialkyldithiocarbamate with corresponding metal chloride in dichloromethane/water mixture. The organic layer was dried over anhydrous sodium sulphate to get the crystals of resulting metal dialkyldithiocarbamate. The various synthesized complexes were characterized by elemental analysis, melting point, solubility, and infrared spectral studies (Arora *et al.* 2003) [1].

$$\underset{1}{n\,[(CH_3)_2NCS_2\text{-}Na]} + \underset{2}{MX_n} \xrightarrow{CH_2Cl_2/H_2O} \underset{3}{[(CH_3)_2NCS_2]_n\,M} + n\,NaX$$

$$\underset{4}{n\,[(C_2H_5)_2NCS_2\text{-}Na]} + \underset{5}{MX_n} \xrightarrow{CH_2Cl_2/H_2O} \underset{6}{[(C_2H_5)_2NCS_2]_n\,M} + n\,NaX$$

M = Mo, W or Pt

Metal dialkyldithiocarbamates as nitrification inhibitors

The soil samples were treated with metal (namely molybdenum, tungsten and platinum) complexes of dimethyldithiocarbamate and diethyldithiocarbamate at three different concentrations i.e. 10 µg g^{-1} soil, 50 µg g^{-1} soil, and 100 µg g^{-1} soil. The data pertaining to nitrification inhibition capacity of different complexes are given in Table 1. Perusal of the table reveals that at 10 µg g^{-1} soil, tungsten dimethyldithiocarbamate showed maximum nitrification inhibition (42.53%). Platinum dimethyldithiocarbamate registered 32.76% inhibition and proved to be significantly better than molybdenum dimethyldithiocarbamate (27.21%), which was at par with the parent salt sodium diethyldithiocarbamate (27.67%). Diethyldithiocarbamate complexes of molybdenum, tungsten and platinum exhibited poor activity pertaining to less than 10% nitrification inhibition.

At 50 µg g^{-1} soil, tungsten dimethyldithiocarbamate again proved to be the best inhibitor exhibiting 57.66% nitrification retardation. Molybdenum dimethyldithiocarbamate was at par with platinum dimethyldithiocarbamate and both were significantly better than the diethyldithiocarbamate complexes of Mo, W and Pt as well as sodium diethyldithiocarbamate, one of their parent salts also.

At 100 µg g^{-1} soil, molybdenum dimethyldithiocarbamate proved to be most effective in retarding nitrification (92.79%). The parent salt sodium diethyldithiocarbamate inhibiting 79.41% nitrification was at par with tungsten dimethyldithiocarbamate (78.64%), followed by platinum dimethyldithiocarbamate (73.98%).

To summarize, among the various test compounds/ complexes, tungsten dimethyldithiocarbamate proved to be best nitrification inhibitor at 10 µg g^{-1} soil and 50 µg g^{-1} soil whereas molybdenum dimethyldithiocarbamate superceded the former at 100 µg g^{-1} soil and became the best nitrification retardant. The order of per cent nitrification inhibition of the various synthesized complexes in soil at maximum concentration (100 µg g^{-1} soil) is MoDMDTC > WDMDTC > PtDMDTC > WDEDTC > MoDEDTC > PtDEDTC. None of the synthesized metal diethyldithiocarbamate exhibited activity better than or at par with their parent salt i.e. sodium diethyldithiocarbamate. In general metal dimethyldithiocarbamates proved to be better retardants than corresponding metal diethyldithiocarbamates. In view of the vast biological properties, these complexes can be exploited as agrochemicals. However integrated research is needed to study other environmental consequences.

Nitrification inhibitors not only influence nitrification in soil, but also affect other physical, chemical and biological processes affecting N-transformations such as the transport, movement and persistence of N in soil and its gaseous loss to the atmosphere. The use of nitrification inhibitors also provides an alternative approach to reduce the emission of green house gases such as nitrous oxide and methane (Sahrawat 2004) [8]. Despite great interest in nitrification inhibitors, only a few compounds have been adopted for agricultural and environmental use. The main problem seems to be the high cost involved in development and subsequent use of the nitrification inhibitors in the low input agriculture in developing countries like India. However, under field conditions especially in tropical regions, the effects of nitrification inhibitors are quite difficult to predict. However, there is a continuous need to identify and develop nitrification inhibitors which are inexpensive, readily available, and are effective at reasonable rates of application (Sahrawat 2003) [7]

Table 1: Per cent Nitrification Inhibition in Soil by Metal Dialkyldithiocarbamates

Compound/Complex	Denoted as	Amount of Metal Dialkyldithiocarbamate Applied		
		10 μg g^{-1} soil	50 μg g^{-1} soil	100 μg g^{-1} soil
NaDEDTC	1	27.67	42.37	79.41
MoDMDTC	3a	27.21	52.63	92.79
MoDEDTC	6a	07.73	14.95	32.52
WDMDTC	3b	42.53	57.66	78.64
WDEDTC	6b	09.08	39.01	42.25
PtDMDTC	3c	32.76	52.57	73.98
PtDEDTC	6c	07.29	11.30	32.00
LSD (0.05)		1.47	1.16	1.64
LSD (0.01)		2.06	1.63	2.29

DMDTC = dimethyldithiocarbamate
DEDTC = diethyldithiocarbamate

Acknowledgement

Author is highly thankful to Dr. Bijay Singh, Retired Professor, ICAR Fellow, Deptt. of Soil Science, Punjab Agricultural University, Ludhiana and Dr. C.L. Arora, Retired Professor, Deptt. of Chemistry, Punjab Agricultural University, Ludhiana for providing necessary research guidance, laboratory facilities and paper writing.

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