UNIVERSITI PUTRA MALAYSIA

USE OF PALM OIL MILL EFFLUENT (POME) AND PEAT TO REDUCE AMMONIA VOLATILISATION FROM FERTILISER UREA

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By

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Dedicated to

'the estimable nucleus in my life who championed my struggle'

Thank you Mother dearest

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LIST OF ABBREVIATIONS

Non symbolic

ANOVA	Analysis of Variance
ATS	Ammonium thiosulfate
BOD	Biochemical Oxygen Demand
BTPT	N-butyl thiophosphoric triamide
CRD	Completely Randomised Design
DMRT	Duncan's Multiple Range Test
DPOME	Decomposed Palm Oil Mill Effluent
FTIR	Fourier Transform Infra-Red
H	Humin
HA	Humic Acid
HAD	Humic acid derived from decomposed POME
HAP	Humic acid derived from peat
HAUD	Humic acid derived from clarified POME
HD	Humin derived from decomposed POME
HP	Humin derived from peat
HUD	Humin derived from clarified POME
NMR	Nuclear Magnetic Resonance
PPDA	Phenylphosphorodiamidate
SCU	Sulfur-coated urea
Soil A	Alkali soil
Soil B	Acid soil
TEA	Triethanolamine
UAN	Urea-Ammonium nitrate
UDPOME	Clarified Palm Oil Mill Effluent
UP	Urea-Phosphate

Symbolic

$(NH_4)_2\ CO_3.\ H_20$	Ammonium carbonate
$(NH_4)_2\ SO_4$	Ammonium sulfate
B	Boron
C	Carbon
$Ca(OAc)_2$	Calcium acetate
Ca^{2+}	Calcium ion
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
$CO(NH_2)_2$	Urea
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
Cu	Copper
H	Hydrogen
H_2O	Water
H_2SO_4	Hydrogen sulfate
HCl	Hydrogen chloride
HF	Hydrogen fluoride
K	Potassium
KBr	Potassium bromide
KCl	Potassium chloride
Mg^{2+}	Magnesium ion
Mn	Manganase
N	Nitrogen
$NaHCO_3$	Sodium hydrogen carbonate
NaOH	Sodium hydroxide
NH_4NO_3	Ammonium nitrate
OH^-	Hydroxyl ion
P	Phosphorus
SO_4^{2-}	Sulfate ion

Abstract of the thesis submitted to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the Degree of Master of Agricultural Science.

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May, 1997

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Ammonia (NH_3) volatilization is a major pathway of nitrogen loss which limits the efficiency of urea as a fertilizer when surface-applied to soils. High pH and low cation exchange capacity in soils have been identified as the principal causes of NH_3 volatilization from urea. The several approaches proposed to correct such inefficiency in urea, thus far, were fundamentally based upon delay of urea dissolution and impedance of urea hydrolysis.

An attempt was made to establish a preferred environment within the urea-soil reaction zone (microsite) using palm oil mill effluent (POME) and peat. Both POME and peat are organic matter-rich, and contain humic substances across their respective organic matrix. Humic substances have been shown to interact with ammoniacal compounds and urea. As such, a study was engaged to explore the effects of POME and peat, and their respective humic derivatives on NH_3 volatilization from urea surface-applied to two Malaysian soils of contrasting pH values.

The organic materials and their humic derivatives were separately matrixed with urea into pelletised form and evaluated under laboratory regimes for % NH_3 volatilization, pH change and NH_4^+-N recovery. Estimation of NH_3 volatilization was carried out using a closed-dynamic air-flow system. Determination of the chemical and physical attributes of soils and materials, and measurement of the parameters studied were done using standard procedures. Characterisation of the POME- and peat-derived humic substances was performed using chemical and spectral methods.

Results showed that reduction in NH_3 volatilisation by peat-treated urea was more pronounced than that of POME in both soils. Such reduction was accompanied by a corresponding increase in NH_4^+ recovery and decrease in pH, particularly at the microsite. The use of differing matrixing ratios did not yield significant variation in the performance of matrixing agents. Acidification of POME and peat resulted in impedance of urea movement from microsite to outersite.

However, with humic substances, particularly humic acid, reduction in volatilisation was not accompanied by a corresponding increase in NH_4^+ recovery.

Generally, results indicated that the mechanism governing the ability of peat and POME to reduce NH_3 volatilisation from urea was NH_4^+ adsorption. With humic substances, there appeared to be possible involvement of other mechanisms, i.e. urease inhibition, urea absorption and NH_3 fixation. The chemical and spectral attributes of humic acids and humins closely corresponded with those reported elsewhere. Nevertheless, higher functional group values were obtained from the fractions under study.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains Pertanian.

PENGGUNAAN EFFLUEN KILANG KELAPA SAWIT (POME) DAN GAMBUT UNTUK MENGURANGKAN PEMERUAPAN AMONIA DARI BAJA UREA.

Oleh

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Pemeruapan amonia (NH_3) merupakan mekanisme utama kehilangan unsur nitrogen yang menghadkan kecekapan baja urea, khasnya apabila ditabur atas permukaan tanah. Ketinggian nilai pH dan keupayaan pertukaran kation yang rendah dalam tanah telah dikenalpasti sebagai punca utama pemeruapan NH_3 dari urea. Setakat ini, pendekatan yang telah diutarakan untuk mencegah pemeruapan NH_3 berlandaskan penangguhan pelarutan urea serta halangan proses hidrolisis urea.

Percubaan telah dijalankan menggunakan effluen kilang kelapa sawit (POME) dan gambut untuk mewujudkan persekitaran kimia yang sesuai di zon reaksi urea-tanah (kawasan mikro). Penggunaan POME dan gambut didorong oleh ketinggian kandungan bahan organik serta kehadiran bahan humik dalam matrik organik tersebut. Justeru itu, kajian berikut dikendali untuk menyelidik kesan POME dan gambut bersama dengan bahan humik masing-masing terhadap pemeruapan NH_3 dari baja urea yang ditabur pada dua jenis tanah tanah di Malaysia yang berbeza nilai pH.

Baja urea dirawat secara berasingan dengan POME/gambut dan bahan humik yang diekstrak, dijadikan matrik dalam bentuk pelet dan dinilai dari segi % pemeruapan NH_3, perubahan pH serta kedapatan NH_4^+ dalam rejim makmal. Anggaran pemeruapan NH_3 telah dibuat menggunakan kaedah sistem pengaliran udara dinamik pada keadaan tertutup. Penentuan sifat fizikal dan kimia tanah dan bahan organan serta pengukuran parameter kajian dibuat menggunakan kaedah piawai. Pencirian bahan humik berdasarkan kaedah kimia dan spektroskopi.

Keputusan menunjukkan penurunan dalam pemeruapan NH_3 dari rawatan urea-gambut lebih ketara daripada rawatan urea-POME pada kedua jenis tanah. Penurunan NH_3 teruap selari dengan peningkatan kedapatan NH_4^+ dan pengurangan nilai pH, terutamanya di kawasan mikro. Penggunaan nisbah rawatan tidak menunjukkan perbezaan yang bermakna terhadap prestasi agen rawatan. Pengasidan POME dan gambut telah menghalang pergerakan urea dari kawasan mikro. Namun, rawatan menggunakan bahan humik, khasnya asid humik, tidak menghasilkan penurunan NH_3 teruap yang selari dengan peningkatan dalam kedapatan NH_4^+.

Secara keseluruhan, keputusan mengimplikasikan bahawa penjerapan NH_4^+ merupakan mekanisme yang beroperasi dalam penurunan NH_3 teruap pada rawatan urea-POME dan urea-gambut. Bagi rawatan urea-bahan humik, adalah disyaki mekanisme lain seperti perencatan enzim 'urease', penyerapan urea dan pengikatan NH_3 beroperasi secara serentak. Sifat kimia dan spektroskopi bahan humik yang dikaji didapati selaras dengan hasil kajian lain yang telah dilapurkan. Walaubagaimanapun, analisa kumpulan berfungsi bahan humik yang dikaji menunjukkan nilai yang lebih tinggi.

CHAPTER I

INTRODUCTION

Nitrogen (N) is the most common and widely used fertiliser nutrient. Produced primarily as ammonia, it can be applied as such or further processed into a variety of liquid or solid N fertilisers. Among solid N fertilisers, urea is most popular because of its low handling, storage and transportation costs, low energy consumption and less pollution during manufacture, and high N analysis (46%). Urea is suitable to be applied in solution, as solids, foliar spray, components of high analysis compound fertiliser and bulk blends (Nayan, 1982).

Although urea is equivalent to other nitrogenous fertilisers (Van Lierop and Tran, 1980) poor crop responses to urea have frequently been observed. A number of studies have identified ammonia (NH_3) volatilisation as the major cause of low N efficiency in urea (Mikkelsen *et al.*, 1978; Fillery *et al.*, 1984) where as much as 80% of the applied urea-N may be lost within 2-3 weeks of application (Torello *et al.*, 1983; Hargrove and Kissel, 1979). As the major pathway of N loss in urea, NH_3 volatilisation not only reduces N turnover in agricultural systems but also causes environmental pollution.

In soil, urea is first molecularly diffused and then hydrolysed to ammonium bicarbonate by the microbially-produced enzyme urease under favourable conditions. The resultant high pH, often exceeding 8.5 (Fenn and Richards, 1986), within the area surrounding urea granules renders instability to ammonium ions (NH_4^+) thus promoting NH_3 volatilisation. The magnitude of NH_3 volatilisation can be ascribed to soil properties, external factors and agrotechnical procedures which operate interactively in dimensions not easily perceptible. Remedial efforts to address the problem of NH_3 volatilisation have accentuated over the years yielding potential control methods such as urease inhibitors, urea coatings, slow-release urea polymers, and addition of neutral salts and mineral acids. These approaches have principally dealt with either impedance of urea hydrolysis or delaying dissolution of urea.

Numerous findings have attributed NH_3 volatilisation to high pH and low cation exchange capacity (CEC) in soil (Whitehead and Rainstrick, 1990, 1993; Santra *et al.*, 1988) while a few have elucidated in terms of soil hydrogen buffering capacity (HBC) (Ferguson *et al.*, 1984; Hargrove, 1988). In general, soil pH, CEC and HBC are factors that interact reciprocally, whereby high pH catalyses an increase in CEC resulting in a decline in HBC. Urea inefficiency due to NH_3 volatilisation has been demonstrated on relatively low pH-tropical soils (Khanif, 1992), which was attributed to sufficient increase in pH at the urea-soil reaction zone (microsite). This concept sanctioned the search for a material that could introduce a preferred environment within the microsite. One such material has been the palm oil mill effluent (POME) (Aminuddin, 1994), while the other being peat (Aminuddin *et al.*, 1994). In both studies, NH_3 volatilisation was successfully reduced to 8% and 4% of the applied N, respectively. Palm oil mill effluent and peat, both rich in organic matter, are believed to contain varying amounts of humic substances across their respective organic matrix.

As bulk constituents of organic matter, humic substances have been reported to interact with ammoniacal compounds (Banerjee and Basak, 1978; Thorn and Mikita, 1992) *via* adsorption and fixation mechanisms respectively, and urea (Patti *et al.*, 1992) through inhibition of nitrification. Structural explication of humic substances have indicated presence of quinones (Schnitzer, 1982), a widely documented class of urease inhibitors, in fractional amounts. Thus, there appears to be a potential for humic substances, derived either from POME or peat, to address the problem of NH_3 volatilisation. At present, there is no published reports which have elucidated the effect of POME or peat-derived humic substances on urea *per se* which leads to alleviating NH_3 volatilisation.

As such, a study was engaged with the following objectives:

i) to investigate the effects of POME and peat on NH_3 volatilisation

ii) to characterise humic substances derived from POME and peat, and to study their effect on NH_3 volatilisation

iii) to elucidate the chemistry between humic substances and urea, in retarding NH_3 volatilisation.

CHAPTER II

REVIEW OF LITERATURE

Urea

In the past, ammonium nitrate (NH_4NO_3) was widely available as a non-volatile N source but economics of production now favour urea. The new generation of urea production facilities have the advantage of the latest technology and economies of size. Hence, the proportion of urea procurable in the fertiliser market is rapidly increasing.

Despite being the cheapest dry N fertiliser available to agriculture, use of urea is plagued by the problem of NH_3 volatilisation. An upsurge of interest in NH_3 volatilisation has occurred over the years due to evidence from agronomic nitrogen-balance studies that generally showed an unexplained 10-80% loss of applied fertiliser nitrogen (Hargrove and Kissel, 1979; Legg and Meisinger, 1982; Torello *et al.*, 1983). Various efforts have been undertaken to address the problem, however, the problem still persist to an extent which significantly limits urea efficiency.