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EVALUATION OF OPTIMUM METHODS FOR DIFFERENT NITROGEN FORMS DETERMINATION IN SEWAGE SLUDGE SAMPLES OF INDUSTRIAL AND RESIDENTIAL AREAS

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Abstract

Sewage sludge contains many essential nutrients, present in several chemical forms, important for plant growth, such as nitrogen, phosphorus, sulphur.In present paper determination of different forms of nitrogen by two methods is reported. In first, extraction followed by spectrophotometer was employed to determine nitrate and nitrite in sewage sludge. Second method depends upon the determination of ammonia, nitrate and nitrite in sewage sludge samples extraction, followed by titration with standard acid and colorimetry using Nesseler's reagent. Recovery of added nitrate and nitrite was optimum.

Key words: optimum methods, Nitrogen determination,

Introduction

The application of waste water sludge to agricultural lands as a supplemental fertilizer and soil conditioner has been adopted an alternative to disposal of this bothersome waste material. In wastewater sludge, nitrogen may be present as ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and/ or a wide variety of organic nitrogen compounds. Nitrates are the most soluble forms of nitrogen and therefore present the most potential contamination.
Kazi, T.G., Katz, S.A, and jenniss, S.W., Spectroscopy Letters, 20 (6 & &), 509-517, 1987.
The regulatory agencies of many nations have developed standard methods for the determination of these nutrients in wastewater sludge, but their applicability to waste water sludge has not been fully explored.

Loading rate of sewage sludge is based on nitrogen content of the wastewater sludge. While procedure for total Kjeldahl's nitrogen and ammonia nitrogen have been successfully applied to wastewater sludge, the chemical speciation of the oxidized form of nitrogen, nitrite and nitrate, lack adequate methodology.

In order to fully assess the impact of applying wastewater sludge to the land, reliable methods are needed for the determination of ammonia, nitrate and nitrite present in this complex matrix. The following is an evaluation of such an optimum method for the routine determination of nitrate nitrogen and nitrite nitrogen in wastewater sludges.

Experiment

Air-dried.
sewage sludge samples were collected from Karachi, Hyderabad and Mirpurkhas, were

Extraction of sewage sludge samples
1. Extraction with Water and 2M KCl

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Bremmer, J.M., and Keene, D.R., Anal. Chim. Acta. 32, 485-495, 1965.
Morgan, G.B. Lackey, J.B., Anal. Chem. 29, 833, 1957.
5g of each sewage sludge sample were extracted with 100ml of deionized water and 2M KCl separately, and shaken for two hours. and filtered through whatman No. 42 filter paper. The sample for determination of exchangeable ammonia - nitrogen, nitrite and nitrate colorimetrically were obtained by distillation method.
Holty, J.G., Potworowski., Environ. Sci. Technol. 6, 835-37, 1972.

Extraction with $CaSO_4$

5 g sample of sludge was suspended in 70 ml of deionized water in separate triplicate flasks and treated with 0.5 g of calcium sulphate . The suspension was shaken mechanically for 30, 10 and 5 minute interval. Then 1 % solution of 10 ml of silver sulphate, 10 ml magnesium carbonate and 10 ml calcium hydroxide were added, and the suspension was mixed well. The suspension was filtered through whatman No. 42 paper. Filtrate was used for determination of ammonium nitrate and nitrite nitrogen, by distillation and spectrophotometry.

Determination by distillation Procedure
Step 1
Determination of exchangeable ammonium -nitrogen

Take 20 ml of potassium chloride, water and calcium sulpate extract of each sewage sludge samples into the distillation flasks separately. Placed 20 ml of 2 % boric acid solution in a conical flask beneath the condenser. Add 0.5 g of dried magnesium oxide to the solution through a long stemmed funnel placed through the second neck of the flask, stopper the flask and steam distill ammonia into boric acid solution. Then titrate with 0.1 M HCl, using mixed indicator.

Step 2
(i) Determination of nitrate and nitrite - nitrogen
(ii) Determination of nitrate- nitrogen

(i) After distillation of the ammonium - nitrogen, remove the stopper of the second neck of the flask and add 0.2g of Devarda's alloy. Rapidly replace the stopper and steam distill ammonia into fresh portion of boric acid solution. Titrate the distillate with standard HCl

(ii) Take 20 ml extracted sample of sewage sludge, add 2ml of 2% sulphamic acid, the mixture was shaken for 2-3 minutes and the nitrate and ammonia determined. Sulphamic acid decomposes nitrite rapidly and quantitatively to nitrogen. After distillation of ammonia a new portion of boric acid is placed below the condenser, and 1 g Devarda's alloy (Cu : Al:Zn :: 50:5:5), added to the reaction flask, and heating to distill out the ammonia formed in boric acid and titrate with standard hydrochloric acid.

Determination of nitrate by spectrophotometer

Duplicate 0.5 ml aliquots of all the extracts of sewage sludge samples, were pipetted out into separate tubes. one of these was used as the interference control for dissolved coloured material in the samples. The contents of the tubes were cooled in a cold water bath and treated with 10 ml of cold sulphuric acid reagent. The content of tubes were mixed and again cooled. 0.5 ml of brucine-sulphanilic acid reagent was added to one of the tubes but not to the other which served as the interference control. The contents of the tubes were mixed , and the tubes were heated in a boiling water bath

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for 25 minutes. Then the contents of the tubes were cooled in a cold water bath to 25C°, and the absorbance were measured against nitrate standards containing 0.002 to 0.01 pm nitrate-nitrogen / ml. The absorbance of the interference control was subtracted from that of the corresponding sample, and the nitrate - nitrogen content of the sample was determined with reference to the absorbance of standards

Determination of nitrite by Spectrophotometry

Duplicate 0.5 ml aliquots of all three extracts of sewage sludge samples, were pipette out into separate 50 ml volumetric flask. One of these was used as interference control for dissolved colored material in the samples, diluted to 45 ml with distilled water . One ml of diazatizing reagent was added, and the solution was mixed well. Five minutes later, 1 ml of the coupling reagent was added. The solution was mixed well, brought to volume with distilled water, and allowed to stand for 25 minutes. Standards containing 0.002 to 0.01 pm of nitrite nitrogen were carried through procedure. The absorbance at 520 nm measured at the end of 25 minute period, and the nitrite nitrogen content of the samples was determined.

Recovery of ammonia, nitrate and nitrite- nitrogen spikes

Replicate 5 g sludge samples were spiked with standard mixture of ammonia-nitrogen 200µ g, nitrate- nitrogen 200 µg and nitrite -nitrogen 100 µg . The ammonium, nitrate and nitrite nitrogen contents of these spiked samples were also determined by extraction/ distillation / and spectrophotometry.

Discussion and Results

Exchangeable ammonia, nitrate nitrogen were extracted with KCl and $CaSO_4$ and hot water. As a general extraction of ammonium from sewage sludge, 2M neutral KCl was most suitable and gives reproducible results. Extraction of sewage sludge samples for nitrate and nitrite – nitrogen with KCl; water and $CaSO_4$ were applied. Nitrate and nitrite are extracted from sewage sludge with aqueous solutions. Extraction with $CaSO_4$ is reproducible., because chloride ion inhibit the formation of the brucine - nitrate chromophore, calcium sulphate was added to precipitate chloride ion[1].

Jenkins, D. and Medskin, L; Anal. Chem., 36610-612, 1964.

Magnesium carbonate and calcium hydroxide are clarifying agents used to prepare a colourless solution for distillation/ spectrophotometry[2].

Price, A.L. Soil Science, 59, 47-52, 1945.

The spectrophotometry of nitrate and nitrite required careful control of incubation time and temperature. The accuracy (based upon the recoveries of spikes) and precision of extraction / Spectrophotometry are improved with the inclusion of the interference controls.

The distillation method has the advantage of permitting the estimation of ammonia, nitrate and nitrite (by difference) in the same aliquot of different extracted samples of sewage sludge.

Ballinger, D.g., EPA-600/4 – 79 – 200, U.S. E.P.A., Emsl, Cincinnati, Ohio, 1979.

Smith, K.A., Commun. Soil Sci., Plant Anal. 15 (12), 1437-51 1984.

In that, once filtered from the sewage sludge samples, the extract needs no further preparatory treatment and that colored extracts make no difficulty. The method depends upon the soil extract treated with a base magnesium oxide

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Bremmer, J.M., and Shaw, K., Journ., Agric. Sci. 51, 22-39, 1955.

(preferably it is easier to handle and is less likely to creep around the glass joints of the apparatus.) and the mixture distilled, ammonia is expelled and absorbed in boric acid solution if it is also desired to measure the nitrite with nitrate in different extracts. The method depends upon reduction of nitrate and nitrite to ammonia by added Devarda's alloy and distilled ammonia as nitrate and nitrite nitrogen. In other portion of extract destroy nitrite with sulphamic acid and determine nitrate only. The distillation method was also applied to spiked samples of sewage sludge with standard mixture of ammonium, nitrate and nitrite, to determine the % recovery.

Nitrite – Nitrogen

Sample	TKN	Extraction A		Extraction B		Extraction C	
		Method1	Method II	Method	MethodII	Method1	Method II
MPS	4580±128	5 ± 0.4	4 ± 0.5	9 ± 0.6	8 ± 0.6	9.5 ± 1	8 ± 0.8
HDS	2800±90	6.±0.8	5±0.8	8±0.5	6±0.4	7±0.4	6.5±0.4
HIS	2940±120	4±0.7	4±0.6	7±0.2	6±0.5	7±0.52	6.5±0.5
KDS	5540±250	5±0.2	4±1.6	8±3.5	6±0.4	8±0.5	7±0.6
KIS	7330±285	5.5±0.4	4±0.4	7±0.4	6±0.2	7±0.8	6±0.5

Method 1 = Determination of different forms of nitrogen by distillation
Method II = ----------Spectrophotometry
MPS = ---------- Sewage sludge samples from Mirpurkhas
HDS = ---------- -residential areas of Hyderabad
HIS = ----------Industrial ----------
KDS = ----------residential areas of Karachi
HIS = ----------industrial----- ----------

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DETERMINATION OF DIFFERENT FORMS OF NITROGEN IN SEWAGE SLUDGE SAMPLES
(mg/Kg dried basis)

	Exchangeable NH_4. N			Nitrate - nitrogen					
Sample	Ext.A Methd 1	Ext.B Method I	Ext. C Metthod I	Extraction A Method 1	Method II	Extraction B Method 1	Method II	Extraction C Method I	Method II
MPS	7.8± 0.8	8.6 ± 0.4	9.0 ± 1	29 ± 2.4	28 ± 15	36 ± 2.6	32 ± 2	40 ± 2.8	41±1.8
HDS	9 ± 1	10 ± 0.8	12.5 ± 1	34 ± 2.8	30 ± 0.8	38 ± 1.5	35 ± 2.4	47 ± 2.4	43 ± 2.4
HIS	8 ± 1	8.5 ± 0.6	10 ± 1	22 ± 0.7	21 ± 0.6	27 ± 1.2	24 ± 1.5	30 ± 2	28 ± 2
KDS	9.5 ± 1	11 ± 0.6	12 ± 0.8	52 ± 2	50 ± 1.6	58 ± 3.5	53 ± 2.4	62 ± 3.5	58 ± 2.6
KIS	11 ± 1.2	14 ± 0.5	17 ± 2	45.5 ± 3	42 ± 3.6	47 ± 2	45 ± 2	49 ± 3	46 ± 2

Key:
Ext. A = Sewage sludge samples extract with hot water
Ext. B = ----------2M KCl
Ext. C =-- ----------$CaSO_4$

References

1 Kazi, T.G., Katz, S.A, and jenniss, S.W., Spectroscopy Letters, 20 (6 & &), 509- 517, 1987.

1. Bremmer, J.M., and Keene, D.R., Anal. Chim. Acta. 32, 485-495, 1965.
2. Morgan, G.B. Lackey, J.B., Anal. Chem. 29, 833, 1957.
3. Holty, J.G., Potworowski., Environ. Sci. Technol. 6, 835-37, 1972.
4. Jenkins, D. and Medskin, L; Anal. Chem., 36610-612, 1964.
5. Price, A.L. Soil Science, 59, 47-52, 1945.
6. Ballinger, D.g., EPA-600/4 – 79 – 200, U.S. E.P.A., Emsl, Cincinnati, Ohio, 1979.
7. Smith, K.A., Commun. Soil Sci., Plant Anal. 15 (12), 1437-51 1984.
8. Bremmer, J.M., and Shaw, K., Journ., Agric. Sci. 51, 22-39, 1955.

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