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Potential Utilization as Fertilizer of Waste Liquid from Bio-Trickling Reactor for Greenhouse Gases Treatment

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This research mainly focused on the exploration of the possibility to utilize the liquid by-products (the circulating alkaline fluid of a bio-trickling reactor, containing NO3-, 7.0 ≦ pH ≦7.5) as a fertilizer, with reduced environmental impact and economic benefits. The composition of the exhausted bio-trickling liquid (TL) was analysed in accordance with Dlgs. 75, 2010 of Italian Republic, which recognizes the CE Rules n.2003/2003 and n.834/2007. In particular, the TL discharged from a bio-trickling filter can be recognized into the category of nitrogen mineral organo-fluid fertilizers.

1. Introduction

Nowadays, air contamination is gradually acknowledged as a major problem for the environmental and public health. In particular, the stringent sulfur dioxide (SO2) and nitrogen oxide (NOx) emission regulations increase a demand for innovative gaseous pollutants abatement technologies, such as: (i) wet scrubbing(Xia et al., 2011), (ii) adsorption (Sumathi et al., 2010), (iii) oxidation (Liu et al., 2010), (iv) pulse corona (Xu et al., 2009). Moreover, in the last years, biotechnologies have demonstrated to be a robust and reliable alternative to conventional technologies. The biological treatment has particular advantages, such as: easy preparation conditions, low cost and energy consumption, suitability for processing low concentration of contaminants. On the other hand, the generation of by-products is inevitable. Given the growing emphasis on sustainable development and "zero waste" politic, the possibility of utilizing these by-products would, even more, stimulate the application of the biological technology. Bio-trickling filtration is one of the many promising biological techniques for odor and VOC control (Oh & Bartha, 1997; Mpanias & Baltzis,1998; Cox, Nguyen & Deshusses, 2000; Gabriel & Deshusses 2003). Bio-trickling filters exploit a distinct liquid phase to control pH, salt or metabolite concentration, and to supplement nutrients to the process culture. TL treatments are rarely explored and studied. However, they constitute a waste and often a process significant cost, which has contributed to hinder the practical application of the bio-trickling technology. Most of the solid organic waste produced by biological treatments, dry sludge and bio-filters (peat, soil, compost, wood bark) can be included in a scheme of recovered resources in terms of land application or composting. For example, in France, about 60% of activated sludges produced in "wastewater treatment processes" (WWTPs) were recovered to be applied on land as fertilizer for agricultural soils. The use as compost has numerous points in favour, it allows during the degradation of the organic components the development of heat which can inactivate pathogenic components (Shareefdeen & Singh, 2005). Moreover, some literature examples report the use of bio-filtration liquids as feedstock for the catalytic conversion in fertilizers (Zhou et al., 2013). A remarkably innovative alternative can be the usage of the liquid component at the discharge of a biological reactor directly as fertilizer. This research mainly focuses on the possibility to utilize the liquid by-products (the circulating alkaline fluid of a bio-trickling reactor, containing NO3-, 7.0 ≦ pH ≦7.5) as a fertilizer, with reduced environmental impact and economic benefits. The composition of the bio-trickling liquid (TL) was analysed in accordance with Dlgs. 75, 2010 of Italian Republic, which recognizes the CE Rules n.2003/2003 and n.834/2007. In particular, the TL discharged from a bio-trickling filter was analysed for pH, carbon-nitrogen ratio (C/N), and nitrogen content. The analyses overall demonstrate that it can be recognized into the category of nitrogen mineral organo-fluid fertilizers.

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2. Experimental and Results

2.1 Materials

Methyl red ($C_{15}H_{15}N_3O_2$), Bromocresol green ($C_{21}H_{14}O_5Br_4S$), Pumice stone, Nessler reagent, Potassium dichromate, Iron(II) sulfate heptahydrate, Sodium nitrate, Silver Sulfate (Ag_2SO_4), 4-diphenylamine sulfonate of barium, Devarda's alloy, Sulphuric Acid (H_2SO_4, 96%), Phosphoric Acid, Sodium Hydroxide, Sodium tetraborate decahydrate, Boric Acid, Hydrogen peroxide solution (H_2O_2) were acquired from Aldrich Chemical Co. All chemicals were of analytical grade.

2.2 Methods

The aim of this paper was to evaluate the properties of the exhausted liquid, from an industrial bio-trickling reactor (Configuration in Table 1) for greenhouse gases emission abatement.

Table 1 Configuration and operating parameters of the bio-trickling filter

Parameter	Value
Bed height	3 m
Bed cross-sectional area	6 m^2
Packaging	• Oak woodchips: 10-200 mm • Compost
Gas feed Rate	10000 m3/h
Typical gas feed composition	O_2 7%; N_2 68%; CO_2 14%; H_2O 7%; NOx/m^3 598.5 mg; SO_2/m^3 25 mg
Gas temperature	10-30 °C
TL Rate*	0,5 mh^{-1}
Typical monitored Parameters	• temperature, • pH, • dissolved oxygen and conductivity of recycle liquid, • liquid feed • rate, • trickling flow rate, • pollutant inlet and outlet concentrations, • pressure drop
Typical controls	• liquid feed rate, • pH control, • low-level liquid • alarm or pump shutdown

• *Initial TL was water

In particular, the goal is to evaluate the feasibility of using it as liquid fertilizer in the agricultural field. In particular, the reactor outlet is equipped with an ultrasonic cavitation apparatus for fluid homogenization and microbial inactivation (Piyasena et al., 2003; Chen 2017), and of an electrostatic precipitator at the entrance of the gaseous stream. The gaseous stream at the reactor was split by the outlet current from a diesel combustion boiler. The abatement capacity per pass was about 80% for the greenhouse gases. After 1 months, 30 different sampling (CE n. 2003 of 13/10/2003, All. IV, Method A) were analysed with this purpose.
In particular, the procedure concerned:

- samples preparation
- determination of the nitrogen content
- determination of the total organic carbon content (TOC).

2.3 Sample preparation

The procedure, involves the following steps: preparation of the elementary sample (minimum number of samples 7): the fluid is divided into a number of roughly equal parts; a number of parts corresponding to the number of elementary samples is randomly selected and at least one sample is taken from each part; global sample formation: assembly of elementary samples to obtain a single global sample.

2.4 Sample preparation for analysis

Once the final sample was obtained, which thanks to the procedure indicated by the EC Regulation represents a significant amount of the sample, it was subjected to a series of steps (Method 1 EN 1482-2), i.e.: sieving, grinding and homogenization (for fluid, liquid or suspended fertilizers it is prescribed a suitably homogenization at a temperature of 20 °C before analysis) .

2.5 Determination of the content of the different Nitrogen (N) forms

Nitrogen is a primary growth ingredient which can be found in numerous chemical compounds such as fertilizers, food, oils, water/wastewater, etc .... Nitrogen can be found in many forms, including: ammonia, organic, nitrate and nitrite forms. The two most common tests for nitrogen consist in the evaluation of organic and inorganic nitrogen. Organic nitrogen is the nitrogen of different organic compounds (amines, amides, imines, etc.) including albuminoidal nitrogen. Its presence in the waters is mainly due to substances with animal and vegetable origin, such as amino acids, polypeptides and proteins. For the determination of organic nitrogen content the procedure of Total Kjeldahl nitrogen (TKN, Total Kjeldahl Nitrogen) evaluation was used. TKN is defined as the sum of ammonia nitrogen and organic nitrogen, which are transformed into ammonium sulfate under the mineralization conditions adopted by the method:

$$TKN=\text{Organic N}+\text{Ammoniacal N} \quad (1)$$

Following the procedure for TKN determination, the sum of ammonia N and organic N was determined by: (i) digestion of the sample (mineralization); (ii) followed by distillation of ammonia and; (iii) titration with a reference solution of a strong acid or measurement by spectrophotometric method. After removal of free ammonia, the same procedure allows to evaluate the organic N. With this method, nitrates and nitrites are not determined. To determine nitrate and nitrite forms the residue of distillation of formed ammonia at the end of the TKN step (ii) can be used.

2.6 Determination in Kjeldahl total nitrogen content

2.7 Digestion process (Mineralization)

First of all TKN was determined according with Dlg. 75/2010 and related Annexs.
In details, the mineralization method is based on a complete oxidation of the sample with sulphuric acid and hydrogen peroxide to transform organic nitrogen into ammonia nitrogen. The procedure carried out is the following: 2.5 g of the collected sample and 11 mL of sulphuric acid (H2SO4, 96%) were added to a 300 mL flat-bottomed Kjeldahl flask. Then 4 mL of hydrogen peroxide (H2O2) were slowly added in anti-splash glass beads. At this point, the flask was brought to a boil with a Bunsen flame and left to boil for 30 min (see Figure 3). After 30 minutes the flask was cooled and 4 mL of hydrogen peroxide was added slowly through a funnel. Then the flask was heated again and kept boiling for 30 min. The flask was cooled and the suspension was sent into a 250 mL volumetric flask and brought to volume with water (H2O). Finally, the solution was homogenized and the solid particles were removed by decantation.

2.8 Distillation process

Distillation allows us to determine the nitrogen content after carefully mineralization of the sample considered. The distillation process was carried out as follows, 200 mL of the clear supernatant obtained after the mineralization was poured into a flask, to this supernatant 2 ÷ 3 pumice granules were, then, added. The flask was connected to the distillation apparatus (see Figure 3). Subsequently, 50 mL of the solution (0.01 molL-1) of the previously prepared sulphuric acid were transferred into a 500 mL beker. At this point: the extension of the refrigerant was immersed in the sulphuric solution (the tip of the extension does not touch the bottom); the tap was opened to allow 30 mL of a previously prepared solution (300 gL-1) of sodium hydroxide to flow into the flask, all using the funnel placed above the flask. Before closing the tap, the funnel was washed with water, then it was closed and left full of water. After these operations, the distillation begins by boiling the solution in the flask with a Bunsen flame for 30 ÷ 45 min.

2.9 Quantification of ammonia by titration

The excess of sulphuric acid present in the beker after distillation was titrated with a solution (0.02 molL-1) of sodium hydroxide, the indicators used for the acid/base titration were: bromocresol green and methyl red. In particular, the indicator for basic acid titration was obtained by mixing 0.99 g of bromocresol green ($C_{21}H_{14}O_5Br_4S$) and 0.66 g of methyl red ($C_{15}H_{15}N_3O_2$) in 1000 ml of ethanol. After the titration the evaluation of the total nitrogen content was calculated according to the following expression:

$$TKN=\frac{B*(K-B_1)*K_1*0.28*D}{V} \quad (2)$$

where:
TKN = total nitrogen content present, expressed in g/L;
B = volume of the sulphuric acid solution (0.01 molL-1), expressed in millilitres (50 mL);
K = correction factor of the sulphuric acid solution (0.01 molL-1);
B1 = volume of the sodium (or potassium) hydroxide solution (0.02 molL-1) expressed in millilitres;
K1 = correction factor of the sodium hydroxide solution (0.02 molL-1);
0.28 = volumetric equivalent • 1000;
D = dilution factor (250 mL / 200 mL = 1.25)
V = sample volume

2.10 Determination of the organic nitrogen content

For organic nitrogen the sample under test is subjected to a process of distillation of the free ammonia before submitting it to the digestion process according to the Kjeldhal methodology. The procedure performed for the removal of free ammonia was as follows: a known volume of the sample diluted with water and neutralized at pH = 7 was introduced into a Kjeldahl flask; then, 25 ml of previously prepared borate buffer solution and NaOH 6 N were added until a pH of 9.5 was achieved; after that the free ammonia was distilled, up to distillate no longer reacts positively with the Nessler reagent. The solution left after ammonia distillation was used for the determination of organic nitrogen. Once the digestion process has been carried out as described above, the distillation was then promoted by connecting the Kjeldahl flask to the distillation apparatus as described in the previous paragraph.
The organic nitrogen content was obtained by:

$$\text{Organic N=C}=\frac{B*(K-B_1)*K_1*0.28*D}{V} \quad (3)$$

where:
C = total nitrogen content present, expressed in g / L;
B = volume of the solution (0.01 molL-1) of sulphuric acid, expressed in millilitres (50 mL);
K = correction factor of the solution (0.01 molL-1) of sulphuric acid;
B1 = volume of the solution (0.02 molL-1) of sodium hydroxide expressed in millilitres;
K1 = correction factor of the solution (0.02 molL-1) of sodium hydroxide;
0.28 = equivalent volume • 1000;
D = dilution factor (250 mL / 200 mL = 1.25)
V = Sample volume

2.11 Determination of ammonia nitrogen content

Ammonia nitrogen was evaluated by the difference between total Kjeldahl nitrogen and organic nitrogen:

$$\text{Ammonia N=TKN-Organic N} \quad (4)$$

2.12 Determination of the content of nitric and nitrous nitrogen

The residue of the distillation present in the flask was used for the determination of nitrous and nitric nitrogen forms. The carried out process was the following: 2 g of Devarda's alloy were added to the distillation residue (to reduce the nitrous and nitric forms in ammonia), the flask was connected to the distillation apparatus previously used. The extension of the refrigerant was immersed in 10 mL of a solution of sulphuric acid (30 g/L), the system was allowed to react at room temperature for 15 ÷ 20 minutes, then the distillation and titration process described previously was continued. A blank test was performed following the same operating procedures.
The mineral nitrogen content (N-NO2 + N-NO3), for example expressed in gL-1, can be calculated by the expression:

$$\text{Nitric and Nitrous nitrogen}=\frac{(A-B)*4*0.14}{V} \quad (5)$$

where:
nitric and nitrous nitrogen = nitric and nitrous nitrogen content in the sample
A = volume of the solution (0.005 molL-1) of sulphuric acid consumed for titration of the sample, expressed in millilitres
B = volume of the solution (0.005 molL-1) of sulphuric acids consumed for titration of the

blank test, expressed in millilitres
0.14 = equivalent volume
4 = 200 mL / 50 mL = volumetric ratio
V = sample volume

2.13 Determination of total organic carbon (TOC)

The determination of TOC (Total Organic Carbon) is a rapid, precise and concrete analytical technique both in environmental and in industrial chemistry. The TOC measures the concentration of organic carbon in a sample; "organic carbon" means: carbon in the form of well-defined compounds (sugars, fatty acids, hydrocarbons, etc.), carbon from bacteria and other microorganisms, other form of C.

2.14 Determination of carbon according to Springer-Klee

The measurement of TOC (Total Organic Carbon) was evaluated according to the "Springer-Klee" method. The principle is based on the oxidation of the organic substances by treatment at defined conditions of acidity and temperature (160 °C) with known amount of potassium dichromate. The amount of potassium dichromate consumed in the reaction can be measured by titration with ferrous sulphate. For manual titration the 4-diphenylamine sulfonate of barium is used as indicator.The sample is sieved and dried in an oven and transferred, in a known amount, into a flask. With 20 ml of a solution (0.3334 molL-1) of potassium dichromate (K2Cr2O7) were collected in a precision burette and transferred in the flask containing the sample to be examined. The flask was placed in a bath of water and ice, than 26 mL of H2SO4 were added. After inserting the thermometer, the bulb must not touch the bottom of the flask, the mixture was heated, with a Bunsen flame, up to a temperature of 160 ± 2 °C. This temperature was kept constant for 10 minutes. After 10 minutes the solution was cooled rapidly and transferred to a 200 ml graduated flask and taken to a volume with H2O. After sedimentation of the mineral solid residue, Ag2SO4 crystals, were added.The volumetric titration was performed by taking 20 ml of the clear solution with a precision pipette and transferred to a conical flask of 250 ml Erlenmeyer a wide neck. 100 ml of H2O and, in succession, 8 ml of H3PO4 and 0.5 ml of oxide hardener were added. The Erlenmeyer conical flask was placed on the agent and the titrated with sulfate iron solution until the solution changed from dark violet to green. The process was repeated under the same experimental conditions, and in a blank test to ascertain the error caused by the possible decomposition of the dichromate due to heating.
The organic carbon content is expressed in g / kg.

$$C\%\left(\frac{m}{m}\right)=\frac{(A-B)*N_1*0.003*200}{(20*M)} \quad (6)$$

where:
A = volume, expressed in millilitres, of ferrous sulphate solution consumed for the blank test;
B = volume, expressed in millilitres, of ferrous sulphate solution consumed for the analysis of the sample;
N1 = normality of the ferrous sulphate solution;
M = mass, expressed in grams, of the sample analysed

3. Characterization of the process liquid.

In the following, the results of the experiments on the various samplings are reported, (see Table 2).
The total nitrogen and carbon contents are due to residues in the TL derived from the contact with the biofilm and molecules coming from the reacted gas stream with the microorganism beds (Yang et al., 2012; Liang et al., 2012; Frutos et al., 2016).

Table 2 TL Parameters

Parameter	Value*
TN (mg/l)	835.1±18
TKN (mg/l)	325.1±15
$N\text{-}NH_4+$ (mg/l)	122.2±13
Total organic N (mg/l)	215.4±10
$N\text{-}NO_2^-$ e $N\text{-}NO_3^-$ (mg/l)	529.2±14
TOC (g/kg)	240.1±16

*The results are the average of three experiments replicated on the liquid after sampling.

In particular, in the second column of the Table 2 the mean values (the mean of 3 different values obtained on three different TL collected at the end of three consecutive months) of total nitrogen, organic and inorganic

nitrogen and of TOC were reported. The latter evidently shows the highest values of inorganic nitrogen deriving from the microbial action.

4. Conclusion

Most of the organic solid waste produced by biological treatments, dry sludge and bio-filters (peat, soil, compost, wood bark) can be included in a scheme to recover resources in terms of land application or composting. The results of the experiments highlight the increase of the inorganic nitrogen content due to the microbial action. In general, all the values suggest the possibility of using these liquids as a base for fertilizers or as fertilizers. Due to their characteristics, and also thanks to the sterilizing action of the ultrasonic cavitation treatment before discharge, the recovered TL can be recognized into the category of nitrogen mineral organo-fluid fertilizers (Annex 1 of Dlgs. 75/2010 Table 6.1.1). It should also be stressed that nitrogen in the nitric form is absorbed faster by plants, producing visible results in the short term. Moreover, the N/C ratio ensures good biodegradability of the material. Finally, the high moisture content makes it possible to produce more concentrated fertilizers, thus determining an increase in nutrient contents at the same weight. It is worth noticing, that the microbial charge after ultrasonic cavitation, which evaluation is not object of this paper, is non-pathogenic.

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