

Renewable energy from ammonium-rich anaerobic wastewaters and liquid sludges

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Abstract

The Italian adoption of the recent European legislation on nitrates has further restricted the parameters for the discharge of water containing ammonium. This adoption has prompted the operators of wastewater treatment plants to invest in abatement equipment for ammonia within the parameters set by the law. This situation is particularly problematic for the anaerobic digestion plants that often have wastewater discharge with concentrations of ammonia nitrogen which also exceeds 3000 ppm. The technologies currently considered for eliminating ammonia include biological processes (*NITRO/DENITRO*, *ANAMMOX*, *SHARON*, *CANON*) [1] (which are difficult to apply to concentrations larger than 700-800 ppm) and stripping ammonia (that requires complex plants and the supply of large quantities of energy). To the end of introducing a technology providing a competitive removal of ammonium, an abatement process with energy recovery of ammonia (that is particularly effective for wastewater with high load of ammonium) has been developed and tested. From the energetic point of view the ammonia has a lower calorific value (18.6 MJ/kg) and contains 17.6% by weight of hydrogen. This is a remarkable (it exceeds by 41% the hydrogen content (by weight) of liquid hydrogen) result and may turn the effluent ammonium into a renewable energy source.

Introduction

The current regulations allow the discharge or disposal of wastewater containing ammonia nitrogen only in very low concentration. These regulations are designed to limit the problems deriving from the leaching of nitrogen compounds (nitrates) into groundwater intended for drinking and/or surface waters, contributing to elicit eutrophication processes. The wastewater containing ammonia nitrogen may be civil, livestock and/or industrial. In all cases, it is necessary a process of reduction of the ammonia load before their discharge into the sewer system or into surface water, or, where required by the regulations, before their spreading on land. Various biological and physico-chemical methods are known and available for to the reduction of ammonia nitrogen load. Biological methods are based on the action of particular bacterial species that, through various and different redox processes, eliminate ammonium by converting it, even in high quantities, into molecular nitrogen. The chemical-physical methods are based on the principle of separation. Among these methods the most commonly used consists in stripping gaseous ammonia from alkalized wastewater, by means of air or vacuum, often also with heating or air stripping of the wastewater itself. Other methods employ ion exchange resins or zeolitic that capture minerals by exchanging the ammonium ion and, to a small extent, also the gaseous ammonia. When the material that produces the exchange is exhausted as the exchange

sites are occupied by various cations (NH_4^+ , Ca^{++} , Mg^+ , Na^+ , K^+ , etc.) it must be brought about the regenerated with acid solutions or sodium chloride. The eluates from the regeneration of the resins or the zeolites contain high concentrations of ammonium that can be retrieved precipitating the ammonium as struvite or in the form of gaseous ammonia by stripping it off the alkalized solutions. Biological methods require bulky and costly aeration tanks and are conveniently applicable only at concentrations of ammonia nitrogen not exceeding 700-800 ppm, since at these concentrations biological processes can undergo phenomena of inhibition. Moreover, ammonia stripping process is not very efficient for the high costs of chemicals and energy as it requires high amounts of alkali to raise the pH up to the high values required for the process to occur and has high costs both for heating (especially in winter) and for the creation of vacuum necessary for blowing off ammonia. It also requires specialized personnel and all that makes it convenient only for cases in which there is a high quantity of wastewater to be treated to justify the economic investment. Among the chemical-physical methods also exists the possibility of capturing the ammonium present in the wastewater precipitated as insoluble salt. There are few insoluble salts and ammonium and Magnesium Ammonium Phosphate (MAP) is deemed to be the most suitable for the purpose. The addition to the effluent of magnesium and phosphorus salts in such quantities to obtain a stoichiometric ratio Mg: N: P equal to 1:1:1 leads to precipitation of the complex salt $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ known as "**struvite**" or more commonly **MAP** [2]. This application of MAP is well known so far and is used in various systems of wastewater treatment. For the removal of phosphorus only addition of magnesium salts is needed because the ammonium is already present in the wastewater in a concentration high enough to satisfy the stoichiometric ratios required. Ammonium, which can reach values over 3000-4000 ppm, can thus technically be removed using the precipitation of MAP. *Shigeru Sugiyama, et al* [3], propose to recycle the MAP obtained after removing ammonium thermally by decomposition of it, in order to eliminate the ammonium as NH_3 gas and recycle the magnesium and phosphorus salts for a new production cycle of MAP, with the ammonia gas being physically removed from the system. This procedure, although interesting, is energetically expensive. Moreover, *M. Iqbal H. Bhuiyan et al.* [4] show that it is rather troublesome to address the process of thermal decomposition into the formation of the MHP (acid phosphate magnesium), a salt useful for a iterative cycles of MAP production. *Shujun Zhang, et al.* [5] and *Shilong He, et al.* [6] propose to chemically decompose MAP by acidifying or alkalinizing the recovered MAP, in order to decompose it and obtain the magnesium and phosphorus salts needed for a new MAP production cycle. These methods solve the problems of thermal decomposition but they are costly in terms of high quantities of acids or alkali needed. Furthermore, the addition of alkali or acid may lead to a excessive concentration of Na^+ , Cl^- , SO_4^{2-} due to their accumulation in the various recycling processes. Among the methods listed for the abatement of ammonium, the precipitation of the MAP is particularly appealing for being a very simple process and that it be applied over a wide range of plant sizes. However, none of the methods here mentioned takes into account the energy value of the ammonia content of the effluent. Ammonia show a high energy content, equal to 18.6 MJ/Kg and it is possible to decompose it electrochemically, both ammonium and

ammonia by obtaining hydrogen and nitrogen. *Gerardine G. Cask*, in US2009127094A1 [7], propose a method to decompose electrochemically the ammonium present in an alkalized solution and claim the applicability of such a method also for the decontamination of the ammonia contained in wastewater. The energy balance of the process would be positive because the electrodecomposed products are hydrogen and nitrogen. Hydrogen has a high energy density and is easily convertible into electrical energy. The amount of electrical energy required by electrolysis appears to be low compared to the energy content of the obtainable hydrogen. However, this method is much more efficient because of the high concentration of ammonium of wastewaters. The process patented *MI2009A001156* developed by *SERECO-BIOTEST snc*, is based on the idea of concentrating the ammonium content in wastewater to make the electrolytic decomposition process more efficient, while reducing the volume of wastewater to be treated. The method of concentration is based on the precipitation of MAP, which concentrates the ammonium in a solid phase precipitated as a ternary salt. Subsequently, with a suitable pH control, the ammonium content in the MAP precipitate, can be electrolytically decomposed into H₂ and N₂ whereas the MAP source is converted into Magnesium Hydro Phosphate (MHP). The MHP is an excellent candidate for the next cycles of capturing H⁺ of ammonium by exchanging it with ammonium ion. In this way, the ammonium content in the wastewater is firstly abated through the precipitation of MAP, then energetically recovered by electrolytic decomposition; finally the MHP resulting from such electrolytic decomposition is used in a new cycle of capture by recycling the chemical species therefore necessary to a subsequent precipitation of MAP, thus significantly cutting down process costs. In order to demonstrate the practical feasibility of this process, *SERECO-BIOTEST snc* in collaboration with LCSTE carried out several MAP electro decomposition tests. Samples of 10 g at 96.8% content of MAP, obtained from pig manure were finely ground and soaked in 100 ml of distilled water. The solution was then conditioned to a pH 11.0 by addition of NaOH 0.05 N. Two electrodes in AISI 316 with flat and parallel faces were immersed in the solution and applied a potential of 1.00 V. Passage of a current of 25 mA triggers the electrolytic conversion of NH₃ in H₂ and N₂. After 24 h of electrolysis the ammonium content of the solutions was determined with Kjeldahl method showing a concentration of N-NH₄ between 13-25 ppm. In parallel, six sample of MAP obtained from swine livestock waste, has been subjected to analysis in powder X-ray diffraction (XRPD) showing the presence of struvite (**Fig.1**). During the process of electro decomposition a certain amount of hydrogen and nitrogen is released from the electrolytic cell. At the end of the process, the electro-decomposed supernatant persisted even in the presence of a precipitate of crystalline nature that has been subjected to determination of the content of ammonium according to the Kjeldahl procedure showing a concentration of N-NH₄ less than 15 ppm. The precipitate was in turn subjected to XRPD.

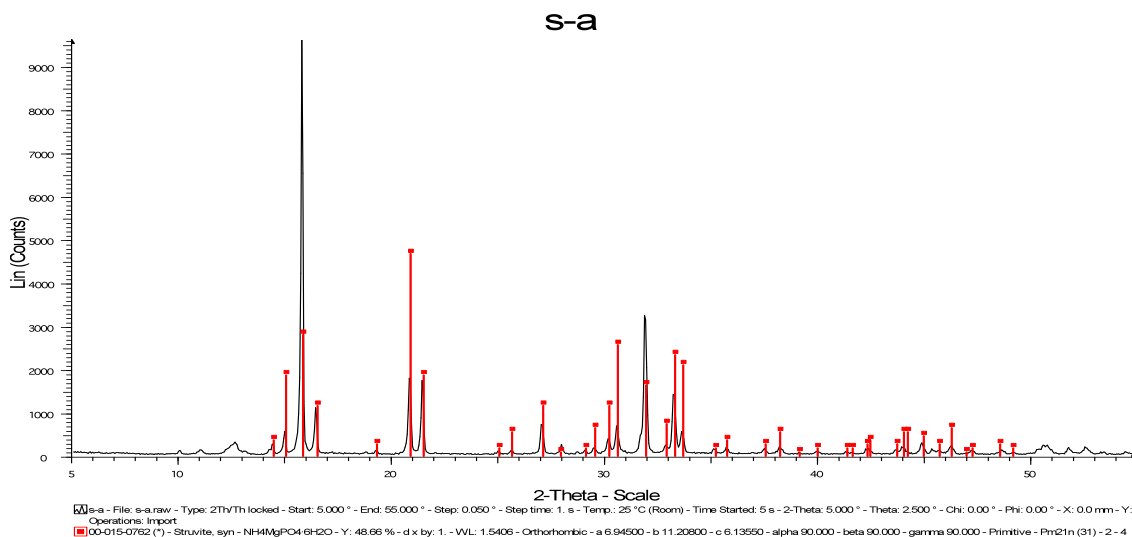


Fig.1

The same sample of MAP subjected to XRPD investigation (**Fig. 2**), was decomposed electrolytically, with the above mentioned method.

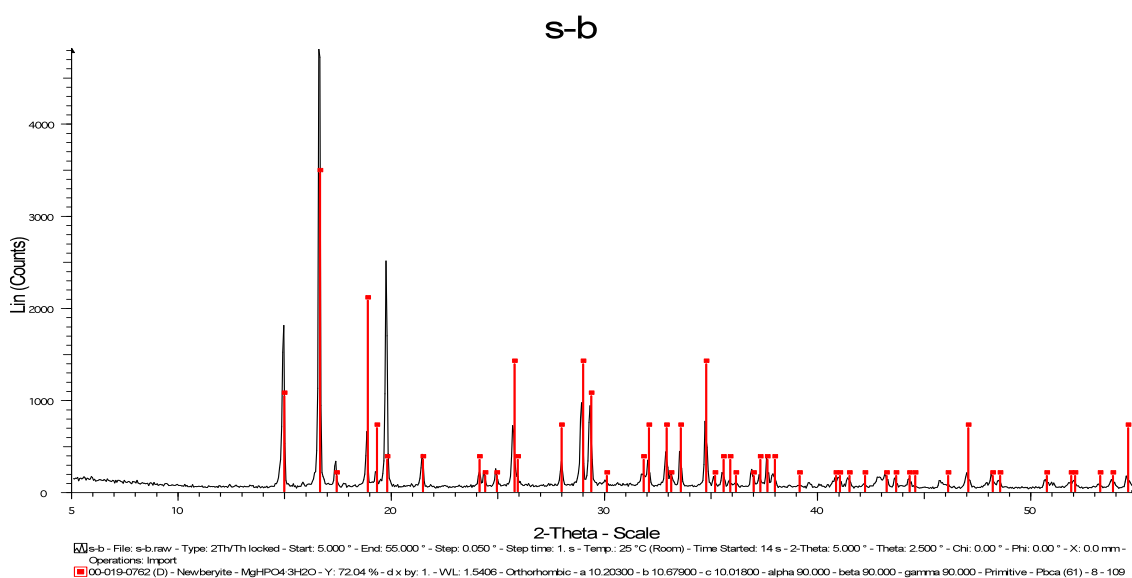


Fig. 2

The spectrum of **Fig. 1** shows the result of the analysis XRPD on the crystalline residue from electro decomposition and shows the absence of the crystalline phase "**struvite**" and the appearance of new phase "**newberiyte**" i.e. the magnesium acid phosphate MgHPO₄, (MHP). The spectrum of **Fig. 2** shows the disappearance of the signals relative to struvite demonstrating that the process of electrodecomposition is exhaustive and that the residual electrolyte is MHP newberiyte, i.e. the best salt of Mg and PO₄ to be used for a new cycle of precipitation of MAP of untreated wastewater. This example demonstrates how the precipitation of MAP and its subsequent electro decomposition is a method effective for the abatement of ammonium / ammonia and for the recovery of its energy content.

Discussion

According to the process mentioned in patent MI2009A001156 and here described, it is possible to decompose the struvite electrochemically, where, under suitable conditions of pH and temperature, the ammonium in equilibrium with MAP is decomposed into H₂ and N₂. This mixture of gases containing hydrogen can be energetically recovered and co-fired with biogas or by means of suitable fuel cells. The MAP subjected to electrolysis is converted into acid phosphate magnesium (MHP). The wastewater resulting from the anaerobic digestion plants exhibits high content of ammonia nitrogen variable between 1000 and 4000 ppm. The study suggests the application of the process to a facility for production of biogas from anaerobic digestion of piggery wastewaters for which are known and measurable parameters of biogas production and energy. In particular, for a typical plant producing biogas from the anaerobic digestion of wastewater from a 13000 pig farm, the following mean value from 10 samples were obtained: flow of sewage input 1200 m³/24 h; N-NH₄ 1540 mg/l; Volatile Solids 14.28 Kg/m³; COD 29,290 mg/l. Flow of wastewater centrifuged out 1170 m³ / day ,N-NH₄ 1370 mg/l; Volatile Solids 6.85 Kg/m³ , COD 5600 mg/l. The amount of biogas produced by the plant is 0.45 Nm³ per kg of volatile solids content in the slurry input. This leads to a daily production of biogas of 7716 Nm³/day. By considering a biogas lower calorific value of 23.3 MJ/Nm³ , the biogas plant has a production energy of 179.6 GJ/day. The biogas is converted into electric energy from the cogeneration system with a typical yield of 35%. This plant therefore produces 17.5 MWh/day of electricity that corresponds to a specific power of 728 KWe. The effluent leaving the digester is centrifuged to be separated from the mud and should be treated in order to reduce the content of ammonium nitrogen that, in the specific case, has a mean value of 1370 ppm. By applying to the centrifuged effluent the process of abating ammonium according to tested process and assuming that the process is adjusted in order to remove 90% of the nitrogen content of the effluent , the treated wastewater exhibits a nitrogen content of 137 mg/l as N-NH₃. The process of removal of ammonium through electro decomposition of MAP would produce a significant amount of hydrogen and nitrogen. The amount of hydrogen producible by the process according to the load content of ammonium nitrogen in the centrifuged wastewater is 1370 mg/l which corresponds to a quantity of ammonium equivalent equal to 1750 Kg/day. This amount of ammonium corresponds to an amount of hydrogen equal to 308 Kg/day. The hydrogen can be converted into electrical energy through fuel cells or directly sent to CHP for co-combustion. From 308 Kg/day of hydrogen 315 MWhe/day of extra electricity production is available that, if compared to 17.5 MWhe/day produced by the plant, would result in an increase in production of electricity of 18%.

Conclusions

The extra production of energy derived by the application of the invention to the real process of biogas production here analyzed, increases plant capacity by **18%** bringing it from **728** to **859 KWe without increasing CO₂ emissions** .

Bibliography

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