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Use of the Modelling in the Development of a Technology for Treating Wastewater from a Dangerous Process

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The production process of nitro aromatic hazardous compounds, with the generation of acidic wastewater, represent a significant dangerous for the health and safety of the workers and the environment. This wastewater containing solid particles of the nitro aromatic compounds and nitric acid in a concentration range between 58-62 %, constitute a potential danger to the environment where the occurrence of accidents are the main concern and reason for its urgent elimination. The present study is focused on to develop an efficient installation to treat acidic wastewater resulting from the synthesis process of nitro aromatic compound, considering workers safety and environmental criteria.
In this research, a detailed study of the different alternatives that can be used for effective and safety treatment of acidic wastewater was performed. The analysis of several technological schemes for the acidic wastewaters neutralization and the selection of the most feasible alternative from a technical-economical point of view were carried out. The ammonia was selected as neutralization compound due to its low cost and high demand of the product (ammonium nitrate) in the agriculture. An experimental design to carry out mass and energy balances was performed in order to define the most appropriate parameters to achieve the greatest effectiveness for the contaminated wastewater treatment. A lack of available information about the parameters of the chemical reaction that takes place between the ammonia and nitric acid (ammonium nitrate formation) as well as the reactor operating conditions was observed. The simulation and mathematical modeling developed in this research represent a significant advance in the knowledge of this process for working in a much more secure form.
The technological scheme of the process was defined and the design of the main and auxiliary equipment as well as the piping system was carried out using different computational programs. Finally, this paper proposes a technological design for the treatment of acidic wastewater generated by the production process of nitro aromatic compound, it which represents the basic criteria for the further design, construction and equipment installation of the plant.

1. Introduction

In Cuba, the environmental problems represent one of the major concern since 1981 when the Law of environmental protection and rational use of natural resources was approved. Several studies to improve the treatment of hazardous wastes generated from explosive production industry have been conducted.
The production process of nitro aromatic hazardous compounds, with the generation of acidic wastewater, represent a significant dangerous for the health and safety of the workers and the

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environment. This wastewater containing solid particles of the nitro aromatic compounds and nitric acid in a concentration range between 58 – 62 %, constitute a potential danger to the environment where the occurrence of accidents are the main concern and reason for its urgent elimination.
The present study is focused on to develop an efficient installation to treat acidic wastewater resulting from the synthesis process of nitro aromatic compound, considering workers safety and environmental criteria.

2. Methods

In this research, a detailed study of the different alternatives that can be used for effective and safety treatment of acidic wastewater was performed. The analysis of several technological schemes for the acidic wastewaters neutralization and the selection of the most feasible alternative from a technical-economical point of view were carried out.

2.1 Economic Technical Analysis of Alternatives

A possible alternative is based on the HNO_3 recovery, where the acid waters are concentrated achieving a nitric acid that could be reused in the process. The use of this alternative is recommended for process having significant amount of acids. A considerable reduction of the production cost (by raw material concept) can be obtained with this alternative. This alternative has many advantages, however, as a main economic disadvantage could be highlighted that the acquisition of a recovery plant is required.
Other alternatives for the treatment of this type of effluent are based on the neutralization by the use of different products. It has been reported by Cruz and Guerra (2002) that the best neutralization compounds are: ammonia, urea, carbonates or oxides of alkali metals and alkaline- earth.
Carbonate rocks and metal oxides. For this method, calcium carbonate, calcium oxide and dolomite can be used. Due to in the Central region of the country can be found huge natural reserves of these compounds, its use make less expensive the production process. From a comparison of these compounds, the dolomite represents the most suitable compound due to its least cost. Besides, the technology does not present major technological complications. Nevertheless, due to the great demand that the dolomite has for the glass production an insufficient amount of this compound for the use in the neutralization process could be observed. With respect to the product obtained, the calcium carbonate and calcium oxide as well as the dolomite may have some application in agriculture. However, the use of calcium carbonate and calcium oxide (in solution or granulated form) is difficult but for the specific case of dolomite, its use is impossible due to the climate conditions of the country. Other compounds that can be used in this alternative are calcium nitrate and potassium carbonate where the first one can be employed in certain soils with lack of calcium (this is not the Cuba situation) and second compound needs to be imported.
Urea and ammonia. The use of ammonia and urea shows higher production cost in comparison with carbonate rocks but analyzing the possible use of the final product, this alternative has the best results. Specifically, the neutralization with ammonia obtaining ammonium nitrate shows greatest advantages due to this fertilizer has a significant demand in our country, incorporating 35 % of nitrogen to the Cuban soils.
The neutralization with ammonia represents the best alternative because it offers a viable solution for the acidic wastewater treatment obtaining a final product with demand in the agriculture. Although, obtaining ammonium nitrate pearl has several advantages, the equipment and production cost are very high. The option of obtaining the liquid fertilizer 32-0-0 (called by its composition) represent the best alternative due to a feasible economic balance was found. Moreover, it can be dosed to the ground together with irrigation water (fertirrigation), is non-corrosive and it is not possible to harden at decreasing temperatures. Furthermore, a significant advantage for the plant development can be observed preventing damage to the rootlets by the intensive use of dry fertilizers. The disadvantages are outweighed by the overall efficiency and are also relatively simple solution. This technique can be applied in a wide range of situations with regard to crop types as well as the soil and water characteristics (Lipinski and Bermejillo, 2008).

2.2 Definition technological scheme

The flow diagram of the treatment plant is shown in the Figure 1.

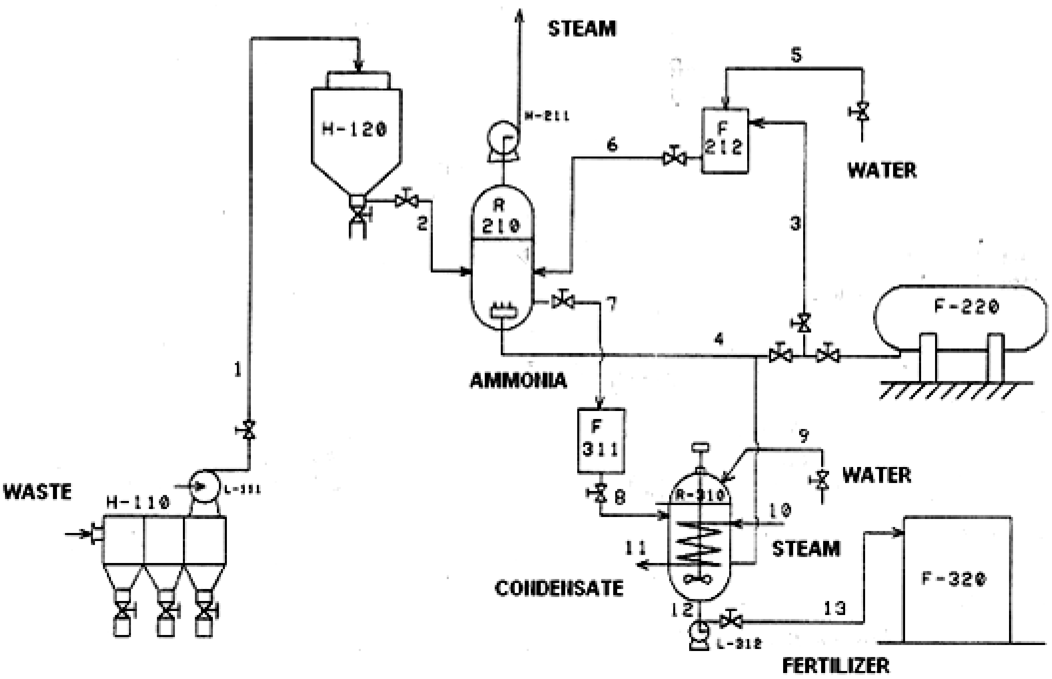

Figure1. Technological scheme. H – 110: Settler; H – 120: Filter Nutsh. ; R – 210: Bubbling reactor; F – 220: Bullet ammonia. R – 310: Stirred tank of fertilizer preparation. F-320 Fertilizer storage tank; L – 111: Pump of residual (HNO_3); H – 211: Extractor; F – 212: Tank of ammonia solution; F – 311: Intermediate storage tank of ammonia nitrate; L – 312: Fertilizer pump

The technological scheme defined is consist of three basic steps: cleaning or preparation of residual, neutralization step and obtaining the final product. The same is described then: during the production of aromatic nitro compound, the acidic wastewater drag small amounts of solid particles, that if pass to the neutralization stage, would jeopardize the process and operator’s life by the occurrence of violent reaction with high heat release. A sedimentation-filtration system was used for purifying the acidic wastewater. In the settling section to precipitate the dissolved solids in the wastewater a long time of settling was required. As the process will works at batch conditions, a suitable volume settler with the greatest possible area of sedimentation was designed. This equipment consists of two rectangular chambers where the first one (largest) was used as a sedimentation region, in which the residual arrives for a pipeline that discharge in its depth. After seven days, the first chamber is filled and the liquid passes smoothly per shawl through the second chamber. Subsequently, when the second chamber has a residual volume stored for one day, the pump installed on the surface feeder it extracts and pushes it into the filter. During the sedimentation the 75 % of solids are eliminated and the remaining particles are trapped in the thin fabric Nutsh filter which operates discontinuously and to vacuum. The settler sludge is unloaded by hand each certain time by the top of the settler. When the filtrate is obtained, is passed until the neutralization stage flowing the obtained liquid by gravity to a batch reactor with gas bubbling operating at atmospheric pressure. This equipment consist on a stainless steel cylinder 304, uncoated, in which the acid solution will be discharged and the neutralizing NH3 (g) will be provided by the background through a bubbler of stainless steel coated with Teflon.

In the neutralizer, the next chemical reaction takes place: $NH3+HNO3 \rightarrow NH4NO3$. The violent conditions that occur when these two substances react, are placated with the addition of an ammoniacal solution containing 15 % of NH3 (g) which passive the medium, decreasing the reaction of ammonia gas and the acid. Due to the effect of this reaction and the heat release that take place, the water vapor obtained from this stage crawl with them small amounts of ammonia and the solution formed. Product of this reaction and heat release that occurs, water vapour that is obtained carry with them small amounts of ammonia and the solution formed. These slightly contaminated vapors (1.5 – 2 % NH3 and < 1 % de HNO_3) are discharged to a suitable height using an extractor, avoiding the negative impact to the environment and human health.
In order to define the most appropriate parameters to achieve greater effectiveness in the treatment of polluted wastewater, laboratory experiments (using a small set up) as well as the needed experiments design to develop mass and energy balances for sizing the whole plant were performed (Cañizares and Ríos, 2003).

2.3 Process simulation

According to Ríos et al. (2003) and with the use of the software "PSI", which allowed model, simulate and scale the chemical reaction stages, were developed mathematical methods and procedures for evaluating and predicting the behavior of dangerous reactions; achieving integrated designs of the reactors that minimize the consumption of material resources, reduce waste disposal to the environment and ensure more security when working with hazardous substances.
Simulation was accomplished with a process's dynamic model. The model this constituted by the component's balance, the energy balance, the process's kinetics, and the electric load balance. The kinetics of the process was limited by gas-liquid mass transfer. To determine the mass transfer coefficient, several equations which are previously reported by Alves et al. (2003), Gang and Xi (2004), and Shimizu et al. (2000), were used in the present research. The model's fundamental equations are.
Component mass balance:

$$\frac{dN_i}{dt} = \sum R_j Vl \qquad (1)$$

Energy balance:

$$\frac{dT}{dt} = \frac{1}{mCp} \sum Q_k \qquad (2)$$

$$Q_i = f_{nh3} Cpg_{nh3} T_{input,} Q_r = 104.5\, R_{nh3} Vl\,,\ Q_s = 34.6\, f_{nh3}, Q_v = -(23.33\, Rv_{nh3} + 40.67\, Rv_{h2o} + 39.09\, Rv_{hno3}) \qquad (2a)$$

Charge balance:

$$c_{hno3} + 10^{Ph+14} + \frac{c_{nh4oh}}{1+10^{4.75+Ph-14}} = 10^{-ph} + \frac{c_{nh4^+ + nhs}}{1+10^{-9.25-Ph}} \qquad (3)$$

$pH=-\log [H^+]$ (4)

Table1. Rate terms in the mass balance equations

Component i	Evaporation rate	Mass transfer rate	Reaction rate
NH_3	$Kv_i(p_i - py_i)$	$kla(c_{eq} - c)$	$-kc_{nh3}c_{hno3}$
HNO_3	$Kv_i(p_i - py_i)$	-	$-kc_{nh3}c_{hno3}$
NH_4NO_3	-	-	$kc_{nh3}c_{hno3}$
H^2O	$Kv_i(p_i - py_i)$	-	-

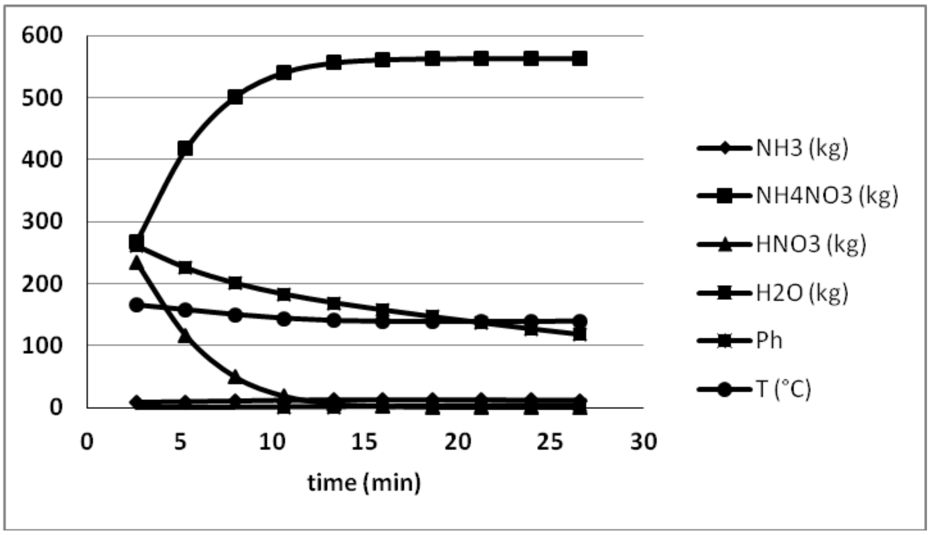

Figure 2. Mass of ammonia, ammonium nitrate, nitric acid and water vs. time

The ammonium nitrate obtained has a concentration of 80 %, and flows by gravity to a storage intermediate tank where it is stored to half of the solution formed, and the other half continues on his way to a tank provided with agitation and a heating coil. In the stirred tank is prepared liquid fertilizer known for its land application as ferti-irrigation and for its composition and 32-0-0. The agitator selected is propeller type and both he and the cylindrical container with conical bottom and the coil to be manufactured in stainless steel.

In order to obtain the fertilizer mentioned above, the ammonium nitrate is mixed with the required amounts of urea, phosphoric acid, ammonia and water. To carry out this research, the archived tables obtained from the Enterprise of Nitrogenised Fertilizer of Cienfuegos were consulted. The fertilizer formed has excellent characteristics when applied to cultivated soil. Other significant advantages can be shown from its use such as: is non corrosive, for this reason can be used in pipelines and irrigation equipment and storage of carbon steel or aluminum. Furthermore, this type of fertilizer can be dosed to the ground according to the crops need and does not represent danger by the crystallization effect.

The technological scheme of the process was defined and the design of the main and auxiliary equipment as well as the piping system was carried out using different computational programs and for determining the thickness of insulation required in each case. The spatial distribution of the equipments in the proposed plant was carried out. For this purpose the characteristics of the gravity for the different transport fluids involved in the process were taking in to account to place the equipments in each corresponding level of the plant. Moreover, the interlinked equipments compaction without affecting the workers comfort and safety and the environment was considered, establishing the conditions for the chemical safety handling and the process management without risk of accidents (Cañizares and Ríos, 2003).

3. Results and discussions

The neutralization of waste of plant of synthesis the nitro aromatic compound using ammonia is the most feasible, because it combines a lower economic cost and high demand of the product (ammonium nitrate) in agriculture. The ammonium nitrate obtained will be used as fertilizer in liquid form. The technological scheme alternative was defined for obtaining the called fertirrigation due to its several advantages for the land application.

We determined experimentally that the temperature of the reaction between nitric acid and ammonia is in a range between 120 -130 °C, and the material and energy balances were made for a production capacity of 600 t/y. The simulation results are well adjusted with the obtained laboratory data in regards to the prevalent operating conditions of the process and the obtained conversion.

The results of simulation agree with the results of laboratory in regards to the prevalent operating conditions and the conversion obtain. The last temperature finds around 130 °C, the pH approximately 1, 80 % of conversion, the losses of nitric acid and ammonia are little; younger than a 3 % in total, the heat of reaction is enough to concentrate the solution and the process presents good level of controllability, in regards to the temperature behavior.

The economic evaluation is positive, giving a net present value or net present value (NPV) of $ 924 399.35 with a return on investment (ROI) of 26 %.

4. Conclusions

From this study was determined that the use of neutralization with ammonia, for obtaining the fertilizer (32-0-0), represents a feasible alternative to treat acidic wastewater generated during the production process of nitro aromatic compound from technical, economical and environmental point of view.

A lack of available information about the parameters of the chemical reaction that takes place between the ammonia and nitric acid (ammonium nitrate formation) as well as the reactor operating conditions was observed. The simulation and mathematical modeling developed in this research represent a significant advance in the knowledge of this process for working in a much more secure form.

This paper proposes a technological design for the treatment of acidic wastewater generated by the production process of nitro aromatic compound, it which represents the basic criteria for the further design, construction and equipment installation of the plant.

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