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Technological Proposal for Treating Wastewater Contaminated with Nitro Aromatic Compounds by Simulation

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During the process of producing nitro aromatic hazardous compounds are generated wastewater highly polluting and dangerous for the health and workers safety and to the environment. The present study focuses on carrying out the project of a technology viable in the conditions of the country, for the treatment of wastewater contaminated with nitro aromatic compound (TNR). This compound is dissolved in the wastewater from the production process can form metal salts and very sensitive compounds that accumulate can lead to accidents, hazardous to human health and the environment, which is why it is vitally important disposal. The role of treatment is to achieve the destruction and elimination of nitro aromatic compound wastewater from the synthesis, purification and washing of this product.
In this research, methods and mathematical procedures have been developed to evaluate and predict the behaviour of nitro-aromatic compounds complex reactions during the TNR production process. An integrated design of semi continuous stirred tank type reactors was achieved in order to minimize the consumption of material resources and to reduce the dumping of waste into the environment. Programs developed by using PSI software were used to obtain the main variable profiles, consistent with the values taken by the experimental runs. The obtained phenomenological models by modelling were validated and the technological scheme of the proposal process was defined.

1. Introduction

The nitro-aromatic compounds are organic compounds containing one or more functional groups nitro ($^{-}NO_2$). They are often highly explosive and if it contains miscellaneous impurities or are improper handling can easily trigger a violent exothermic decomposition. Perhaps less well known is how low the danger threshold can be in practice: very small quantities of these chemicals (or of contaminant within these chemicals) can, in some circumstances, generate substantial explosions (Vince, 2013). Based on the importance that our country has been given to this environmental problem, several studies have been carried out to improve the treatment of hazardous waste generated by different manufacturing processes.
The wastewaters of the technological process of obtaining of TNR nitro aromatic compound are contaminated mainly by organic and inorganic compounds, which have a marked character acidic. This compound is dissolved in wastewater from the production process and can be very sensitive metal compounds and salts which cumulatively may cause accidents, dangerous for both human health and the environment; which is why it is important its elimination and requires carrying out the project and the design of an installation efficient for this purpose.
In earlier researches (Escobar and Velazco, 2004) and later Carballo et al. (2006), has been demonstrated poor efficiency of treatment that has been in place for many years, because it does not occur the total destruction of the nitro aromatic compound TNR, as is evidenced their presence in wastewater at the exit of

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the process. The role of treatment is to achieve the destruction and elimination of aromatic nitro compound wastewater from the synthesis, purification and washing of this product.

Investigations follow by Hernández (1994) and later Díaz (1997) reported the use of bleach mixtures, mainly sodium and calcium hypochlorite in discoloration of wastewater contaminated with various organic compounds (small and medium installations) and in the specific case of sodium hypochlorite, it is readily available, for being a cheap and domestically produced product. Previous investigations reported by Carballo and Guerra, (2006) have shown that the use of sodium hypochlorite as an oxidizing agent can significantly reduce pollution by TNR.

In Cuba, the environmental problems represent one of the major concerns 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 (Ríos et al., 2012). EMI industry "Ernesto Guevara" is one of the major industries of explosives who it is still in production at the country and it is located at the central region of the country. Currently, the industry is maintained with the production of TNR-PB (type of explosives) using a Spanish technology that generates wastewater with high pollution by the presence of nitro-aromatics compounds. It has been found that this treatment does not meet the standards for industrial wastewater dumping established in the country.

The present study focuses on carrying out the project of a technology viable in the conditions of the country, for the treatment of wastewater contaminated with nitro aromatic compound (TNR) using hypochlorite sodium.

2. Material and methods

2.1 Description of experimental procedure

In this research, a detailed study of the different variables for the treatment of wastewater contaminated with nitro aromatic compounds was performed to obtain optimal process conditions. First, the main variables of the process were established by experiments at laboratory scale. The principal variables that influence on the removal of nitro aromatic compounds in the reaction with sodium hypochlorite (NaClO) were: the pH, concentration ratio TNR: Sodium hypochlorite: r c(TNR) / c(NaClO), sodium hypochlorite concentration: C(NaClO), agitation speed: Vag., Response Time: treac and the Temperature: T (Rios and Peralta, 2008) and later (Rios and Peralta, 2010). After, an integrated design of semi continuous stirred tank type reactors was achieved in order to minimize the consumption of material resources and to reduce the dumping of waste into the environment. Finally, a phenomenological model was designed by modelling using PSI software to obtain the main variable profiles, consistent with the values taken by the experimental runs.

2.2 Description of wastewater treatment plant of TNR production process

The wastewater treatment plant of TNR production process has the function to achieve the destruction and elimination of the compound T1 of wastewater from the synthesis, purification and washing of this product. It consists of the following steps: addition of hypochlorite, aeration, dechlorinating, neutralization and sedimentation. The same is described then: First, it intends a storage tank where wastewaters remain before treatment if there any interruption in the system and as a primary treatment of sedimentation. The wastewater will undergo a filtration process, from where they will spend a reactor (R – 810) equipped with agitation to contact sodium hypochlorite (NaClO) arriving from a feeder tank. During this stage there is an oxidation reaction occurring total bleaching wastewater. After that the reaction occur, the wastewaters passed to a Nutsh type filter where the solids present are removed, and hence will be driven to a collection tank filter, for safety reasons, before being pumped to the next processing step.

After treatment with hypochlorite are a number of gases dissolved in these waters as Cl_2 (g), so is the aeration process in another type stirred tank reactor (R – 910), in order that these gases dissolved in move wastewater to dissolve into the air and can be evacuated (for this was studied in air flow l/h and the aeration time needed). In the same reactor, the wastewater passed out to the dechlorinating process to remove dissolved chlorite and chlorate by reacting with sodium thiosulfate ($Na_2S_2O_3$) 10 % to be reduced to chloride. The flow diagram of the treatment plant is shown in the Figure 1.

So far, the wastewater has an acid pH and it is necessary the addition of CaO or whitewash, to bring it to a neutral or slightly basic pH, before moving to the stage of sedimentation; here will be subject to a phase of coagulation-flocculation using as coagulant the iron sulfate (II) ($FeSO_4 \cdot 7H_2O$) 8 % and pH = 10. The settler is obtained good quality treated water according to the results of concentration of TNR, concentration of Cl_2, ClO^- and pH (Rios and Peralta, 2010).

We carried out the technical design of the main and auxiliary equipment and piping systems, using computer programs for calculating the pumping systems and for determining the thickness of insulation required in each case. It also conducted the physical layout in plant, based primarily on the use of gravity to transport fluids between the teams placed at different levels in the plant; also taken into account the compaction of interlinked equipments, without affecting the comfort and safety the workers and the environmental protection, as well as, the establishment of conditions for the safe handling of chemicals and the driving the process without risk of accidents (Rios and Peralta, 2010).

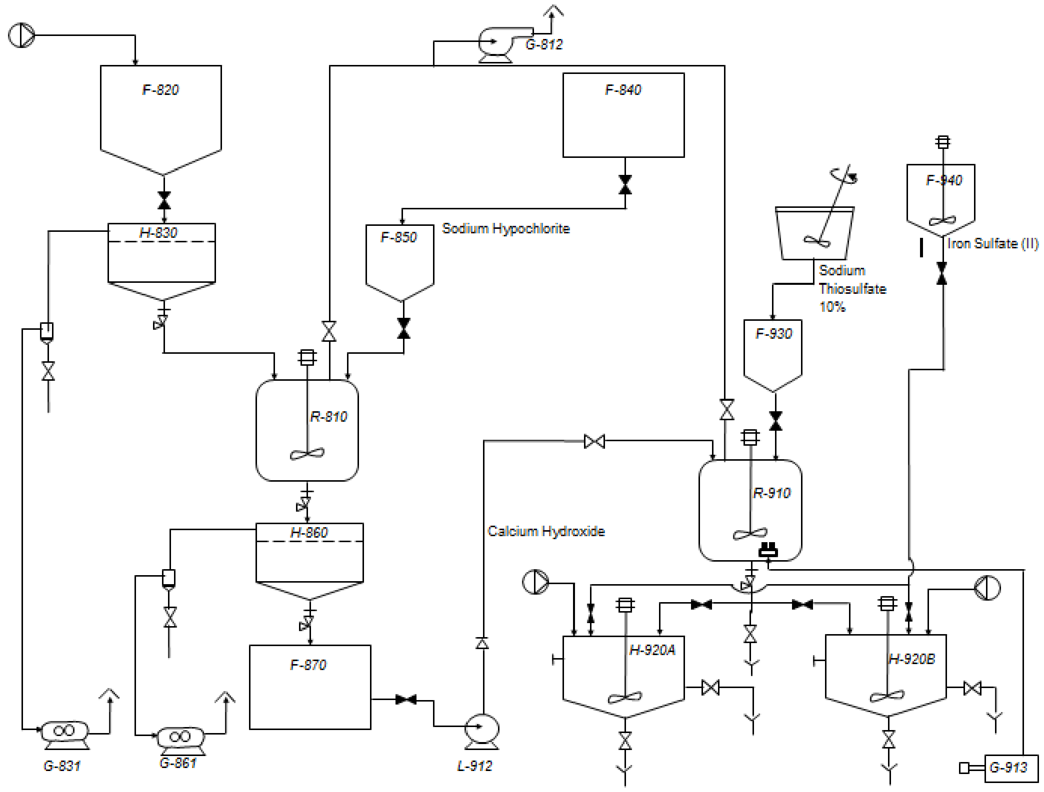

Figure 1: Technological scheme of the wastewater treatment plant.

R – 810: Reactor for treating wastewater with sodium hypochlorite; F – 820: Storage tank of wastewater; H - 830: Filter Nutsh; F – 840: Storage tank of hypochlorite sodium; F – 850: Dosing tank of hypochlorite sodium; H - 860: Filter Nutsh; F – 870: Filtrate collection tank; R – 910: Reactor for treating with sodium thiosulfate; H – 920 A: Settler; H – 920 B: Settler; F – 930: Dosing tank of sodium thiosulfate; F – 940: Flocculant preparation tank; G – 812: Centrifugal fan; G – 831: Vacuum pump; G – 861: Vacuum pump; L – 912: Centrifugal pump

2.3 Process simulation

According to Ríos and Peralta (2008) and later Ríos et al. (2010) 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 Shimizu et al. (2000) and later Alves et al. (2004) and also Gang and Xi (2004), were used in the presented research. The model's fundamental equations used specifically during the chemical reaction stage (R-810 and R-910) of the process are:

Mass balance of sodium hypochlorite:

$$\frac{dn_n}{dt} = F_n - r_n \tag{1}$$

$$r_n = K_0 \cdot e^{-E/RT} \cdot c_n \cdot c_{tr}$$

Mass balance of T_1 compound:

$$\frac{dn_{tr}}{dt} = -0.5 \cdot r_{tr} \tag{2}$$

Mass balance of water:

$$dh = Fh \tag{3}$$

Mass balance of dissolved chlorine:

$$dCl = r_n - r_{Cl}$$

$$r_{Cl} = 8 \cdot 10^{-8} \cdot a_r / a_{r_1} \tag{4}$$

Energy balance:

$$\frac{d(c_{p_m} n_t t)}{dt} = q_n - q_t + q_r - q_{Cl} \tag{5}$$

Scaling equations:

$$N_2 = N_1 \left[\frac{V_2}{V_1}\right]^{-2/9}$$

$$D_2 = \left[\left(\frac{V_2}{F}\right) \Big/ a + \left(\pi/4\right) R\right]^{1/3} \tag{6}$$

3. Results

3.1 Optimal conditions of the wastewater treatment process

From the study carried out to establish the optimal process conditions for the treatment of wastewater contaminated with nitro aromatic compounds, was determined that the most influence factors are: the pH, r C_{TNR}/C_{NaClO} and the concentration of sodium hypochlorite, and influencing much lesser extent are the stirring speed, the temperature and the reaction time.
The design method of the reactors was based on the experimental design performed at laboratory scale and with this data; a phenomenological model was conceived at industrial scale by process scaling procedure. The combination of scaling itself with the dynamic modelling allows a correct prediction and integral operation in the reactor on a larger scale.

3.2 Feasible alternative to revitalize the wastewater treatment system

The Figure 2 and Figure 3 show the performance of the main variables of the process during the reaction simulation of reactors R-810 and R-910 at industrial scale (Rios and Peralta, 2010). The most significant variables of the process and their values were taken at the end of reaction time were assessment and. The implementation of a dynamic model can be represented graphically to discover output values at any instant of time of either programmed variables.
The results of the simulation of one industrial scale reactor demonstrated that both the mass of the product TNR (mtr), as the number of moles (ntr) become zero at about 6 min of chemical reaction. Meanwhile, a performance (ren) very close to 100 % was observed at this interval of time. The number of moles of sodium hypochlorite (nn) increases to the extent that the same be added and finally reaches a stable value. The number of moles of chlorine (ncl) increases progressively until the sixth minute and on that slowly decreases progressively. The heat of reaction was determined experimentally and found that there are no problems with heat transfer. The temperature remains constant, showing that a value exceeding 20 % does not create problems or raising the temperature or heat transfer.
An analysis of the graph showing the results of the simulation of two industrial-scale reactor can be concluded that in the first stage of treatment shows that the number of moles of chlorine (ncl) is zero as air is added with a flow value constant, during a time of 12 min. The number of moles of chlorate (na) remains constant until it begins the second stage of treatment in which the addition of sodium thiosulfate chlorate makes disappear about 16 min after the start of the reaction. The number of moles of sodium thiosulfate (nto) will increase as it adds up that takes a constant value at the end of the reaction. Likewise, the power flow of sodium thiosulfate (fto) increases rapidly at first takes a constant value and decreases to zero when it completes its addition. The total volume of wastewater (vtt) undergoes an increase, which takes a constant value, with bubbling air, then takes the initial value during the second phase will increase as will adding sodium thiosulfate to reach a constant value. The gas flow (qg) ensures total dispersion of gas in the vessel and was determined experimentally and industrial scale at which we calculated the dimensions and parameters of an air bubble in a ring.
The modelling and simulation studies of chemical reaction steps showed that there are no problems with heat transfer and the temperature remains almost constant throughout the interval, reaching the end of treatment a yield 100 %, approximately 16 min, which confirms the accuracy and reliability of the experimental results.

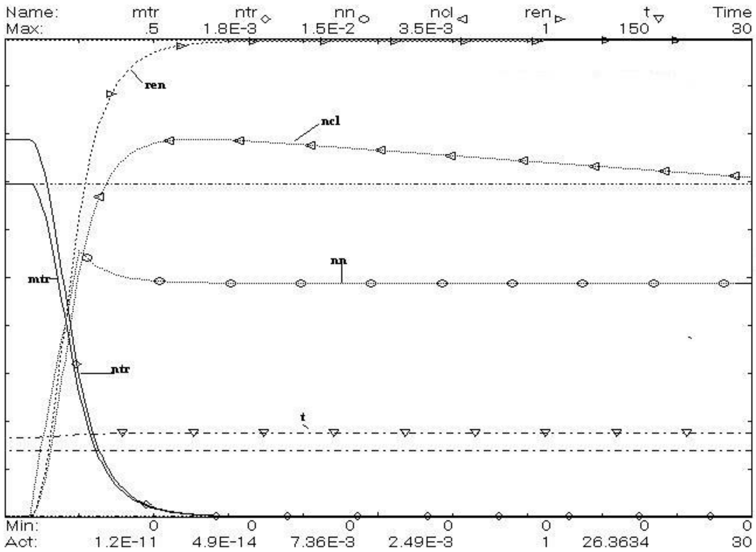

Figure 2: Perfomance of the process variables at different stage for the Reactor R-810. na: chlorates flow [kmol/h]; nto: thiosulfates flow [kmol/h]; qg: gases flow [m^3/h]; ntt: total flow [kmol/h]; fto: feed flow of sodium thiosulfate [kmol/h]

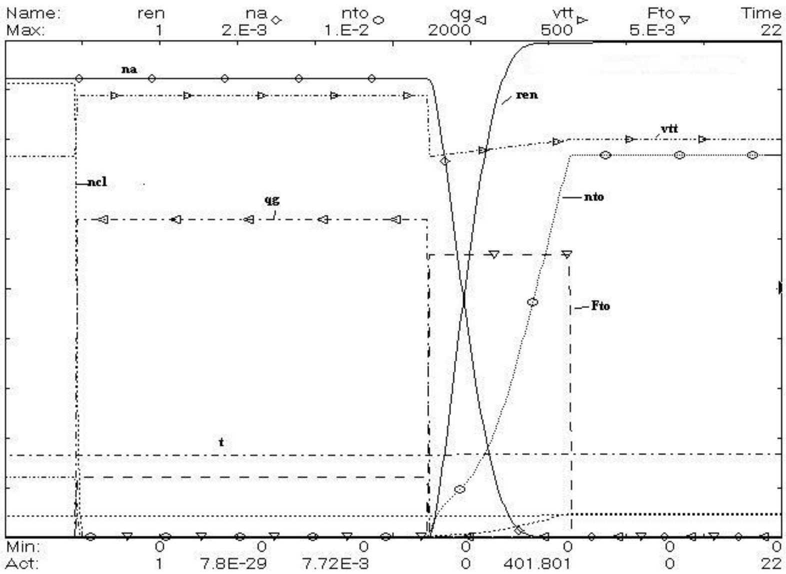

Figure 3: Perfomance of the process variables at different stage for the Reactor R-910. na: chlorates flow [kmol/h]; nto: thiosulfates flow [kmol/h]; qg: gases flow [m^3/h]; ntt: total flow [kmol/h]; fto: feed flow of sodium thiosulfate [kmol/h]

3.3 Comparison between experimental and simulation parameters:

A comparison between experimental and simulation operational parameters was conducted to evaluate the adjust level of the proposal phenomenological model. As it can be observed in Table 1, the values obtained by simulation keeps a very well correlation level with the parameters obtained experimentally for the both evaluated reactors (Reactor R-810 and R-910).

Table 1: Operational parameters obtained experimentally and by simulation in the reaction stages

Parameters	Experiment	Simulation
	Reactor R-810	
Temperature (°C)	25	25
Conversion (min)	0.999551 (10 min)	1 (10 min)
c_fT_1 (kmol/L)*	$1.7\cdot10^{-16}$	0
	Reactor R-910	
Temperature (°C)	25.16	25
Conversion (min)	0.999654 (15 min)	1 (15 min)
$c_{fclorhides}$ (kmol/L)**	$1.95\cdot10^{-31}$	0

* c_fT_1 is the final concentration of the compound T_1 obtained in the reactor R-810; ** $c_{fclorhides}$ is the final concentration of chlorides obtained in the reactor R-910.

4. Conclusions

The study undertaken is determined that is feasible the treatment from contaminated wastewater with TNR, by use of sodium hypochlorite as an oxidizing agent. The best results (100 % removal of TNR) are achieved when pH = 1 is used, r CTNR / CNaClO = 0.14 and concentration of 4.8 % sodium hypochlorite.
Simulation models developed using PSI software was able to obtain profiles of main process variables; consistent with the values taken in the experimental runs developed strongly validated phenomenological models made in the development of programs. The models obtained allow us to assess the sensitivity of the processes against different failures and / or accidents, especially for the synthetic processes of hazardous substances, which is achieved by predicting the course of the reactions of safely.
The integrated design, that includes the optimization of operating parameters and fundamental geometric dimensions of semi continuous stirred tank reactors with heat transfer, to minimize material consumption in the manufacturing process and reactor. The proposal technological design of the wastewater treatment system of the plant for the production of nitro aromatic compound (TNR), representing the basic criteria for the subsequent design, construction and installation of equipment and plant as a whole.

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