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ENHANCED ELECTRO-OXIDATION FOR TKN REMOVAL FROM HIGHLY POLLUTED INDUSTRIAL WASTEWATER

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ABSTRACT

Many industrial effluents contain concentrated Total Kjeldahl Nitrogen (TKN), which may might be also accompanied with ammonia, sulfur, iron, total solids, etc. Conventional wastewater treatment plants are unable to remove TKN, to a level acceptable for the ecosystem, thus, such wastewater has to be treated at the source; however, adequate methods have not been demonstrated yet. The industrial wastewater of concern, which contained 14 g TKN/L and 11 g NH4/L had a low probability to be biologically treated, therefore, an enhanced electro-oxidation method was proposed in this study. The industrial effluent was subjected to a series of tests, where finally the electro-Fenton oxidation demonstrated the best results; however, the method was designed to be effective without an addition of external iron; iron pollutant contained in wastewater was used instead. DC electrical field permitted to keep iron at an adequate state for the Fenton reactions. The results from batch reactors of 2.2L showed an excellent removal of TKN and ammonia - 98.7% and 99.5%, respectively. In order to decrease the detention time to 24h, an Electro-Fenton Sequential Batch Reactor (EF-SBR) was invented and designed. Considering a low degradability of TKN in the form of amides, the developed Enhanced Electro-Fenton Oxidation method based on wastewater components, is an effective approach in preventing the discharge of organic nitrogen to the sewage system and therefore protecting the environment. Moreover, the proposed design is sustainable since limits supplying additional chemicals and optimizes energy use. The technology is ready for a full-scale application.

Keywords: Industrial wastewater treatment, Enhanced Electro-Oxidation, TKN, Ammonia, Electro-Fenton Sequential Batch Reactor, Detention time, Electro-Fenton Oxidation, Sustainable design.

1. INTRODUCTION

Highly polluted industrial wastewaters require adequate treatment before discharge since it is mostly considered as one of the greatest threats to the ecosystem. Moreover, at conventional treatment facilities, total Kjeldahl nitrogen (TKN) removal may not reach the allowable discharge concentration before being released to the receiving waterbodies because of its low degradability. Furthermore, the high concentration of ammonia in wastewater increases the complexity in TKN removal. Therefore, an operation unit based on Advanced Oxidation Processes (AOPs) appears to be an appropriate approach to obtain a satisfactory TKN removal. Unfortunately, no such treatment is available at this moment.

There is a number of Advanced Oxidation Processes (AOPs) such as: Ozonation, Photolysis, Fenton Oxidation, Photo-Fenton Oxidation and Electrochemical Advanced Oxidation Processes (EAOPs); however, they have never demonstrated successful treatment of such harsh wastewater. The first disadvantage that limits the use of ozonation in this study are the fact that the compounds with an amide structure are resistant to ozone (Nakada et al., 2007). An additional disadvantage is the side effects of the by-products from ozone treatment, which may be more harmful than the parent ones (Li et al., 2008). Moreover, the mass transfer of the ozone molecule from the gas to liquid phase is a limiting step, which reduces removal efficiency and increases the cost of treatment (Homem and Santos, 2011).

There are two types of photolysis processes: direct and indirect. In the direct process, organic compounds absorb UV light and undergo self-decomposition (Boreen et al., 2004). Since photolysis can be applied to low COD loads and photosensitive compounds (Kummerer, 2009), it cannot be used to the wastewater of concern since its chemical oxygen demand (COD) is 44000 mg/L. Fenton Oxidation requires the presence of Fe^{2+} and H_2O_2, where ferrous ions act as a catalyst while hydrogen peroxide produces hydroxyl radicals to degrade organic compounds. Moreover, H_2O_2 can act as an OH scavenger as well as an initiator (Venkatadri and Peters, 1993). The disadvantages include expensive treatment of sludge and a limited pH range (pH 2-3), as well as the fact that not all organics are susceptible to this type of oxidation (Nidheesh and Gandhimathi, 2012). However, the costs might be reduced if the addition of chemicals (e.g. iron) can be avoided.

Photo-Fenton Oxidation, which is the combination of Fe^{2+}/H_2O_2/UV, which can use solar radiation instead of UV to decrease the costs (Bauer and Fallmann, 1997). However, the process needs a reactor with a chamber that limits the design parameter selection (e.g. detention time and dimensions of the reactor); furthermore, it requires a continuous source of light, which would not be always available. Likewise, UV resource installation causes a significant increase of costs. Thus, Photo-Fenton Oxidation was not applied in this study.

Electro-Fenton Oxidation is one of the electrochemical advanced oxidation processes that has a possibility of a high mineralization of persistent organics. The feasibility of Electro-Fenton Oxidation reactions and anodic oxidation was studied in this research for the first time on such complex wastewater (Tab. 1). The proposed Electro-Fenton process was modified, since wastewater contained already iron. The application of an adequate direct current (DC) electric field would keep the iron in an adequate state for Fenton reaction. The sustainable approach to this industrial wastewater treatment lies on using contaminants instead addition of chemicals to initiate Fenton reaction. The concept of electro-bioreactor (Elektorowicz et al., 2011) where electrochemical processes might be prevalent over biological processes, or vice-versa (Ibeid et al., 2013; Hasan et al., 2012), was previously applied; however, it has not included Fenton process yet.

2. MATERIALS AND METHODS

2.1 Methodology

The objective of this study was to achieve the lowest possible concentration, or highest removal, of TKN using the modified Enhanced Electro-Oxidation without the addition of iron. Instead, this study used iron contaminant contained within the industrial wastewater (Tab. 1). Generally, the Electro-Fenton is an indirect oxidation that generates hydrogen peroxide by the reduction of oxygen at cathode surface (Eq. 1). Then, the oxidizing power is enhanced by the production of OH radicals in bulk solution trough Fenton reaction (Eq.2). This reaction is catalyzed from electrochemical re-generation of ferrous ions (Eq. 3).

[1] $O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$

[2] $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH$

[3] $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Hydroxyl radicals lead the process to a higher oxidation potential level and ferric ions are produced in the result of oxidation potential increase. Effective destruction of wastewater contaminants is due to generation of highly reactive radicals (HO^-) – a strong oxidizing agent.

[4] $H_2O_2 + Fe^{+2} + H^+ \rightarrow HO^{\cdot} + Fe^{3+} + H_2O$

They react with persistent organics and may mineralize them into inorganic ions or convert to biodegradable organic compounds. Electro-Fenton process removes organic nitrogen (Eq.5), ammonia (Eq. 6 and 7) and TKN (Eq. 8) in the following equations:

[5] $R + OH^{-} \rightarrow CO_2 + H_2O$ (or ROH)

[6] $2NH_3 + 6OH^{-} \rightarrow N_2 + 6H_2O + 6e^{-}$

[7] $6H_2O + 6e^{-} \rightarrow 3H_2 + 6OH^{-}$

[8] $NH_3+ + O_2 + 2e^{-} + H_2O \rightarrow NO^{2-} + 5H^{+} + 4e^{-}$

2.2 Materials

The industrial wastewater in this study, containing high concentrations of TKN, were sampled at the “end-of-pipe” at industrial facilities and analyzed within 12 hours. The initial concentration of its compounds and physiochemical properties are provided in Table 1 and Table 2, respectively. Hydrogen peroxide 30% was used as an associated oxidant in order to produce hydroxyl radicals and to occur the Fenton reactions during Enhanced Electro-Oxidation process. Hydroxyl radical led the process to higher oxidation potential where ferric ions produced in the result of oxidation potential increase. Effective destruction of wastewater contaminants was due to a generation of highly reactive radicals (HO^{-}) – a strong oxidizing agent. The initial pH of the wastewater was maintained without any adjustment.

Table 1: Initial concentration of wastewater pollutants

Compound	Concentration [mg/L]
TKN	14000
Ammonia	11000
TN	14500
Nitrate/Nitrite	519
Organic nitrogen	3000
Ferrous ion	2760
Sulphate	4190

Table 2: Initial physiochemical value of industrial wastewater

Parameter	Average Value
pH	6.85
Conductivity [mS/cm]	54.8
ORP* [mV]	-10.7
Temperature [°C]	15.7

2.3 Equipment and Setup

Enhanced electro-oxidation experiments were performed in the laboratory in a single electro-Fenton reactor (Fig. 1). The studies consisted of 3 phases, namely small-scale, higher (medium) scale and EF-SBR (Electro-Fenton Sequential Batch Reactor). In the first phase, graphite sheet and rods were used as the anode. They were characterized by very fine carbon grains that improved strength and heat-resistant comparing to other typical graphite materials. Stainless steel was used as the cathode in both forms: mesh and sheets. The selection of the electrodes materials was based on preliminary experiments. Two individual power suppliers, 30V/5A and 20V/76A, were applied for a small scale and higher (medium) scale tests, respectively.

In the first phase, small-scale tests were conducted in 0.5 L electro-reactor (Fig. 1), while a various number of carbon rods were used as an anode and mesh stainless steel as a cathode. Using carbon rods enhanced the flexibility of the anode exposure surface area; it also helped to provide a larger anode surface area in a smaller volume reactor. The first phase of the study focused on the investigation of the optimal value of parameters in order to design electro-reactor properly on a small scale. Four approaches were considered and 43 experiments were conducted in order to investigate the influence of each approach. In the first approach different electrode materials were considered. In the second approach, the anode to cathode surface area ratio was investigated. The third approach consisted of studying the effect of varying the time interval of hydrogen peroxide supply. The fourth approach assessed the impact of adding ferrous ions ($FeSO_4$).

The scale-up design in phase 2 kept a constant current density and distance between electrodes. The medium scale tests were referred to experiments in 2.2 L effective volume reactor (Fig. 2). The carbon rods were used as the anode and stainless steel plate as the cathode. Carbon rods provided optimal current density in scale-up process. The distance between electrodes was kept constant; however, a fluctuation in the distance between the electrodes by more than 20% influenced TKN removal. Supply of hydrogen peroxide was adjusted and optimized over time.

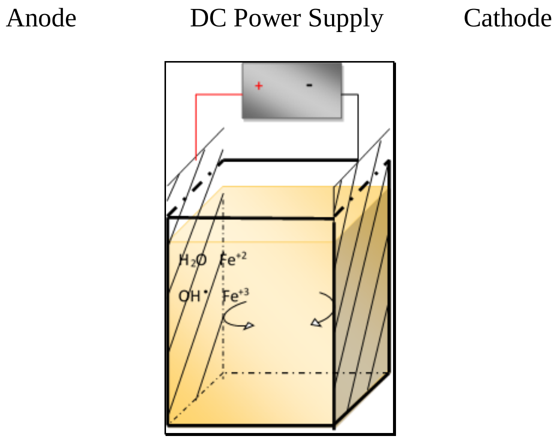

Figure 1: Schema of experimental setup for small and medium

In phase 3, the Electro-Fenton Sequential Batch Reactor (EF-SBR) of the effective volume of 6.7 L, was designed in order to optimize the energy use by considering exposure and detention time of the process. In the proposed EF-SBR design, a specific percentage of the volume was remaining after each sequence of treatment and discharge. This study demonstrates the initial stage of EF-SBR when the first three days was considered with subsequent two days of the process. EF-SBR is a novel process for TKN removal developed in this study. . It permitted to obtain in 24 hours better results than in a single reactor.

3. RESULTS AND DISCUSSION

In approach 1, the best results were achieved with very fine grain carbon graphite as the anode and stainless steel as the cathode after running 10 experiments with various combination of different electrode materials. For the second approach, according to achieved outcome, the best results were obtained in 1:1 anode to cathode surface area ratio (Fig. 2) among nine combinations from 0.125:1 to 1.25:1. The increase of TKN removal from 73.5% to 98.1% was observed when ratios 0.625:1 to 1:1 were applied, however the removal efficiency tended to decrease while the anode to cathode ratio is increased more than 1:1. Therefore, the optimal ratio was considered as 1:1.In the third approach, the optimal removal of ammonia (99.7%) and TKN (98.1%) was achieved when the 12h-interval supply of H_2O_2 was implemented (Fig. 3). The best removal efficiency was achieved in the fourth approach with respect to removal of TKN (98.4%) and organic nitrogen (96.7%). However, due to adding sulfate ions, the probability of producing hydrogen sulfide gas was increased. So the third approach was finally selected as a primary aim in experimental plan setting for scaling-up (Phases 2 and 3). The best achieved results in each small scale approach are provided in Tab. 3.

Operation conditions with 12h-interval of hydrogen peroxide supply led to a significant decrease in real-time of treatment process (60h) and helped to achieve higher removal efficiency comparing to all previous approaches (Fig. 3). A significant removal was achieved after 48 h when the amount of TKN was reduced from 14 g TKN/L to 1.08 g TKN/L (Fig. 2). Furthermore, an important reduction of the TKN concentration was achieved after 36 h when the addition of H_2O_2 was optimized.

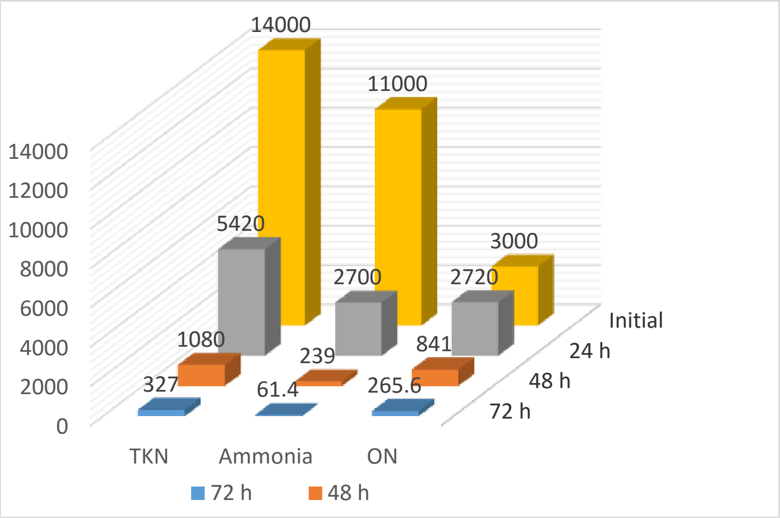

Figure 2: TKN, NH_3, and organic nitrogen concentrations (mg/L) in small scale experiments (Phase1, 2nd approach)

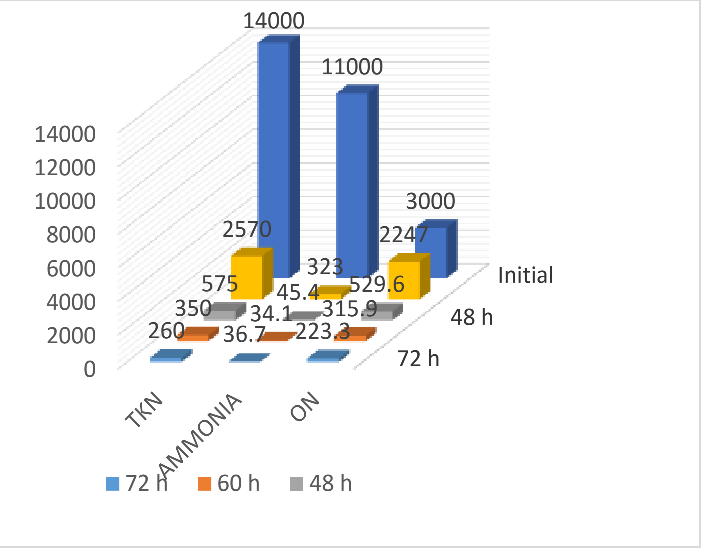

Figure 3: TKN, NH_3, and organic nitrogen concentrations (mg/L) in small scale experiments (Phase1, 3rd approach)

The second phase of the study focused on scale up the process in a reactor of medium size with an effective volume of 2.2 L. This phase used electrodes, current density, and interval of hydrogen peroxide application selected in phase 1. The results demonstrated high removal of ammonia and TKN, 99.3% and 97.8 %, respectively (Tab. 4). Significant removal efficiency was achieved in Phase 3 (Fig. 4) with new EF-SBR at higher (medium) scale because its second cycle demonstrated a removal of 98.6% for TKN. Furthermore, the designed EF-SBR reduced the energy consumption to one-third of previous setups due to 3 times shorter exposure time. Moreover, the capability of TKN treatment increased three times compared to the volume treated in other phases. This approach has been recommended for further scale up.

The results in all phases also showed a decrease in pH levels, which indicated acidity of the effluent. Therefore, pH adjustment after treatment was suggested, for example using sodium hydroxide (2M NaOH). An optimal volumetric ratio of treated wastewater and 2M NaOH solution was 1:1.42, which. means that 1 L of effluent with pH 1 needs 1.42 L of 2M NaOH to neutralize effluent to pH=7. No significant sludge generation was observed.

Table 3: The optimally achieved results in small scale experiments (Phase 1)

Description of Experiments	Current [A]	Voltage [V]	NH3 [mg/L]	TKN [mg/L]	ON [mg/L]
Initial Wastewater Properties	-	-	11000	14000	3000
Small scale 2nd approach after 72 h	2.87	4.4	61.4 (99.4%)	327 (97.7%)	265.6 (91.1%)
Small scale 3rd approach after 48 h	2.87	4.6	45.4 (99.6%)	575 (95.9%)	529.6 (82.3%)
Small scale 3rd approach after 60 h	2.87	5.4	34.1 (99.7%)	350 (97.5%)	315.9 (89.5%)
Small scale 3rd approach after 72 h	2.87	5.2	36.7 (99.7%)	260 (98.1%)	223.3 (92.5%)
Small scale 4th approach after 72 h	2.62	5.0	130 (98.8%)	228 (98.4%)	98 (96.7%)

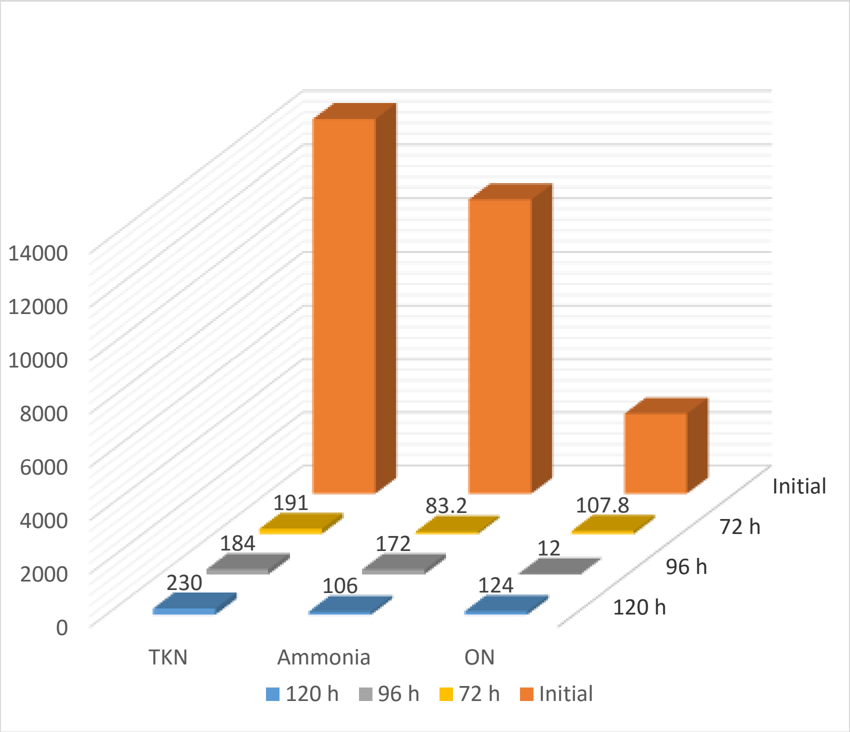

Figure 4: Concentrations (in mg/L) of TKN, ammonia and organic nitrogen after treatment using EF-SBR (1 cycle at medium scale), Phase 3.

Table 4 - The best achieved results in medium scale experiments

Description of Experiments	Current [A]	Voltage [V]	NH_3 [mg/L] % removal	TKN [mg/L]	ON [mg/L]
Initial Wastewater Properties	-	-	11000	14000	3000
Phase 2 after 72 h	10.54	6.45	71.8 (99.3%)	313 (97.8%)	241.8 (92%)
Phase 3 after 72 h	10.21	4.18	83.2 (99.2%)	191 (98.6%)	107.8 (96.4%)
Phase 3 after 96 h	11.66	4.11	172 (98.4%)	184 (98.7%)	12 (99.6%)
Phase 3 after 120 h	9.33	4.07	106 (99.0%)	230 (98.3%)	124 (95.9%)

4. CONCLUSIONS

The Enhanced Electro-Oxidation method using modified electro-Fenton phenomena was applied for the first time to industrial wastewater polluted with iron and TKN in the form of amides. This study optimized the process at a number of stages for efficient scale up of the reactor design. Results demonstrated that the proposed process is capable of reaching 99.5% and 98.7% removal efficiency for ammonia and TKN, respectively. Electro-Fenton Sequential Batch Reactor (EF-SBR) design, applied at a medium scale, also led to reduce the treatment time to 24 h, and therefore decrease treatment costs. The proposed successful and innovative technology is an important achievement with respect to treatment of TKN in industrial wastewater. It represents a sustainable design as it uses existing pollutants in the wastewater instead of relying on the addition of external chemicals allowing the process to be easily automated. Moreover, the proposed design is ready to be applied at full scale, and may be easily adjusted and implemented to both existing and newly built treatment facilities due to the fact that the configuration of existed setups don't require complete redesign.

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