الغرفة الإسلامية للتجارة والصناعة والزراعة
Islamic Chamber of Commerce, Industry & Agriculture
La Chambre Islamique de Commerce, d'Industrie et d'Agriculture

No. 57/OIC/0266

السلام عليكم ورحمة الله وبركاته

Sub: **'Design of a Fenton Oxidative Waste Treatment Plant'**
Federal Republic of Nigeria

The General Secretariat of Islamic Chamber of Commerce, Industry & Agriculture (ICCIA) presents its compliments to its Member Institutions and has the honor to state the following:

The ICCIA has received a letter from the General Secretariat of the Organization of Islamic Cooperation (OIC) informing that the Government of Federation of Nigeria has initiated a project entitled 'Design of a Fenton Oxidative Waste Treatment Plant' which is aimed at rehabilitating and building a water treatment plant to help address the acute shortage in the area.

Since the above mentioned initiative is in line with the relevant OIC resolutions on economic assistance to its member states, Member Institutions are requested to kindly circulate the said information among the interested members, who may support the execution of the said initiative. It is further requested that Honorable Members may kindly publicize the project details on their websites / newsletters / periodicals / magazines or in any other printed materials. Interested parties may contact the General Secretariat of the ICCIA:

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A copy of the project details is **enclosed** herewith

The General Secretariat of the ICCIA avails itself of this opportunity to renew to the Member Institutions, the assurances of its highest consideration.

Rajab 17, 1434
Karachi, May 28, 2013

The General Secretariat of the Islamic
Chamber of Commerce, Industry & Agriculture

ALL MEMBER INSTITUTIONS

ana/rz280502

جمهورية باكستان الإسلامية - ص. ب ٣٨٣١ كراتشي٧٥٦٠٠ هاتف: ٠٠٩٢٢١٣٥٨٣٠٥٣٥/٣٥٨٧٤٩١٠ فاكس ٠٠٩٢٢١٣٥٨٧٠٧٦٥/٣٥٨٧٤٢١٢ البريد الإلكتروني icci@icci-oic.org
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National Research Institute for Chemical Technology (NARICT), Zaria

An Industrial and Environmental Technology
Department Research Proposal on

Design of a Fenton Oxidative Wastewater Treatment Plant

February, 2013

4-8

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EXECUTIVE SUMMARY

Environmental pollution control continues to receive attention due to negative impact for ecosystems and humans from industrial wastewaters. These discharges can be toxic, carcinogenic and with mutagenic properties (Busca et al., 2008). Available data in 2009 indicates that 42 % of the global wastewater generation traces their origin to process industries (Doan et al., 2009) and among the organic wastewaters that attract significant environmental concern are recalcitrant wastewater. Textile, pharmaceuticals and petroleum refinery wastewaters are among these discharges with adverse environmental consequences and most active industries in Nigeria (Busca et al., 2008; Iurascu et al., 2009; Diya'uddeen et al., 2011a; Diya'uddeen et al., 2011b).

A robust and environmentally clean technology that minimize the generation of secondary waste phases is the advanced oxidation processes (AOPs). Here, highly oxidizing hydroxyl radicals (•OH) which potentially oxidize and mineralize almost any organic contaminant indiscriminately are generated [18]. Of the many AOPs - photocatalytic degradation, ozonation, and sonolysis, etc, Fenton oxidation is adjudged as the most cost effective, requires minimal energy input [20], with easy-to-handle reagents and no mass transfer limitation also make the method attractive [20, 21].

To the best of our knowledge, there exists no treatment plant utilizing the Fenton Technology or any other AOP in the country and thus the proposed research work aim to design and develop a pilot plant operating on classical Fenton oxidative technology for the abatement of recalcitrant effluents. The appropriate sequence of the process and the conceptual equipment design required for developing this system has been identified by the team members. Additionally, the team has work extensively on bench scale studies and published same in many high impact factor journals. More in depth data would be carried out to further enhance and materialize the concepts from the pilot plant scale perspective. Successful development of the plant would go a long way in addressing environmental issues related to the discharge of partially or untreated effluents.

The project in its entirety is to be carried out by a technical team from the National Research Institute for Chemical Technology (NARICT), Zaria in collaboration with researchers form the Ahmadu Bello University Zaria. The plant is intended to be located within the NARICT premises. The NARICT team is also advantaged by the fact that there is already an existing infrastructure related to fabrication (NARICT Fabrication Division) and a full-fledged Pilot Plant Division both located within the Research Institute.

2.0 LITERATURE

2.1 Background

2.1.1 *Textile Effluents*

The textile industry wastewaters poses serious environmental challenge due to large amounts of wastewater generated due to large quantities of water used. In a recent review, Oller et al. (2011) summarised the range of textile wastewater as 150 to 12000 mg/L, 2900 and 3100 mg/L and 80 to 6000 mg/L for COD, total suspended solids and BOD, respectively. Based on the biodegradability index ratio, BOD_5/COD, It's vivid from the ranges presented that this category of wastewater is recalcitrant with the average ratio being 0.25.

2.1.2 *Petroleum refinery wastewater (PRE)*

The refining process of crude oil produces over 2,500 refined products [1] and generates large volumes of effluents containing light fractions of aliphatic and aromatic petroleum hydrocarbons. As reported by Alva-Argaez et al. [2], the estimated average water consumption in processing a barrel of crude oil is 246 - 341 L of water. Approximately 0.4–1.6 times the volume of the processed crude oil is discharged as petroleum refinery wastewater (PRE)[3].

Generally, the effluents are made of numerous organic and inorganic components arising from the feedstock nature, which is composed mainly of hydrocarbons along with a wide range of other components [5]. Discharge of contaminants from the petroleum industries form residual chemical oxygen demand (COD), which has detrimental environmental consequences due to high oxygen demand and toxicity of the individual components in wastewater. Thus, strict regulations are in place in terms of minimum levels allowable for their disposal [6-8].

Concerted efforts to replace fossil fuels have been made; however, crude oil remains a strategic raw material. The need to augment the ever increase in global energy demand, which is expected to soar by 44 % over the next two decades (Doggett and Rascoe, 2009) makes the processing of crude oil and generation of PRE a global phenomenon. The forecast for world oil demand is a rise to 107 mbpd over the next two decades and oil is to account for 32 % of the world's energy supply by 2030 (Doggett and Rascoe, 2009). Biofuels, including ethanol and biodiesel, are expected to account for 5.9 mbpd by 2030 while contribution from renewable energy sources like wind and solar power is estimated at about 4-15 % only (Doggett and Rascoe, 2009; Marcilly, 2003). This vividly indicates that wastewaters from the oil industry would continually be produced and discharged into the main water bodies. This necessitates the need for a treatment approach that effectively treats these categories of wastewaters.

2.2 *Current Treatment Technologies*

Significant advancement has been made by several novel approaches for petroleum refinery effluent (PRE) treatment through COD reduction. Among them are cross flow membrane bioreactors [9], adsorption of pollutants onto date-pit activated carbon [10], coagulation and coagulant aids [11], electrocoagulation [1, 12], electrochemical oxidation [1] and catalytic vacuum distillation [13]. These techniques have limitations, as they only partially degrade the effluent, produce toxic intermediates, need an external source of energy and generate secondary phases that incur additional cost in the treatment process. In fact, for electrocoagulation, a recent work by Yavuz et al. [1] has established the method as ineffective in the treatment of petroleum effluents. It is evident that much research has gone into the development of these methods; however, the emphasis of wastewater treatment is gradually metamorphosing from partial degradation to complete destruction [8], as the constituents contaminants are hazardous. In the case of dye treatment technologies highlighted by Malik et al. [5] several drawbacks mitigate against the successful and effective treatment from environmental and health perspectives.

A critical review of most of the processes currently adopted for the treatment of recalcitrant WW has shown that these methods are bedeviled with many problems (Diya'uddeen et al., 2011b). These range from phase transfer of contaminants from one medium to another, the generation of a high amount of sludge, low treatment efficiencies and slow reaction rates (Kuyukina et al., 2009; Laoufi et al., 2008). Additionally, these treatment options do not mineralize the wastewaters. Thus, a robust approach is required to satisfactorily decontaminate the effluents completely.

2.3 Adverse effects of recalcitrant streams

The environmental concern over these discharges is related to their lack of biodegradability, toxicity and large volume generation (Alva-Argáez et al., 2007; Coelho et al., 2006). The disposal of PWW into water, as a priority pollutant (Mrayyana and Battikhi, 2005; Wake, 2005), results in decreased algae productivity, thereby affecting the food chain (El-Naas et al., 2009; Pardeshi and Patil, 2008) and depleting oxygen in receiving water bodies (Attiogbe et al., 2007; Poulton et al., 2002). PWW generally have a carcinogenic character and cause considerable damage to the ecosystem and human health (Abdelwahab et al., 2009; Pardeshi and Patil, 2008).

Effluents from the textile industry are highly complex and their composition varies significantly due to the presence of several contaminants. They generally contain synthetic dyes, surface-active agents and textile additive materials [1]. Their mutagenic effects are well-established; aesthetically, they impart strong colouring to the effluent, and adversely affect aquatic life [2].

2.4 Advanced Oxidation Processes (AOPs)

These are oxidative processes utilising hydroxyl radicals and have demonstrated effectiveness of treating recalcitrant and non-biodegradable products [6]. However, the petroleum industry has yet to benefit from the many opportunities these processes offer [14] and in the case of textile effluent the researches are limited to bench scale. Advanced oxidation processes (AOPs) are becoming an attractive alternative for the treatment of recalcitrant and high-COD-containing wastewaters [15]. They are regarded as environmentally clean technologies that minimise the generation of secondary waste phases, as the final product discharged is environmentally benign [16]. Advanced oxidation processes are basically physicochemical processes in nature that generate highly oxidising species, mainly hydroxyl radicals ($^{\cdot}OH$) with redox potential of approximately $E^0 = 2.8$ V (second only to fluorine with 3.06 eV) [17]. Advanced oxidation processes have successfully been employed in the treatment of myriad organic contaminants and can potentially oxidise and mineralise almost any organic contaminant [18]. The indiscriminate and strong reaction between organic compounds and $^{\cdot}OH$ mineralises almost all organic and inorganic components of the effluent into CO_2, H_2O and stable states of inorganic matter [19].

Application of AOPs have been reported using TiO_2-mediated photocatalytic degradation [3, 4, 8], ozonation [3] and photo-degradation [3, 19]. Despite the merits of the Fenton peroxidation, work in the open scientific literature reporting use of the process in PRE treatment is limited to one process that has been described by Coelho et al. [3], and more recently, the one that has been described by Yavuz et al. [1]. Both processes were not optimised, and mineralisation was not monitored in the latter work. Investigating interactions of parameters affecting the processes leads to proper utilisation of the reagents and, to a large extent, this promotes the choice of a treatment method with the cost of reagent as a critical determining factor [20].

2.5 *Fenton Oxidation*

There are several AOP's; however, the Fenton and Fenton-like oxidation are the simplest and most cost effective AOP. They have been widely used in the treatment of dye-containing wastewaters [6-11].

Of the many AOPs, Fenton peroxidation has been judged to be rather effective in degradation and mineralisation. The process is cost effective because catalysing the $^{\bullet}OH$ generation from hydrogen peroxide requires minimal energy input [21]. The absence of mass transfer limitation due to its homogeneous catalytic nature and easy-to-handle reagents also make the method attractive [21, 22]. Furthermore, the reaction time required to achieve mineralisation is remarkably less in Fenton oxidation than in other AOPs [23].

In the classical Fenton process, Fe^{2+} is used as the catalyst while the Fenton-like oxidation uses Fe^{3+}. However, the cost of Fe^{3+} is lower than Fe^{2+}, and this informed choice of the latter [12].

Basically, the Fenton oxidation generates the $\cdot OH$ through the cyclic catalytic decomposition of H_2O_2 by iron (II) ions (Fe^{2+}) as shown in Eq. (1), and iron (III) ions (Fe^{3+}) are also produced. The cycle is completed by the reduction of ferric iron by hydrogen peroxide and subsequent generation of perhydroxyl radicals and ferrous iron. The sequences of the reactions resulting in the radical generation are as shown in Eqs. (1) – (3) (Lucas et al., 2007) while the mineralization of the organic substrate (RH) generates free organics as transient intermediates, which are further oxidized to more stable products by $^{\bullet}OH$, Fe^{3+}, Fe^{2+}, H_2O_2 and O_2, (Eqs. (4) – (7)) (Hermosilla et al., 2009; Umar et al., 2010).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}_2 + H^{+} \qquad (2)$$

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (3)$$

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O \qquad (4)$$

$$R^{\cdot} + Fe^{3+} \rightarrow R^{\cdot} + Fe^{2+} \qquad (5)$$

$$R^{\cdot} + Fe^{2+} \rightarrow R^{\cdot} + Fe^{2+} \qquad (6)$$

$$R^{\cdot} + H_2O_2 \rightarrow ROH + {}^{\cdot}OH \qquad (7)$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \qquad (8)$$

1.4 Problem Statement

Currently, the treatment techniques adopted for recalcitrant wastewater possess many shortcomings. Inefficient and incomplete degradation, transfer of the contaminants from one medium to another, generating high amount of sludge, low efficiencies and slow reaction rates are few among them (Shukla et al., 2010; Navalon et al., 2010). Such wastewaters include resin-producing factory discharges (Aparicio et al., 2007), textile wastewaters (Sun et al., 2007; Huang et al., 2010), petroleum refinery wastewaters (Coelho et al., 2006), s-triazine herbicides and dyes containing the triazine ring (Watanabe et al., 2005), metal working fluids (Jagadevan et al., 2011), pollutant from pharmaceutical industry such as ibuprofen (Di Iaconi et al., 2010; Méndez-Arriaga et al., 2009) and aromatics (Garcia-Segura et al., 2011). Literature is replete with studies identifying Fenton oxidation as the most promising approach to the remediation of these wastewaters (Di Iaconi et al., 2010; Ballesteros Martín et al., 2010; Shukla et al., 2010). However, for textile and petroleum wastewater, the most active industrial sector in Nigeria, much is yet to be done.

1.5 Objectives of the Project

The objectives of the proposed project are as follows:

a) To develop design and construct a pilot plant for recalcitrant wastewater treatment.

b) To investigate the unit operations arrangements, alternate catalyst and oxidant with the aim of minimizing operation cost and attaining higher efficiencies.

c) To establish and evaluate the treatment cost based on experimentally determined required amount of oxidant of (hydrogen peroxide, formic acid, etc), amount of catalyst added (iron II or III, nZVI, etc (a factor that also depends on the nature of the pollutant) and amounts of reagents used to change the pH (H2SO4 and/or NaOH). Finally the treatment cost of the sludge generated will be computed and incorporated in the cost analysis.

d) In the case of sludge disposal, experiments would be conducted to establish possible application of the sludge generated.

1.7 Justification for the Project

a. Unreliable power sources do not pose a problem for the Fenton Technology as it relies on minimal power consumption

b. Can be easily integrated into existing wastewater treatment plants with little modification.

c. Treatment process releases little or no odor emissions

d. The utilization of this environmentally friendly technology leads to higher levels of performance, a more compact layouts and more cost effective management improvements in purification, speed of water treatment and enhances application of the treated wastewater. Broadly, the process results in more energy savings and time. In addition, potential disease-causing contaminants are removed and this reduces their risk of entering water sources.

e. The fact that water possesses economic value often goes unrecognized. According to the United Nations, water scarcity is amongst the most serious crises facing the world. Thus the use of treated waste water is a great economic advantage especially as water scarcity is increasing at alarming rate and this can impact consumer cost by reducing the demand for potable water sources. And this waster scarcity is a global phenomenon as the world's supply of fresh water is slowly running dry with an estimated 40% of the world's population already reeling under the problem of water scarcity.
f. It's worth mentioning that, most of the diseases plaguing the world are water-borne and while there is a child born every eight seconds in America, there is a life taken every eight seconds by some water borne disease in other parts of the world (Runion, 2012).
g. A process of wastewater treatment has many associated environmental benefits. However, these benefits are often not computed as they are not set by the market. Recently, Hernández-Sancho et al (2010), proposed a methodology based on the estimation of shadow prices for the pollutants removed in a treatment process to represents value to the environmental benefit (avoided cost) associated with un-discharged pollution. Their findings, by comparison of these benefits with the internal costs suggested the economic importance of wastewater treatment.

2.6 Value to the Nation

i) Success of the project will justify and catalyze proper management of recalcitrant wastewater and allows for enforcing proper wastewater disposal.
ii) Potential of developing local capacity in process and equipment designs, process intensification, optimization and trouble shooting.

iii) Benefit relating to education and training of students and the career development of the researchers involved.

iv) Promoting innovative research and development in environmental technology and establishing an advance research infrastructure

v) Contribution to the conception of advanced wastewater treatment to industries which will invariably enhance the national economy

3.0 DESCRIPTION OF THE PROPOSED WORK

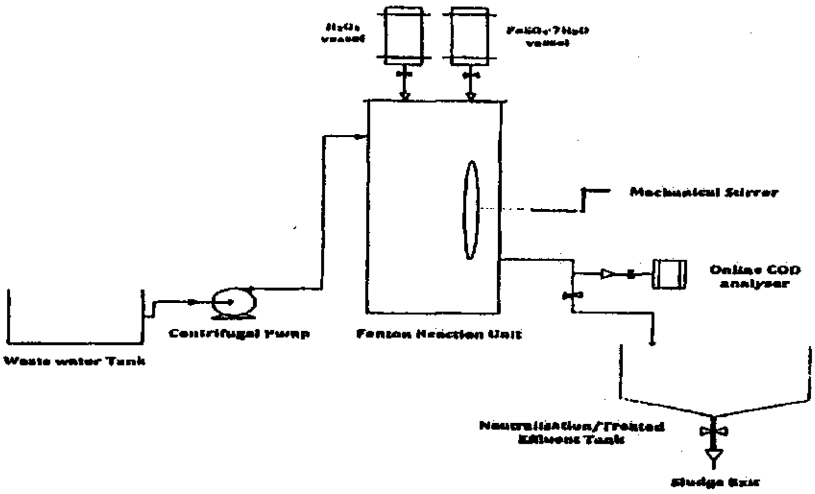
3.1 Research methodology

The proposed plant would be run on a continuous basis and a typical experimental arrangement for the Fenton oxidative process is outlined below

3.1.1 Experimental Procedure

The Fenton oxidation experimental will be run at ambient operating conditions. The required amounts of the oxidant (H_2O_2) and catalyst (Fe^{3+}) in the form of $FeCl_3 \cdot 6H_2O$ will be computed. The reagents will then be added to the reaction mixtures.

A typical experimental arrangement for the Fenton oxidative is as shown in Figure 1. The wastewater will be acidified with H_2SO_4 (3 M) to pH 3 ± 0.1, which is necessary to prevent Fe^{3+} precipitation to Fe $(OH)_3$. Formation of $Fe(OH)_3$ is known to hinder the Fe^{3+}-H_2O_2 reaction, thereby limiting the regeneration step of Fe^{2+}. Moreover, the $Fe(OH)_3$ catalyses the decomposition of H_2O_2 to O_2 and H_2O, thus decreasing the production of $^{\cdot}OH$. Addition of the catalyst, Fe^{3+}, in the form of $FeCl_3.6H_2O$ will be done and the oxidation reaction initiated by transferring H_2O_2 to the reaction mixture under constant stirring. The oxidation reaction shall be terminated by quenching with a NaOH solution (50%, 3 M). The pH adjustment to a value of 8 resulted in immediate precipitation of the oxidised catalyst in the form of iron hydroxide, $Fe(OH)_3$. A solid settling time of 1 h will be allowed and settling proceeded under quiescent conditions.



3.1.2 Analytical measurements

Quantification of residual H_2O_2 in the solution was made using H_2O_2 strips (Merckoquant, Merck). The theoretical correlation (equation 1) proposed by Talini and Anderson [26] to account for the positive interference of trace residual H_2O_2 on COD measurements.

$$COD = COD_S - (R_{H_2O_2} \times 0.25) \qquad (1)$$

The chemical oxygen demand (COD) measurement was made using the dichromate closed reflux and colorimetric methods according to Standard Methods [27]. For the discoloration monitoring, a UV–vis spectrophotometer will be used.

4.0 STRATEGIC PLANNING

The strategic planning gives ideas of the composition of the project team, technical partners/consultants, and the project deliverables.

4.1 Project Team

The project in its entirety is to be carried out by a technical team from the National Research Institute for Chemical Technology (NARICT), Zaria in collaboration with researchers from the Ahmadu Bello University Zaria. The plant is intended to be located within the NARICT premises.

A consultant, Dr. Rui Martins, from Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Portugal, a highly established researcher in the field of AOPs and Environmental related research, will be coopted not only to guide in the design and conduct of the experiments leading to results for publications in high impact journals but to also provide expertise, where necessary, for the smooth running of the project.

4.2 Equipment and Wastewater

The equipment required for the pilot plant will all be sourced locally and fabricated in NARICT. The wastewater would be obtained from collaborative industries, the Nigerian National Petroleum Cooperation, and local textile and pharmaceutical industries. The raw effluent samples (not exposed to any prior treatment) are to be collected in 30-mL plastic containers at the inlet point to the pre-treatment unit.

To avoid composition change through photolysis or biological activities, the wastewater-containing plastic container shall be immediately transported to the laboratory (within 1 hour) in an ice box and stored in a cold room maintained at 4°C.