Fenton Process for Industrial Wastewater Treatment

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Abstract- *This paper is on 'Fenton Process for Industrial Wastewater Treatment'.*

The aim of the study is to introduce the Fenton Process for Industrial Wastewater. This method is based on the use of radical generators like hydrogen peroxide, Metal salts.

The importance of wastewater treatment to the environment is discussed, Fenton processes is effective for the reduction of chemical oxygen demand in wastewaters from industry.

Keywords- Fenton Process, Chemical Oxidation, Fenton Reagent

I. INTRODUCTION

In recent years, with an increase in the stringent water quality regulations due to environmental concerns, extensive research has focused on upgrading current water treatment technologies and developing more economical processes that can effectively deal with toxic and biologically refractory organic contaminants in wastewater. The development and application of several Advanced Oxidation Processes (AOPs) to destroy toxic and biologically refractory organic contaminants in aqueous solutions concentrated significant research in the field of environmental engineering during the last decades.[1]

Advanced Oxidative Degradation Processes (AOPs) comprise of techniques such that, under certain conditions, it could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions.

One of the major environmental problems today refers to the impact associated with the disposal of industrial wastewater and other residues into superficial and underground water bodies. Solutions to this issue require combined approaches, concerning generation, treatment, and disposal into the environment not only of effluents but passive residues produced by specific treatments: physical (resulting primarily from the formation of low-solubility solids and auxiliary reagent for flocculation and precipitation); chemical (promising, but still undergoing up-scaling as emergent processes); microbiological (the most commonly used on industrial scale in terms of versatility and cost); or combined hybrid process. Several techniques are available for wastewater treatment (as mentioned before, chemical, physical and biological processes) as well as the use of combinations of these techniques to an optimal result.

When organic compounds in wastewaters present recalcitrant characteristics precluding treatments by conventional biological methods, chemical oxidation can be used as pre- or post-treatment, decreasing toxicity before applying a conventional biological process or conditioning the effluent to required maximum concentrations (i.e., oxidize non- biodegradable residues).

Chemical oxidation can also be used as a post treatment to oxidize non-biodegradable residues present in wastewater treated by biological processes. Each treatment technique has positive aspects and constraints in relation to applicability, efficiency and cost. (2)

Fenton process is attractive alternative to conventional oxidation processes in effluent treatment of recalcitrant compounds. The oxidation of organic substrates by iron (II) and hydrogen peroxide is called the "Fenton chemistry", and it was first described by H.J.H. Fenton.
There is something intriguing and at the same time fascinating that a simple reaction (of Fe^{2+}ions with H_2O_2), which was observed by H.J.H. Fenton over 110 years ago, proves to be very difficult to describe and understand. It was first described by H.J.H. Fenton who first observed the oxidation of tartaric acid by H_2O_2 in the presence of ferrous iron ions. Alternatively, the name of "Fenton Reaction" or "Fenton reagent" is often used. (3)

We know that the Fenton reagent defined as a mixture of hydrogen peroxide and ferrous iron is currently accepted as one of the most effective methods for the oxidation of organic pollutants.(3)

Among AOPs, the Fenton's reagent is an interesting solution since it allows high depuration levels at room temperature and pressure conditions using innocuous and easy to handle reactants. The inorganic reactions involved in Fenton process are well established and the process has been used for the treatment of a variety of wastewaters. The high

efficiency of this technique can be explained by the formation of strong hydroxyl radical (OH•) and oxidation of $Fe^{2+}$to Fe^{3+}. Both $Fe^{2+}$and Fe^{3+} ions are coagulants, so the Fenton process can, therefore, have dual function, namely oxidation and coagulation, in the treatment processes (Badawy & Ali, 2006). It is essential, though, to investigate and set the operating conditions that best suits the wastewater that are being treated in order to achieve high degradation efficiencies.(1)

Comprehensive investigations showed that the Fenton reagent is effective in treating various industrial wastewater components including aromatic amines, a wide variety of dyes, pesticides, surfactants explosives as well as many other substances.(3)

In comparison to other oxidation processes, such as UV/H_2O_2 process, costs of Fenton oxidation are quite low.

II. THEORETICAL CONTENTS

Treatment methods vary with the wastewater characteristics. In economic point of view, the most economical and efficient methods are preferable compare to the other. Chemical methods, biological methods and physical methods are the general treatment that are being used and further investigations by researchers proves that chemical methods are the most efficient and economical compare to the other two methods.

THEORY OF FENTON PROCESS

In the Fenton reaction hydroxyl radicals are generated from the reduction of hydrogen peroxide.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^- \quad \text{- - - - - - - - - - - - - [1]}$$

In the absence of a substrate or in the presence of high concentrations of Fe^{2+}, the hydroxyl radicals formed can oxidize other ferrous ions to ferric ion, as in Equation:

$$Fe^{2+} + {\bullet}OH \rightarrow Fe^{3+} + OH^- \text{ - [2]}$$

Fenton process requires the usage of hydrogen peroxide (H_2O_2) as the oxidation agents. Further research improves this Fenton process by using transition metal salts, ozone and also UV-light. Oxidation process that use H_2O_2 and metal salts are classically known as Fenton process. The reaction between H_2O_2 and iron salts it will results in the formation of hydroxyl radicals, HO•. This advances oxidation techniques [E. Neyens et. al., 2002] with the presence of HO•, will nonspecifically oxidize target compounds at high reaction rates. (5)

MATERIALS.

The main chemical used for Fenton process is hydrogen peroxide (H_2O_2).Hydrogen peroxide (H_2O_2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Still H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H_2O_2concentrations. Improvements can be achieved by using transition metal salts (e.g. iron salts) or ozone and UV-light can activate H_2O_2 to form hydroxyl radicals, which are strong oxidants. Oxidation processes utilizing activation of H_2O_2 by iron salts, classically referred to as Fenton's reagent is known to be very effective in the destruction of many hazardous organic pollutants in water. Secondly is an iron salt to catalyze Fenton process and aid as the coagulant for coagulation process. It is also known as reducing agent. **(5)**

- **HYDROGEN PEROXIDE IN FENTON PROCESS.**

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- **OXIDATION BY FENTON PROCESS.**

Oxidation is defined as the interaction between oxygen molecules and all the different substances they may contact, from metal to living tissues. Technically, however, with the discovery of electrons, oxidation came to be more precisely defined as the loss of at least one electron when two or more substances interact. Those substances may or may not include oxygen. Incidentally, the opposite of oxidation is reduction the addition of at least one electron when substances come into contact with each other [M. Pollick et al., 2009]. In wastewater treatment, oxidation is done for example, by using hydrogen peroxide (H_2O_2) as the oxidation agent, called as the Fenton process. The agent used for Fenton process is mainly hydrogen peroxide (H_2O_2).

Numerous applications of H_2O_2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine, are known [Venkatadri, Peeters et al., 1993]. H_2O_2 is also useful in the treatment of the gaseous sulphur oxides and nitrogen oxides being converted to the corresponding acids. H_2O_2 has applications in the surface treatment industry involving cleaning, decorating, protecting and etching of metals. Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals which are strong oxidants. **(5)**

FENTON OXIDATION TREATMENT:

Typically a stirred batch reactor is used where the pH is controlled commonly within the 3–3.5 range. Fe^{2+} is most frequently added as ferrous sulphate and H2O2 is usually fed as aqueous solution. The process usually works at ambient temperature and pressure. The reactor vessel must be coated with an acid-resistant material, because corrosion can be a serious problem. Addition of reactants is performed in the following sequence:

Waste-water, followed by dilute sulphuric acid (for maintaining acidic conditions), the catalyst (Fe^{2+} salt) in acidic solution, base or acid for pH adjustment and finally hydrogen peroxide.

The discharge from the Fenton reactor passes to a neutralization tank and after flocculants addition the Fe $(OH)_3$ and other accompanying solids are separated by settling.

One of the advantages of the Fenton process with regard to other oxidation techniques is that no energy input is necessary to activate hydrogen peroxide because the reaction takes place at atmospheric pressure and at room temperature. Furthermore, this method requires relatively short reaction times and uses easy-to-handle reagents. **(6)**

ADVANTAGES OF FENTON PROCESS:

1) There is complete mineralization of organic matter.
2) There is no need for any processing units on the surface.
3) This process reduces organic loading in terms of chemical oxygen demand and done the removal of recalcitrant and toxic pollutants thus allowing for further conventional biological treatment.
4) Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs. Furthermore, both iron and hydrogen peroxide are relatively cheap and safe.

DISADVANTAGES OF FENTON PROCESS:

1) The reactions are efficient at low pH-levels (<6) - which is difficult to maintain.
2) There is a formation of iron sludge.

III. GLOBAL AND NATIONAL SCENARIO

Industrial pollution has been and continues to be a major factor causing the degradation of the environment around us, affecting the water we use, the air we breathe and the soil we live on.

But of these, the pollution of water is arguably the most serious threat to current human welfare. Water is polluted not only by industries but also by households. Both industries and household waste-water contain chemicals and biological matter that impose high demands on the oxygen present in water. Polluted water thus contains low levels of dissolved oxygen as a result of the heavy biological oxygen demand (BOD) and chemical oxygen demand (COD) placed by industrial and household waste materials discharged into water bodies and water systems, both above and below the earth's surface. In addition to low levels of dissolved oxygen in water, industrial wastes(effluents) also contain chemicals and metals that are directly harmful to human health and the ecosystem.(9)

Industrialization has become an important factor to the development of a country's economy, through the establishment of plants and factories. However, the waste or by-products discharged from them are severely disastrous to the environment consists various kind of contaminant which contaminate the surface water, ground water and soil. There are a number of reasons the waste are not safely treated. One of the reasons is mainly due to the lacking of highly efficient and economic treatment technology.

EFFECT OF INDUSTRIAL WASTEWATER ON ECOSYSTEM OR GLOBAL ENVIRONMENT:

Humans are dependent upon eco-system services such as air, water, food, and for provision of materials for development and construction. While the importance of ecosystems and their services cannot be underestimated, a wide range of human and natural processes have altered the way they function, eroding their capacity to deliver these vital ecosystem services for human well-being. Surface water is usually rain water that collects in surface water

bodies, like oceans, lakes, or streams. Surface water can become contaminated in many ways, one of which is direct recharge can come from industries sources. A change in the water chemistry due to surface water contamination can negatively affect all levels of an ecosystem. It can impact the health of lower food chain organism and consequently the contaminated surface water can also affect the health of animals and humans when they drink or bathe in contaminated water or for aquatic organism when they ingest contaminated sediments. Degradation of water quality or depletion of water resources and loss of aquatic biodiversity are prominent features of the environmental landscape requiring urgent attention at global and national level.

HUMAN ACTIVITIES AND GLOBAL WATER QUALITY:

Human development actions have resulted in the destruction of wetlands, diminishing their capacity to prevent floods, filter water pollutants, regulate climate, among others, as they result in simplified systems and reduce their intrinsic resilience to change. Increasing impacts on water and eco systems may result partly from ignorance of human development actions on the environment, and an inadequate understanding of ecosystem values.

Aquatic ecosystems have long been used as a medium for transporting and disposing of human, agricultural, and industrial wastes, discharged directly or indirectly into the water courses. More than 80 per cent of sewage in developing countries is discharged untreated, polluting rivers, lakes and coastal areas (WWAP, 2009) and remains far from satisfactory even in some developed countries. Pollutants including microbes, nutrients, heavy metals, organic chemicals, oil and sediments; heat, which raises the temperature of the receiving water, are typically the cause of major water quality degradation around the world. Major nutrient sources to ecosystems include agricultural runoff, domestic sewage, industrial effluents and atmospheric inputs. Pressures emanating from population growth, urbanization, globalization of trade, consumption patterns, increasing energy demands, growing waste quantities, economic growth, and climate change pose an immediate danger to the current situation. (10)

WASTEWATER AND INDUSTRIAL WASTEWATER IN INDIA

According to India's Central Pollution Control Board, the country has an installed capacity to treat only about 30% of the household waste it generates – the rest is released into open drains or straight into the ground. And just two cities, Delhi and Mumbai, which generate around 17% of the country's sewage, have nearly 40% of its installed capacity. According to Asit K Biswas and Peter Brabeck Letmathe, while 90% of households in Delhi are considered to have adequate sanitation because they have indoor toilets, almost all of Delhi's untreated wastewater flows into the Yamuna River, a source of drinking water for cities downstream. If India were to widely deploy adequate treatment technology, the country would be able to significantly expand its available water supply, both for potable and non-potable use. Our economy, industry and most importantly, our people, would reap the benefits. (11)

Surface water has the highest concentration of cations and anions. Surface water is affected by industrial effluents which have high concentration of Na, Ca, Mg, K, Cl, SO_4 and HCO_3.These parameters are in more than desirable limits which could be the result of direct dumping of effluents into the water bodies. The industrial effluents are let into the stream directly during rainy days thus leading to accumulation of elements in surface water, which together with rain water, flow down to stream and join the major drainage system and these water in due course percolate down to join ground water reservoir.

Some industries like textile industries consume a large quantity of water and generate a huge amount of wastewater, which are generally discharged into a common effluent drain of industrial area. The composite effluents from industries in city consisting high concentrations of heavy metals, organic pollutants and toxic colors, which may affect the quality of surface water, soil, groundwater and plant tissues of the region. Toxic pollutants may percolate down via soil profile and reach in groundwater, which ultimately cause the health hazards among human being and livestock after consumption as daily drinking requirements (Malik and Bharti, 2010). The wastewater without any treatment may cause adverse effect on the health of human, domestic animals, wildlife and environment. Contaminated ground water has deteriorated the drinking water and impacts on soil systems and crop productivity. (12)

IV. APPLICATIONS

- **CHEMICAL INDUSTRY**

The chemical industry is a major contributor to the nowadays problem of industrial wastewaters, not only in terms of discharge volumes, but also looking at the hazardous nature of many of the pollutants found in the effluents. The increasingly stringent regulations have enforced the

application of advanced technologies like Fenton oxidation for complying the discharge limits and allowing for water recycling.

- **PHARMACEUTICAL INDUSTRY**

Fenton oxidation has proved to be a suitable pretreatment for an extremely polluted pharmaceutical wastewater, mostly due to recalcitrant compounds. Fenton oxidation is applied as a pre-treatment for the wastewaters generated by a drug manufacturing, leading to an improvement of the wastewater biodegradability and a reduction of the toxicity of these effluents.

- **PULP AND PAPER INDUSTRY**

Wood extractives (tannins, resin acids, lignin, etc.), others are xenobiotic compounds that are formed mostly in pulp manufacture (chlorinated lignin, phenols, dioxins and furans, among others).

These effluents are highly colored and contain high organic loads. Fenton oxidation is effective for the treatment of pulp bleaching effluents.

- **TEXTILE INDUSTRY**

Textile industry is particularly known for its high water consumption as well as the amount and variety of chemicals used throughout the different operations.

The environmental problems associated with textile effluents are in a great part due to color. The bio-refractory nature of textile wastewaters from the dyeing and finishing stages is mainly attributable to the extensive use of various dyestuffs and chemical additives (such as polyvinyl alcohol, surfactants, etc.). Therefore, the wastewaters are characterized by high organic matter content (COD), color. Fenton process is effective in removing COD and color. (6)

- **DRY-PROCESS INDUSTRIAL WASTE**

There is a need for the development of on-site wastewater treatment technologies suitable for "dry-process industries," such as the wood-floor sector. Due to the nature of their activities, these industries generate lower volumes of highly polluted wastewaters after cleaning activities.

Advanced oxidation processes such as Fenton is potentially feasible options for treatment of these wastewaters. (7)

Fenton is effective in treating various industrial wastewater components including aromatic amines, a wide variety of dyes, pesticides, surfactants, explosives as well as many other substances. Also effective for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for secondary biological treatment. (3)

V. CONCLUSION

Fenton process can be utilized in wastewater treatment for overall organic content such as COD reduction, specific pollutant destruction, sludge treatment and color and odor reduction. Reaction generally occurs in chemical and biological systems as well as in the natural environment. It is successfully used in environment protection. OH radical is a major species in the Fenton reaction causing oxidation.. The overall results of this study indicates that the application of Fenton's process is a feasible method to treat industrial wastewaters, allowing a satisfactory decrease of COD. The Fenton oxidation process can be applied as a pretreatment process to degrade non-biodegradable organic matters in industrial wastewater. So it may conclude that the Fenton process is effective, simple and economical method which causes the oxidation of very toxic wastes in industrial wastewater and helps to maintain the standards to some extent.

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