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Industrial Waste Water Treatment Using Advanced Oxidation Process – A Review

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Abstract: ***Management of Industrial wastewater is one of the complicated problems in this world. Many technologies and methods are implemented for the industrial wastewater treatment and got the maximum efficiency of removal using various chemicals and materials. But, the management of sludge from various treatment technologies is comparatively low. Various methods such as physio-chemical, biological, Membrane process, Adsorption, Advanced oxidation process and electrochemical processes were used for the treatment of different effluents. Due to the limitations of the conventional sludge stabilization processes are not able to remove the heavy metals ions from waste activated sludge to make it reliable enough to be utilized as fertilizer in agricultural lands and farms. Advanced Oxidation Processes (AOPs) is the outstanding technique for treatment of polluted wastewaters containing intractable organic pollutants. AOP utilize the tough oxidising power of hydroxyl radicals that can trim down organic compounds to nontoxic end products. The most studied AOPs are photochemical-based processes (PAOPs), as UV/hydrogen peroxide, heterogeneous photo catalysis (HP), photo-Fenton (PF), UV plus ozone and combination of these technologies. Currently, advanced oxidation process is among the most frequently used approaches to remove pollutants that have low biodegradability or high chemical stability. These methods are depend on the generation of hydroxyl free radical (HO*) as a strong oxidant for the destruction of compounds which cannot be oxidized using conventional oxidants. This paper reviews that, the application of AOP for the removal of different kinds of toxic pollutants from the industrial wastewater.***

Keywords: Advanced Oxidation Processes, hydroxyl free radical, sludge stabilization.

I. INTRODUCTION

Life on the earth would be impossible without water. All living organisms are needed the water especially, humans are using 70% of the water in this world for cooking, drinking, agriculture etc. By, 2025, more than 1/3rd of the population in the world will live in areas with inadequate supply of fresh water for drinking and irrigation. Over 70 billion barrels of wastewater produced in worldwide in each year. Water is becoming one of most valuable resource in the 21st century. Due to excessive amount of toxicity accumulation in water, it causes the severe diseases to the human beings and living organisms. Toxicity removal from the wastewater is one of the serious problems in this world.

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The water bodies have been polluted in very high range because of discharging the Industrial effluent without any prior treatment. The presence of toxic contaminants in aqueous solutions is non-biodegradable, accumulates in nature and contaminates ground water and surface water posing serious threat to the living beings and the environment. Various conventional treatment methods are available for the elimination of inorganic toxicity from water and wastewater. These methods include chemical precipitation, membrane filtration, ion exchange, coagulation, flocculation, electrochemical technique, adsorption, Advanced Oxidation Process and co-precipitation. Due to some kind of regent requirements and Instrumental usages (High reagents, Ion removal prediction, Toxic sludge generation etc.) these methods are having several disadvantages also. Compared to these methods, Advanced Oxidation Process being very simple, effective and versatile has become the most preferred methods for the removal of toxic pollutants from waste water. This review work mainly focused to analyze the efficiency of different kinds of AOPs such as Fenton process, Photo Catalytic Oxidation, Ozone/UV etc.

II. ADVANCED OXIDATION PROCESS

Advanced Oxidation Process (AOP) is the method of treatment of toxic pollutants in wastewater, most widely used in recent days. The remediation of wastewater containing such as pesticides, coloring matters and other inorganic substances are recovered by this process. AOP involves in the two stages of oxidation process. The first stage of oxidation process is the creation of strong oxidants (Hydroxyl Radicals) and the second stage is the reaction of these oxidants with organic contaminants in wastewater. The generation of highly reactive free radical is the major mechanism and a great number of methods are classified under the broad definition of AOP. The most popular technology for wastewater treatment is the combination of the strong oxidizing agents (e.g.H_2O_2 or O_3) with catalyst and irradiation (e.g. ultraviolet, visible). Among different available AOP producing hydroxyl radicals, titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reactions seem to be some of the most popular technologies for wastewater treatment.

a) Fenton process - Fenton's reagent is a solution of H_2O_2 and iron catalyst that is used to oxidize the toxic organic compounds. In this process, the ferric iron (Fe^{3+}), a hydroxyl anion or radical is normally generated by the oxidation of ferrous iron (Fe^{2+}) because of H_2O_2. The net effect is the disproportionate of H_2O_2 to cause formation of two different oxygen radical species, with H_2O (H^++OH^-) as a byproduct. The process of Fenton's Mechanism is given below.

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$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO^\cdot \quad (1)$$
$$Fe^{2+} + HO^\cdot \longrightarrow Fe^{3+} + OH^- \quad (2)$$
$$HO^\cdot + RH \longrightarrow H_2O + R^\cdot \quad (3)$$
$$R^\cdot + Fe^{3+} \longrightarrow R^+ + Fe^{2+} \quad (4)$$
$$Fe^{3+} + H2O \longrightarrow Fe^{2+} + H^+ + HO^\cdot \quad (5)$$

In this process the secondary reactions are engaged by the free radicals which were generated during the reaction. The Fenton's reagent oxidizes the organic compound in a rapid way by the heat producing technique and results in the contaminants oxidation primarily to CO_2 and water. The presence of light accelerates the reaction and large degrees of mineralization are obtained. If the Fenton's process driven in very low energy of photons, the solar irradiation could be used and this reduces the operational cost of the treatment. The optimum pH for the Fenton's process between 2 to 4. In this case, the Fe^{2+} ions are in unstable conditions when the pH goes to above 4. Before the treatment process the pH has been adjusted because the oxidizing power of Fe^{2+} is gradually decreased in alkaline medium due to the collapse of H_2O_2 into O_2 and H_2O. The factors such as pH, amount of ferrous ions, H_2O_2 concentration etc. are commonly affects the Fenton's process and this technique is commonly used for treating the waste from pulp and paper industrial effluent, dyes and chemical processing industrial effluents

b) Super Critical Water Oxidation (SCWO) – It is one of the Advanced Oxidation Process which is used to find out the efficiency of demolition of in industrial wastewater and to understand the feasibility. Two types of reactor systems (Pipe reactor system & Transpiring wall reactor system) are used to destroy the sludge or converted into harmless substances. This is the method which is used to completely destroy the sludge and substances from the industrial effluent. The two types of reactor system stated that in this technique, the pipe reactor system gives 99.9% of efficiency when compare to the transpiring wall reactor system. The pipe reactor system can be used in paper, chemical industrial effluent treatment as well as the sewage treatment also. This waste includes a high range with respect to Total Organic Carbons (TOC), salts and solid contents. Conversion of at least 97% of the organic chemicals could be achieved in SCWO technology. This process (SCWO) can be operated at the temperature between 450^0C - 650^0C and the pressure of 25.35 MPa. Under these conditions most of the organic compounds and water, oxygen, CO_2 forms a single, fluid phase and oxidation rates are not limited by transport process across phase boundaries. According to the matches of acids or salts the hetero are mineralized. In such case, the formation of acid may lead to corrosion, the creation or the occurrence of salts leads to plugging and many attempts have been made to solve this corrosion problem. To overcome this issue, the transpiring wall reactor was developed. As a result, SCWO has got high potential for the demolition of halogenated organic compounds using this transpiring wall reactor system (TWR). In this reactor, using the pumps or a compressor, waste and oxidant (air), are fed at the top. This solution is brought to the supercritical state (with respect to water) using pre-heaters and the exothermic reaction. The salts may be precipitated in the reactor due to the high amount of temperature and pressure. To solve this problem, the water is passed into the annular gap through the porous pipe to form a film or at least an energetic force directed to the centre of the inner effect at a temperature of 550^0C with 30MPa of compression force. Sticking of inner surface of the porous tube by solids, this transpiring effect can be avoided and this may act as a corrosion resistance also. While feeding the quench water in the lower part of TWR, the precipitated salts are again dissolved under the adjustments of subcritical conditions. The complete demolitions of toxic organic compounds are possible in this reactor system. This Super Critical Water Oxidation can produce the CO_2 and H_2O and could not produce the nitrogen oxides

c) Photo Catalytic Oxidation – This can be achieved by the combination of UV light rays with Titanium Dioxide (TiO2) coated filter. Under this UV radiation, the semi-conductor material gets energized by the suitable energy possessing by the photons. As a result of this radiation, the band electrons and valance holes can be produced and this is the basis for photo catalysis. These may react with the absorbed species in the surface of TiO2 particles.

$$.OH + RH \longrightarrow R + H_2O \quad (6)$$

The valance holes have a tremendous positive oxidation potential and it oxidizes almost all chemicals. The formation of hydroxyl radicals are feasible in energetically from the one electron oxidation of water.

$$H2O + h+ \longrightarrow .OH + H^+ \quad (7)$$

TiO2 having the energy band gap of 3.2eV which has been activated by the UV illumination with 387.5 nm wavelength. Also, it interacted with supported phase and not only as catalyst and the solar radiation starts at the ground level about 300 nm wavelength. Hence, the solar energy reaches the ground only 4 – 5 % and it could be used as various components, when TiO2 is used as a catalyst. The process efficiency can be occurred at the optimum pH of 3. When, the pH value is increased up to 6.5, the phenolic degradation increased and attained the maximum level.

$$TiO_2 + hv \longrightarrow ecb- + hvb+ \quad (8)$$

The character of the oxidized compound is purely depends on the optimum pH value. Thus, the phenolics behave differently than aromatic amino compounds. To yield the superoxide radical anions, the surface adsorbed molecular oxygen is interacted with the band electrons and the water interacts with the band holes for producing the hydroxyl radical. These free radicals are having high efficiency to degrade the toxic organic compounds. For Olive processing industrial wastewater treatment, this process can be used. Based on the results, the efficiency of the treatment was increased with decreasing initial COD and increasing contact time and catalyst concentration. But, a pre-treatment method is required to ensure the destruction of toxic biodegradable compound initially present to less toxic biodegradable intermediates. TiO2 with photo catalytic oxidation is an economically variable process and it produces the conduction band electrons & valance band holes before they undergo any chemical reactions. To solve this issue the silver doing has been used for getting effective results.

d) H2O2 / UV Light Processes - In the reactor, the toxic organic compounds and the H2O2 is injected and mixed together. The hydroxyl radical can be produced when the mixing is aided with UV light of radiation of wavelength of 200 to 280 nm which is equipped with the reactor in turn causes the cleavage of O-O bonds and results.

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For dye removal and water disinfection process, this technique can be used. The intermediate formation may be happened when the alteration of pH of hydroxyl radical. Hence the lower pH is maintained in lower level.

To mineralize the organic compounds this is efficient and it cannot use the solar light for the essential UV energy. This is for the photolysis of the oxidizer is not available in the solar spectrum. Due to this reason, the H_2O_2 has very low absorption characteristics and need a special reactors designed for UV illumination. The following factors are the main reason which affects the efficiency of the treatment such as, initial concentration of the target compound, the amount of H_2O_2 used, pH value of the wastewater, occurrence of bicarbonate compounds and the reaction time.

$$H_2O_2 \xrightarrow{hv} 2{\cdot}OH \quad (9)$$

$$H_2O_2 + {\cdot}OH \longrightarrow HO_2^{\cdot} + H_2O \quad (10)$$

$$H_2O_2 + HO_2^{\cdot} \longrightarrow HO^{\cdot} + H_2O + O_2 \quad (11)$$

$$2\,{\cdot}OH \longrightarrow H_2O_2 \quad (12)$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \quad (13)$$

$$HO^{\cdot} + HO2^{\cdot} \longrightarrow H_2O + O_2 \quad (14)$$

e) Ozone/UV Process – The UV radiation can easily absorbed by the ozone at a wave length of 254nm. Then, it forms H_2O_2 to as intermediate to form the hydroxyl radial for decomposition. With the help of low pressure mercury lamps, the UV energy at this wavelength could be generated. Compared to the Fenton's process, the photochemical cleavage of H_2O_2 is the economical and simple method & UV/O_3 process produced more hydroxyl radicals. Usually, the power supplies for UV lamps in the process of ozone photolysis are in watts range against kilowatts for H_2O_2 photolysis. The UV occurs from the viewing of ozone by optically energetic compounds such as phenols. The complete mineralization is not possible though ozone oxidizes.

$$O_3 + hv \longrightarrow O_2 + O\,(^1D) \quad (15)$$

$$O\,(^1D) + H_2O \longrightarrow H_2O_2 \longrightarrow 2{\cdot}OH \quad (16)$$

f) Ozone/H_2O_2/UV Process - The accumulation of H_2O_2 to the O_3/UV accelerates the process and results in the larger creation of hydroxyl radicals. To treat the mixed organic wastes, H_2O_2 is very economical and also it contains some weak absorbent compounds against the UV radiation. This could be considered as a substitute for photo-oxidation process. The capital and operational cost of this process can be varied depending on the type and absorption of pollutants and the degree of removal required.

III. CONCLUSION

Advanced oxidation processes have emerged as an important approach to treat waste water. Majority of the processes for waste water treatment are physicochemical in nature, physical or chemical processes or combine both. As one of the advanced methods, AOPs are based on a basic principle that entails the invention and use of a hydroxyl free radical (HO*) as a well-built oxidant for the destruction of compounds which cannot be oxidized using predictable oxidants. AOPs have shown premises in various water treatment sectors due to its superior efficiency in pollutant elimination.

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