IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 15, Issue 1 Ser. I (January 2021), PP 04-14
www.iosrjournals.org

Treatment of Industrial Wastewater (IWW) and Reuse through Advanced Oxidation Processes (AOPs): A Comprehensive Overview

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Abstract
Though sedimentation, disinfection, filtration and coagulation/flocculation are capable approaches of treatment for IWW, certain chemical contaminants can't be removed with such techniques; therefore, they required applying advanced approaches. Presently, AOPs are amongst the best often applied approaches to eliminate contaminants that may have less-biodegradability or great chemical constancy. AOPs approaches needs free hydroxyl radical (HO) as an oxidant for the degradation of toxic pollutants that can't be removed via traditional methods. In current comprehensive-overview, we have reported several AOPs which revealed evidences in contaminant elimination from IWW.*

***Key Word**: Advanced Oxidation Processes (AOPs), Wastewater, Water treatment, Human health*

Date of Submission: 26-12-2020 Date of Acceptance: 07-01-2021

I. Introduction

Currently human activities and their basic needs of life are increasing fast due to increased population and industrialization in all countries and as a result our water resources have been polluted with a larger amount of hazardous contaminants particularly toxic heavy metals from various sectors (Raghunandan et al., 2018). Several adverse effects of development like water pollution, increasing in carbon dioxide amount and resources depletion are reported locally and globally that are disturbing human health and environment (Ahuti, 2015). Industrialization has also numerous effects on social and economic change of individuals and societies and also required inventions for enhancement (Mgbemeneet al., 2016). Because of industrial practices, enormous quantity of contaminants is discharging into near water bodies and thus producing problems to human health. Industrialization not only producing heavy metals but also generating various types of wastes that effects environment. Due to industrial revolutions, there is huge release of harmful gases and chemical substances to the environment. Water contamination is a severe problem that might disrupt humans. Though several methods had been applied to avoid or control this problem but still it is a concern for humans. Humans and environment together effected by such contaminants globally. Some heavy metals are beneficial in fewer quantities for humans such as Nickel (Ni), Iron (Fe), Copper (Cu), and Arsenic (As) however these become toxic at great amount (Valko et al., 2016). Particularly HMs with great densities is stated to be more poisonous even in less quantity (Iram et al., 2013). Contaminants seriously affect the function of kidney, lungs and brain and also decrease energy level in humans. Several contaminants are carcinogenic since of their often exposure (Jaishankar et al., 2014). Hence, it is vital to suggest appropriate technique for contaminants removal from water systems (Toth et al., 2016). Numerous approaches such as coagulation, adsorption nanotechnology and ion exchange have been applied to remove contaminants from water solutions (Rajasulochanaet al., 2016). All these suggested methods have their specific advantages and drawbacks however these are expensive and required more time. A novel technique must be designed to protect human health and environment from the adverse effects of water contamination and AOPs are stated capable and effective methods for pollutants elimination. AOPs methods have developed as a comparatively cost-effective technique and might show effectiveness for the elimination of contaminants from soil and water resources and make it toxic-free compounds (Biń and Sobera-Madej, 2012). AOPs are progressively being reported as a greatly viable wastewater treatment method for eliminating low-biodegradability or great chemical constancy contaminants (Ning et al., 2007). Although these methods efficient to remove contaminants with great chemical permanence but reported much expensive for complete mineralization. Thus to decrease the costs, the method can be combined with other biological treatment methods (Oller et al., 2011). Though the last is an exciting method to industrial wastewater treatment, the below given description only limited to AOPs.

II. Brief Review of Literature

1. Selection of treatment method for IWW:

The mission of choosing the topmost treatment option for treating wastewater particularly industrial wastewater is typically a difficult one. The key influences that must be considered in making a decision about the IWW method to use including the water quality, traditional wastewater (WW) treatment options, elimination of parental pollutants, flexibility removal, cost-effective studies, cleansing ability of the facility, efficiency of wastewater treatment system, possible usage of cleaned water and life cycle assessments (LCA) of WW treatment method for the determination and compatibility of proposed methods (Biń and Sobera-Madej, 2012). In over-all, the competences and potentials of the traditional methods of treatment presented are broadly well-known. But, in order to regulate the effectiveness of advanced techniques like AOPs, pilot-plant studies and bench-scale must be applied. Such types of research may show significant treatment for pollutants especially heavy metals where numerous methods can be combined for decontamination and reuse of specific industrial wastewater.

2. Process of physicochemical analysis

The physicochemical technique for wastewater treatment includes any physical or chemical method or sometimes the combination of both methods. However the main principles vary, it is typically tough to differentiate the procedures as they might happen instantaneously in a single unit treatment (Srinivasan and Viraraghavan, 2010).

Reliant on on treatment setting, the physical commences of micro contaminants especially (organic) in water and polluted water occasionally linked with biological treatment. Physiochemical properties like lipophilicity or alkalinity regulate the behaviour of micro contaminants throughout adsorption on the surface of solids (Carballa et al., 2005).

Determining the effluent organic matter (EfQM) affinity to certain material and the sorption efficiency mostly complete by two coefficients, which is, Octanol-water partition coefficient (Kow) and organic carbon partition coefficient (Koc). The coefficients consideration take into two key sorption methods: adsorption and absorption (Rosal et al., 2010).

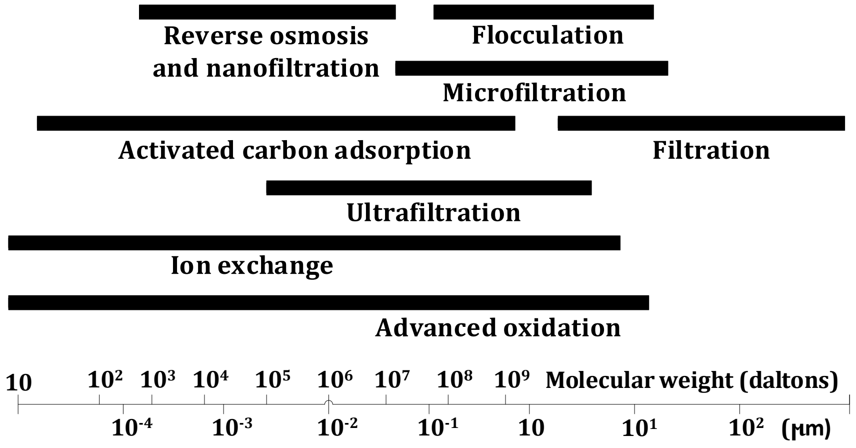

Figure 1: Various sizes ranges of practical treatment methods for the treating of EfQM(Al Mayyahi and Al-Asadi, 2018)

3. Physiochemical processes overview

The main reasons why physiochemical procedures are used for the treatment of IWW that has been treated with biological treatment is the elimination of organic matter (OM). Elimination of EfQM can be presented in terms of endocrine disrupting chemicals (EDCs), dissolve organic carbon (DOC), personal care products (PPCPs) and molecular weight distribution (MWD). Treatment of EDCs and of PPCPs can be applied to show the minimum MW compounds existent in a waste, fraction shows the elimination of several hydrophilic/phobic parts, however MWD offers with particular elimination of different organic sizes.

The usage of DOC mostly significant as it provides an alternate for common organic pollutant elimination via physiochemical procedures. How efficient a particular method in the removal of EfQM is greatly affected by the size and structure of EfQM. Variety sizes of EfQM that are treated with several removal approaches as presented in figure 1. Mostly particulate organic matters (POM) are treated by the methods of flocculation and biofiltration.

The elimination of DOC is mainly reliant on removal methods that were applied. Powdered activated carbon (PAC) and granular activated carbon (GAC) commonly resulted in DOC levels as compared to elimination of EfQM which are greater. It might be seen as suggesting that EfQM contains mostly of minor molecular weight (MW) OM in the IWW that is biologically treated. MWD of EfQM is of most significance for treatment of several tiny contaminants in various sizes with the usage of different removal techniques.

Elimination of various organic pollutants could help in the detection of effectiveness of numerous ranges of physiochemical methods in the treatment of transphilic (TP) hydrophobic (HP) and hydrophilic (HL) fractions. EfQM result in iron chloride ($FeCl_3$) flocculation has been treated at maximum quantity of hydrophilic portion.

4. Advanced Oxidation Processes (AOPs)

Usually known as AOPs, AOPs generally applied to oxidize organic contaminants which are existing in IWW and hard to decompose into simple products with biological methods (Deng and Zhao, 2015).

4.1. Theory of AOPs

The main principle of AOPs involves the production of (HO*) and chemical oxidant see Table 1, as a oxidizing agent for degrading complex organic pollutants that can't be degraded by traditional chemical oxidants like ozone, oxygen and chlorine (Covinich et al., 2014). HO* are efficient for treatment of organic pollutants because of sensitive electrophiles that not only response fast but also non-selective with all organic chemicals which are electron-rich (Munter, 2001). The oxidizing capacity is measured as 2.80V and marks them to show rapid oxidation reactions related to traditional oxidants (Diaz-Elsayed et al., 2019). Once the HO* are produced, they are capable to breakdown the organic compounds via transfer of electron, radical combination hydrogen and abstraction (Angelakis et al., 2018). The reactions that occurred are given below:

$$R+HO^* \rightarrow ROH \; …. \; (a)$$
$$R+HO^* \rightarrow R + H_2O \; ….. \; (b)$$
$$Rn + HO^* \rightarrow Rn\text{-}1+ OH^- \; …. \; (c)$$

Table 1: Oxidation capacity of several oxidants(Deng and Zhao, 2015)

Oxidizing agent	Oxidizing capacity (v)	EOP relative to (Cl)
Molecular oxygen (O_2)	1.23	0.90
Chlorine Dioxide (ClO_2)	1.27	0.93
Chlorine (Cl)	1.36	1.00
Hypochlorite (ClO-)	1.49	1.10
Hydrogen Peroxide (H_2O_2)	1.78	1.30
Ozone (O_3)	2.08	1.52
Atomic Oxygen (O)	2.42	1.78
Hydroxyl radical (OH*)	2.80	2.05
Fluorine (F)	3.03	2.25

This is not essential to conduct whole reaction of a certain chemical compound or set of chemical compounds. In maximum cases the partial oxidation reactions are commonly enough to decrease the harmfulness of several chemicals or reduce them permissible limits. The amount of degradation that might be applied is typically categorized into four categories. They mainly including the primary degradation, defusing, and mineralization and fusing. In primary degradation, the structure changing takes place in the parent compound. For defusing the altering of structure in parent compound take place to reduce the level of toxicity.

In degradation, inorganic carbon dioxide comes from organic carbon compounds (OCC). Fusing basically is the change in structure of the parental compound which augmented the poisonousness and hence it is unattractive (Pouran et al., 2015, Brillas and Martínez-Huitle, 2015).

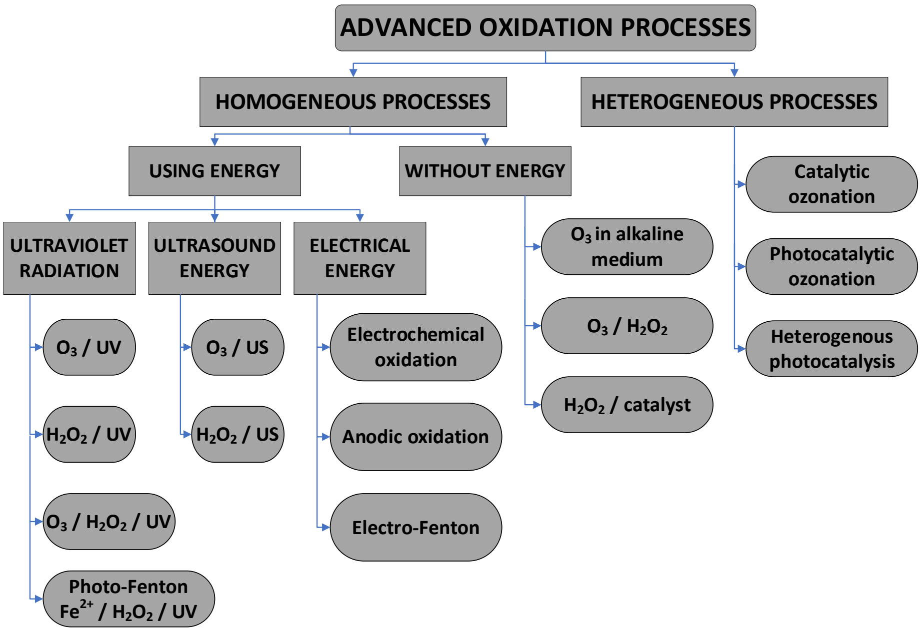

Figure 2: Advanced Oxidation Processes (AOPs) classification

4.2. AOPs classification

There are numerous approaches which are categorized under the wide definition of AOPs. More of these techniques have powerful oxidizing agent such as hydrogen peroxide (H_2O_2) or ozone (O_3) through a catalyst like irradiation such as UV and transition metal ions. Several studies show that Fenton's reactions, TiO_2/UV light method, and hydrogen peroxide/UV light are the best AOPs those generating HO* (Oller et al., 2011). Several AOPs are categorized as each homogeneous and heterogeneous. They are typically further divided on their energy utilization base.

4.2.1. Homogenous AOPs

These types of AOPs usually use UV light for the degradation of chemical compounds that use UV light in the reliable range of the band. The organic pollutants absorbing UV radiation at low band are appropriate for this type of photo degradation procedure.

4.2.1.1. Ozonation/Ultraviolet Radiation (O_3 /UV)

Ozonation/Ultraviolet radiation is an improved wastewater treatment technique that might be efficiently applied to degrade the hazardous organic compounds in industrial polluted water. Usually, water systems saturated with O_3 and then treated with 254 nm UV radiation. It has been observed that this method is so efficient for the degradation of chloro phenols (CPs) as compared to ozonation and UV photolysis (Martins et al., 2015, Kuo, 1999)Though, Leitus and his co-workers (Pera-Titus et al., 2004) have observed that photo catalytic ozonation is most efficient as compared to simple ozonation in several conditions.

4.2.1.2. Hydrogen Peroxide and UV Radiations (H_2O_2/UV)

In current AOP, the HO* are produced by photolysis of H_2O_2 and wide reactions that are consistent to the method. The procedure of photolysis of H_2O_2 happens when UV light is used as presented in the given equation:

$$H_2O_2 + h\nu \rightarrow 2HO^* \quad \ldots\ldots\ldots \text{(d)}$$

This technique needs more UV exposure and a comparatively more dosage of H_2O_2. Several reports revealed the ratio of photolysis of H_2O_2 is mainly pH reliant and increase with rise of basic medium (Tisa et al., 2014). UV lamps with low radiation can be applied for enhancing the molar absorption of H_2O_2 that is less at wavelength of 253.7nm. The major disadvantages of the proposed technique is that in conditions in which the wastewater to be processed has a greater ratio for absorbance, and there is an affinity to contest with the H_2O_2 for energy (Mahamuni and Adewuyi, 2010).

The technique has the capability to fully degrade every organic pollutant, with the end-products such as H_2O and CO_2. Though, the proposed method is typically not much essential as the hazardous of oxidizing materials is not an issue because their decomposition is pretty easy.

Determining the optimum dose of H_2O_2 essential is typically on the basis of bench testing and pilot-scale. Main benefits of the method are that H_2O_2 is extremely solvable and hence be supplement to the water source at great amount and the fact that these techniques are proficient to produce huge quantities of HO* as associated to O_3/UV for same quantity of used energy. Key drawbacks of this technique are, it is costly due to the extra charges of required instruments or energy supplies and the existence of residual H_2O_2 in the treated water inclines to help the re-growth within biological system (Al Mayyahi and Al-Asadi, 2018).

The procedure of direct photolysis includes the contact of molecules with light with water, to assist the particles to be detached into parts with the automatic way presented below:

$$R + hv \rightarrow \text{Intermediates} \ldots\ldots \text{(e)}$$
$$\text{Intermediates} + hv \rightarrow CO_2 + H_2O + R- \ldots\ldots\ldots \text{(f)}$$

The method is less efficient as related to new methods in which UV light is joined with O_3 or H_2O_2, or where heterogeneous, homogeneous catalysis and photo catalysis were used. The utmost collective causes of UV radiation used contain pulsed xenon arc lamps, low-pressure mercury vapour lamps and continuous wave medium pressure mercury vapor lamps (Asghar et al., 2015).

4.2.1.3. Fenton and Photo Fenton's Oxidation

This method has been introduced by Henry J.H. Fenton. Fenton's reagents are the combination (H_2O_2) and iron salt (Zhang et al., 2019).

Fenton defined the oxidizing strength of H_2O_2 on several organic chemicals and compounds and HO* are generated from H_2O_2 with addition of ferrous iron generally Fe (II) as a catalyst (Bautista et al., 2008). This method is reported the utmost capable removal technology amongst various AOPs used for the treatment of IWW which are greatly polluted. Because of its ease, the Fenton reaction is the method often used in conditions where it becomes mandatory to treat non-biodegradable organic compounds. The key drawback of the mentioned technique is that it produced iron sludge as end-product. To remove this problem, the photo Fenton method was introduced and it mainly use sun light and Ultraviolet for changing Fe(III) into Fe(II), thus fallouts in extreme decrease in waste production. The rate of treatment attained by Fenton method is almost 60 to 70 % (Andreozzi et al., 1999).

To increase the reduction rate of organic contaminants, a wavelength of 300 nm of visible light-UV is applied in the process. The method changes from the Fenton method in which photolysis of Fe (III) developments assists the redevelopment of Fe (II), and hence it reacts with more H_2O_2 (Pouran et al., 2015). The method is valuable as linked to Fenton method in which it decreases the production of waste that produces in Fenton method. Though, it is important to thoroughly regulate the pH of reaction medium, within 2.6 to 3 ranges for optimal performance of the method.

The situations in which the both methods such as Fenton and photo-Fenton were done and the elements of the water that have effect on the stoichiometry and speed of reaction and also result as the influences in solution chemistry. pH is the key feature that may effects the methods (Zhang et al., 2005). A reports of existing literature (Zhang et al., 2009) on the method reveal that this method is more effective at 3 pH. At greater pH ranges, there is an inclination for the degradation ratio to reduce as an effect of precipitation of iron(II) hydroxide. For low pH ranges, there is a reduction in the speed and as an effect of minor radiation absorption amount which is related with produced complexes.

Another aspect that has an effect on the these methods is H_2O_2 amount (Maezono et al., 2011). The amount influences the ratio and magnitude of decomposition of organic contaminants. There is a propensity for the rate of reaction to rise with rising amount of H_2O_2(Pesakhov et al., 2007). The chain of intermediates occurring in the method suggests that enough H_2O_2 should be added to drive the reaction. This is typically practiced when performing a pre-treatment of organic pollutants wastewater for its toxicity decrease. As the quantity of H_2O_2 is augmented a stable decrease in COD might occurred with slight or no alteration in toxicity till the achievement of a threshold. Adding more H_2O_2 above the optimal level has no effect on the treatment efficacy and which is attachable to the automatic degradation of H_2O_2 into H_2O and O_2 and also the re-joining of HO* (Maezono et al., 2011).

The catalytic iron ion amount (Fe^{+2}) has also influence on this method. The character of taking an optimal amount ratio for ferrous catalytic agent is typically feature of Fenton's reagent, while a trend for the range to have a difference among polluted WW (Kavitha and Palanivelu, 2004). General ranges for use are 1/5-

25 part of Fe^{+2} per H_2O_2 respectively. Addition of ferrous salt beyond the stated optimal dosage has no influence on the decomposition with the amplifying of amount. The cause is Fe(II) amount which is greater than the optimal H_2O_2 incline to be spent by side reactions afore their use for elimination of contaminants (Asghar et al., 2015).

Basic benefits of this methods is that it required lesser energy as related to former techniques using O_3 or UV light, absence of vapour releases and therefore no air licenses mandatory, absence of mass transmission limits because of that reactions occurred in the homogeneous stage and the procedure is done at room temperature and pressure. Main drawbacks of the methods including iron mining scheme is essential for elimination of remaining iron waste, a low pH of 4 is required to retain Fe in medium and the usage of non-natural radiation for the photo Fenton method needs extra light usage for running of lamps.

4.2.1.4. Electro Fenton (EF)

Another AOP is the electro Fenton technique. This method mainly based on the electro generation of H_2O_2 consistently at a proper cathode that is served with air or O_2, with the adding of catalyst mostly iron based to medium for the generation of OH* of majority via Fenton reaction (Nidheesh and Gandhimathi, 2012). The benefits of the technique contain generation of hydrogen peroxide on-site and maximum treatment rate of organic contaminants and as a consequence of the constant redevelopment of Fe^{2+} at cathode that contribute to the reduction of sludge waste production (Kavitha and Palanivelu, 2004).

4.2.1.5. Anodic Oxidation (AO)

Anodic oxidation (AO) is another AOP that can be used for the wastewater treatment (Candia-Onfray et al., 2018). By definition, (AO) refers to a faster electrochemical method which is strengthened by the coating of natural oxide skin (NOS) of aluminium. Through the passage of time, a new transparent oxide layer develops significantly denser related to the (NOS). An important benefits of applying this method is the high resistance to rust and long-term safety (Nidheesh and Gandhimathi, 2012).

4.2.2. Heterogeneous AOPs

In heterogeneous AOPs, for the treatment of various compounds the catalytic agents are used. The word heterogeneous refers to the existence of pollutants in liquid stage though the catalytic agent is typically in the solid stage. The final consequences in the speeding up of chemical methods because of existence of electron pairs hole. The photo generated holes and electrons effect in reduction and oxidation methods individually. For liquid mediums, decomposition of H_2O molecules attached to catalytic agent produced OH*, the method is usually applied in presence of O_2 with the pollutants to be decreased, a method that produces a super oxide radical.

4.2.2.1. Photo catalysts

For a photo catalyst to be observed as worthy in treatment of pollutants, it must be chemically and biologically immobile, photoactive, capable to use visible or near ultraviolet light, low-cost, photo stable and non-hazardous. Some examples of these catalytic agents contain Zinc oxide (ZnO), Silicon (Si), Tungsten trioxide (WO_3), Cadmium sulphide (CdS),Strontium titanate ($SrTiO_3$), Zinc sulphide (ZnS), Titanium dioxide (TiO_2), Stannic oxide (SnO_2), Iron oxide or ferric oxide (Fe_2O_3), and Tungsten diselenide (WSe_2) (Chong et al., 2010). The best frequently applied of the catalytic agents is (TiO_2) and it has been revealed an outstanding catalytic agent for the degradation of several organic or inorganic contaminants (Bagheri et al., 2014).

4.2.2.1.1. Titanium Oxide (TiO_2)

Titanium (Ti) is the 9th rich essential elements on the earth's surface. Ti can be present in three potential crystalline types in its greatest constant kind as an oxide. The types mainly contain rutile, brookite and anatase. From a photo catalytic view, only anatase and rutile are applicable, with the maximum catalytic action (Oller et al., 2011). Basically, the method occurred with TiO_2 generating electrons pairs and holes via absorption of or sunlight or UV. Electrons become active when lightened with the additional light applied to help the electron for transmission spectrum of TiO_2, hence, the generation of negative electron and positive hole. Main functioning parameters for the method contain quantity of the catalytic agent, primary amount of the reactant and influence of pH values (Oller et al., 2011).

The amount of catalytic agent to be applied must be in optimal level. Usage of extra catalytic agent may cause the decrease in the quantity of sun-light that is moved in medium because of impenetrability which is produced by catalytic agent particles. Optimal amount of catalytic agent to be applied is reliant on the type or quantity of contaminant, in adding to the degree at which OH* are produced. For wastewater which is greatly polluted, no degradation is detected and therefore its dilution is typically important. The way in which pH influences the rates of photo catalytic oxidation is complex but usually reliant on the zero point charge of the catalytic agent to be used and the kind of contaminant, Mostly, the treatment of the contaminant, and hence the rates of treatment should be more close to zero point charge (Bagheri et al., 2014).

Over the last few decades, TiO_2 has been broadly applied as a photo catalyst for organic contaminant decomposition from polluted water (Cuerda-Correa et al., 2020).

Finding of intermediary products and generation of by-products in the photo catalysis have been examined in the previous studies (Mahamuni and Adewuyi, 2010)(Asghar et al., 2015).About 70% of literature is present on photo catalysis for the treatment of wastewater using TiO_2 as a photo catalyst. Amongst them, some studies have tried the metal doped TiO_2nano photo catalysts for the IWW.

Nogueira and Jardim revealed that the removal dyes might be attained by sun light radiation consuming TiO_2 as photo catalyst (Bethi et al., 2016).

(Reeves et al., 1992) planned the usage of great intensity of sun light radiation for the treatment of biological dyes and textile dyes from polluted water using $TiO_{2.}$

During the degradation of dyes and organic contaminants can produce hazardous materials which could be toxic to human and environment. Removal of dyes could create the intermediates and have been stated as cancer-causing and poisonous in nature (Bethi et al., 2016). (Ao et al., 2007) described the decolourization of anthraquinonic dye by sol-gel TiO_2 in the existence of photo catalytic oxidation method. Attained results shows the founding of TiO_2 at lower temperature calcination indicate efficient decolourization in ultraviolet region.

4.2.2.1.2. Zinc Oxide (ZnO)

More specially, among various metal-oxide nanoparticles (NPs), ZnO NPs have their specific significance because of vast applications in many fields, such as gas sensor, bio-sensor, chemical-sensor, cosmetics, packing, electrical and optical instruments, solar cells and medicines (Baxter and Aydil, 2005). Presently, the use of ZnO is drawing the attention of scientists all over the world. ZnO is a non-hazardous and indicate much constancy. ZnO capably works in the pH range of 5.7 to 6.8 and hence attaining the attention currently (Singh et al., 2013).

ZnO is a capable NPs for short-wavelength optical and electronic applications because of its wide-ranging spectrum gap 3.37 eV, huge bond power, as well as great exciting binding radiation (60 meV) at normal temperature. As a wide-ranging spectrum gap material, ZnO is applied in solid form mainly blue to UV optical and electronic, containing laser improvements (Vaseem et al., 2010). ZnO have various commercial and technical applications such as non-toxicity, much stability, photo activity , inexpensive and synergistic effects make this material for waste water treatment (Siriwong et al., 2012). (Singh et al., 2013) checked the elimination of As with acetate activated ZnO at various intervals of time and report a fast arsenic elimination in the start with >99.9%.

ZnO has been widely applied for the treatment of organic contaminants in aqueous systems. Because of well photolytic properties and great surface area (Klaine et al., 2008), ZnO reported as best photo catalysts for water treatment.

(Shukla et al., 2010) examined the decomposition of phenolic complex in the existence of liquid medium by ZnO as a photo catalyst and per sulphate as an extra radicals generating agent in the occurrence of ultraviolet-visible radiation. Results show that ZnO revealed greater photo catalytic decomposition of phenol as compared TiO_2 in the occurrence of sunlight.

(Elamin and Elsanousi, 2013) have been produced the ZnO materials in nanostructured form like nanosheets and nanotubes by hydro-thermal process. The work of both the photo catalysts to the decomposition of Methyl orange has been assessed by applying ultraviolet radiation (λ =253.7 nm). The achieved results show that ZnOnanosheets showed efficient decomposition of MO related to nanotubes. Such outcome was achieved because nanosheets offered great surface area for adsorption as compared to nanotubes.

(Pompermayer et al., 2013) have reported the valuation of ZnOnano photo catalysts production through 6 various techniques. The consistent ZnOnano photo catalysts have been studied for Rhodamine B dye treatment, and decided that treatment ratio of the Rhodamine B dye improved more than 30 times.

(Cheng et al., 2010) studied the assessment of nano sized ZnO/TiO_2 in occurrence of UVC energy for the elimination of E. coli in polluted water at various amount of nano sized ZnO/TiO_2. Results show that the nano sized ZnO is greater in the elimination of E. coli as compared nano sized TiO_2.

(Wu et al., 2010) observed the amplification properties of Pickering emulsions on photo catalytic decomposition of nitrobenzene. ZnO NPs amended with 3 wt % amending agent indicates greatest effects in treatment of nitrobenzene. It was observed that ZnO NPs might efficiently increase the photo catalytic treatment of organic pollutants in the treatment of wastewater.

5. Mechanism prospects of AOPs:

The mechanistic of AOPs eventually cause the production of greatly active OH*. These OH* are extremely reactive with organic contaminants present in the polluted water. OH* typically absorb the electrons from the nearby organic pollutants that is electron-rich might leads to the treatment of organic contaminants completely. The oxidation capability of OH* is observed about 2.33 V, that is greater as related to chemical oxidants like Hydrogen peroxide or Potassium permanganate. The review of mechanism prospects of OH* formation in numerous AOPs contains photochemical and non-photochemical AOPs have been discussed below.

5.1. Non-photochemical approaches:

These AOPs are capable to produce the OH* with-out consuming light source. According to literature, some non-photo chemical AOPs also observed in the pollutants from IWW. The mechanism method for the generation of OH* in non-photochemical AOPs has been argued here.

1.Ozonation (O_3)
2.Ozonation/Hydrogen peroxide (O_3/H_2O_2)
3.Catalytic ozonation
4.Fenton based wet peroxidation (H_2O_2/Fe^{2+})

5.1.1. Ozonation

Ozone (O_3) is the effective oxidisation reagents for the oxidizing of compounds amongst air and pure O_2. O_3 could generate the oxidative radicals in the polluted water. Attacking of O_3 on OH* bounded by organic contaminants could leads to contaminants degradation. The common reaction involved in ozonation process was stated as (Gottschalk et al., 2000).

$$3O_3 + OH^- + H^+ \rightarrow 2{\bullet}OH + 4O_2 \text{ (g)}$$

5.1.2. Wet hydrogen peroxide ozonation (O_3/H_2O_2)

From literature it is observed that the rapid degradation of O_3 could be completed by adding H_2O_2 to O_3 leads to the rapid formation of OH*.

$$2O_3 + H_2O_2 \rightarrow 2\ OH^* + 3O_2 \text{ (h)}$$

The reported reaction might remain unchanged as stated above and the OH* are generated (Bethi et al., 2016).

5.1.3. Catalytic ozonation

Generally homogeneous or heterogeneous catalytic agent could be applied to enhance the ozonation process for effective treatment of organic contaminants. Numerous metallic oxides had planned for catalytic ozonation method like ferric oxide (Fe_2O_3), Aluminium oxide (Al_2O_3), Manganes oxide (MnO_2), Cerium oxide (CeO_2), Titanium oxide **(**TiO_2) and Zinc oxide (ZnO). The basic reaction process of decomposition of different organic contaminants is stayed uncertain in many of the catalytic agent.

5.1.4. Fenton based wet peroxidation (H_2O_2/Fe^{2+})

This method was described by Fenton for the oxidation of maleic acid. Late, researchers have conducted various studies on use of Fenton as a catalytic agent for treatment of many organic contaminants in IWW (Bethi et al., 2016). Some of the studies have also carried out some other oxidants in combination with Fenton method to improve the treatment ratio. The reaction process of joined method of Fenton and H_2O_2 is given below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \text{ (i)}$$

5.2 Photochemical approaches:

Non-photochemical degradation methods like (H_2O_2/Fe^{2+}) and (O_3/H_2O_2) could not fully the degradation of organic contaminants (Bethi et al., 2016). Some of these AOPs can produce most hazardous medium related to first parental material. Whole degradation of organic pollutants might be attained by joining non-photochemical AOPs with UV light. Mostly UV lamps show UV radiation of 200-300 nm wavelengths. Because of nonstop photolysis process, organic compounds could be activated upon the absorption of UV radiation and produce the OH*.

Several photochemical based AOPs have been argued here.

1. Ozone–hydrogen peroxide–UV radiation ($O_3/ H_2O_2/UV$)
2. Photo-Fenton system
3. Photo catalytic system (UV/TiO_2)

5.2.1. (O_3/H_2O_2/UV)

Degradation rate of O_3 might be enhanced by addition of H_2O_2 to the O_3/UV method. Improved degradation of O_3 eventually improved the speed of OH* generation. Adding of H_2O_2 to some AOPs is economical, while the organic contaminant has little absorption of light from UV lamp radiation.

5.2.2. Photo-Fenton system

The H_2O_2 andFe^{3+} ions contact to UV light, H_2O_2 will be degrade under photo catalytic action of Fe^{3+} ions and will produce OH* and Fe^{2+} ions. It has been detected that Fe $(OH)^{2+}$ compound has produced at pH 3.

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H+ \text{ (j)}$$
$$Fe(OH)^{2+} \leftrightarrow Fe^{3+} + OH^- \text{ (k)}$$
$$Fe(OH)^{2+}h\nu \rightarrow Fe^{2+} + OH^* \text{ (l)}$$

5.2.3. (UV/TiO_2)

In visible or UV radiation adopted semiconductor substance could be activated by photons and generate two electron pairs and holes in valence and conduction band individually. Produced charge movers will start the oxidation or reduction reactions correspondingly. On the surface of TiO_2 these can react with absorbent (Matthews, 1986).

$$e^- + O_2 \rightarrow \bullet O^{-2} \text{ (m)}$$
$$h^+ + A^- \rightarrow \bullet .A \text{ (n)}$$
$$h^+ + OH^- \rightarrow OH^* \text{ (o)}$$
$$OH^* + RH \rightarrow {}^*RHOH \text{ (p)}$$
$$OH^* + RH \rightarrow {}^*R + H_2O \text{ (q)}$$
$$h^+ + RH \rightarrow {}^*RH^+ \text{ (r)}$$
$$H_2O + h^+ \rightarrow OH^* + H^+ \text{ (s)}$$

6. Present trends & future prospects:

Previous, studies have been mostly gave attention on conventional systems for the treatment of polluted water. Scientists have been used these traditional treatment methods till 1990’s. Late they moved to AOPs like ozonation and photo catalysis, etc. Mostly previous works have been carried out for the treatment of IWW consuming TiO_2 based photo catalytic AOP.

The recent concern of researchers applying AOPs for water treatment is attaining attention worldwide. The different approaches of AOPs for advanced water treatment method to eliminate pollutants from polluted water or change contaminants into degradable substances, though various AOPs methods are described in current review are tested in the laboratory and pilot scale.

The future prospects for application of ultrasonic treatment and hydrodynamic coating as an AOP on experimental and commercial scale that can enhance the generation of extra OH*. A capable prospect for such AOPs waits. Such AOPs might develop usable on industrial scale when each effective aspect is enhanced and various methods are joined to remove all disadvantages related with the single methods to attain full effectiveness with least energy use. To get this goal in specific, extra efforts are essential to overcome certain main problems, like the improvement of unique catalytic tools (that might be activate in visible bands region or solar centred).

III. Conclusions

AOPs have developed as a vital method for IWW treatment. Mostly the methods for treatment of WW are physiochemical, chemical or physical methods and sometimes the combination of both. As one of the innovative techniques, AOPs involves the formation and use of HO* as a powerful oxidant for the degradation of organic pollutants that can’t be degraded by traditional oxidants. AOPs methods have revealed evidences in many sectors of WW treatment because of its greater competence in contaminant removal. Moreover, the quantity of OH* generated is a significant factor, however further research work has to be conducted in this research area.

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