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Industrial Wastewater Treatment: A Challenging Task in the Industrial Waste Management

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Abstract

This review shows the pros and cons of using the combination of various technologies for industrial waste water treatment plant. Rapid industrialization, intensive agriculture and other human activities cause soil degradation, pollution and lowers the productivity and sustainability of the crops that further increase the pressure on natural resources and contribute to their degradation. Environmental bio remediation is an effective management tool for managing the polluted environment and in restoring the contaminated soil. The use of microbial sources, coupled with advanced technology is one of the most promising and economic strategies for the removal of environmental pollutants. There is a strong scientific growth with both the *in situ* and *ex situ* ways of bio remediation, in part due increased use of natural damping as most of the natural attenuation is due to bio degradation. The degradation of pollutants by environmental bio remediation technology, can be a lucrative and environmentally friendly alternative. This article provides an overview of the important environmental bioremediation technologies and their application in treating the industrial waste water.

Keywords: Bio-remediation; Bio-degradation; Bacteria; Environment; Waste water

Introduction

To deal with effluents, the traditional end-of-pipe solutions coming out of the production plant have gradually been substituted for an increased decentralized approach to treat the selected wastewater streams in the most effective and economical way [1]. Further, additional goals like reducing the overall effluent emissions by recycling the treated wastewater towards zero-discharge strategies or minimizing waste generation and disposal costs have gradually been incorporated to both water and wastewater management approach. The future of industrial wastewater treatment has two main targets:

α. Monitoring and abatement of trace pollutants;

β. Further development of the existing and new wastewater treatment technologies in order to minimize the costs and optimize resource consumption.

Environmental pollution is the most atrocious ecological crisis that man is facing today. Pollution is a global intimidation to the environment and it becomes an alarm word of today's world. The swift growth of human populations fulled by scientific developments in health and agriculture has led to a speedy increase in the environmental pollution. Water has a major impact on all aspects of human life, including but not limited to health, food, energy and the economy. The unprecedented inhabitants' multiplies and the industrial development during the 20th century has not only increased the conventional solid and liquid waste pollutants to critical levels but also produced a range of previously unknown pollution problems for which the society was unprepared. Of the total 220 million deaths per year it was estimated that the causes of death in 12-20 million are due to water and non-fatal infections which is very high [2]. The run- off flow is considered to be the freshwater source on which the people depend. The steady flow of fresh water was estimated at 12.700 to 16.000 km^3 year which is 4200 km^3 per year. It is used for freshwater irrigation, industrial and domestic purposes, and that is estimated to increase by a number of 4350-5200 km^3 per year. Alternatively, the available fresh water is only 0.5% of the worlds 1.4 billion km^3 water, which is also poorly distributed throughout the world [3]. There is a limited ability to increase the supply of drinking water due to the competing demands of the growing populations worldwide and, the problems related to water. It is expected to further increase due to climatic changes and population growth over the next two decades. The most common method of wastewater treatment in the developed countries is centralized aerobic wastewater treatment plants and lagoons for both domestic and industrial waste water. It is estimated that the world's population increases roughly by 2.9 billion people between now and 2050. The lack of delivery of drinking water is the result of the use of water resources for domestic, industrial and irrigation purposes by many due to growing global demand for food, energy, etc. and will be much more increased as a result population growth and the further threat of climate changes [4]. The polluted surface/ground water resources, is another cause of reduced fresh water supplies. The aquifers worldwide are thinner and are contaminated as a result of many problems of intrusion of salt water, soil erosion, lack of hygiene, contamination of soil/surface water algae growth, detergents, fertilizers, pesticides, chemicals, heavy metals, and so on. The domestic wastewater can also be treated on site using septic systems. It is an advanced system which can treat wastewater from one or more households. It consists of an anaerobic underground tank and the drainage field for the treatment of effluent from the tank. The quantity of wastewater treatment varies in many developing countries [5]. In some instances, the industrial waste water is discharged directly into water bodies, while large industrial facilities can have a full race treatment. In some coastal cities, the domestic wastewater is discharged directly into the ocean. Waste pits are lined or unlined holes to a depth of several meters, which can be equipped for comfort. Figure 1 shows the different ways for wastewater treatment and discharge.

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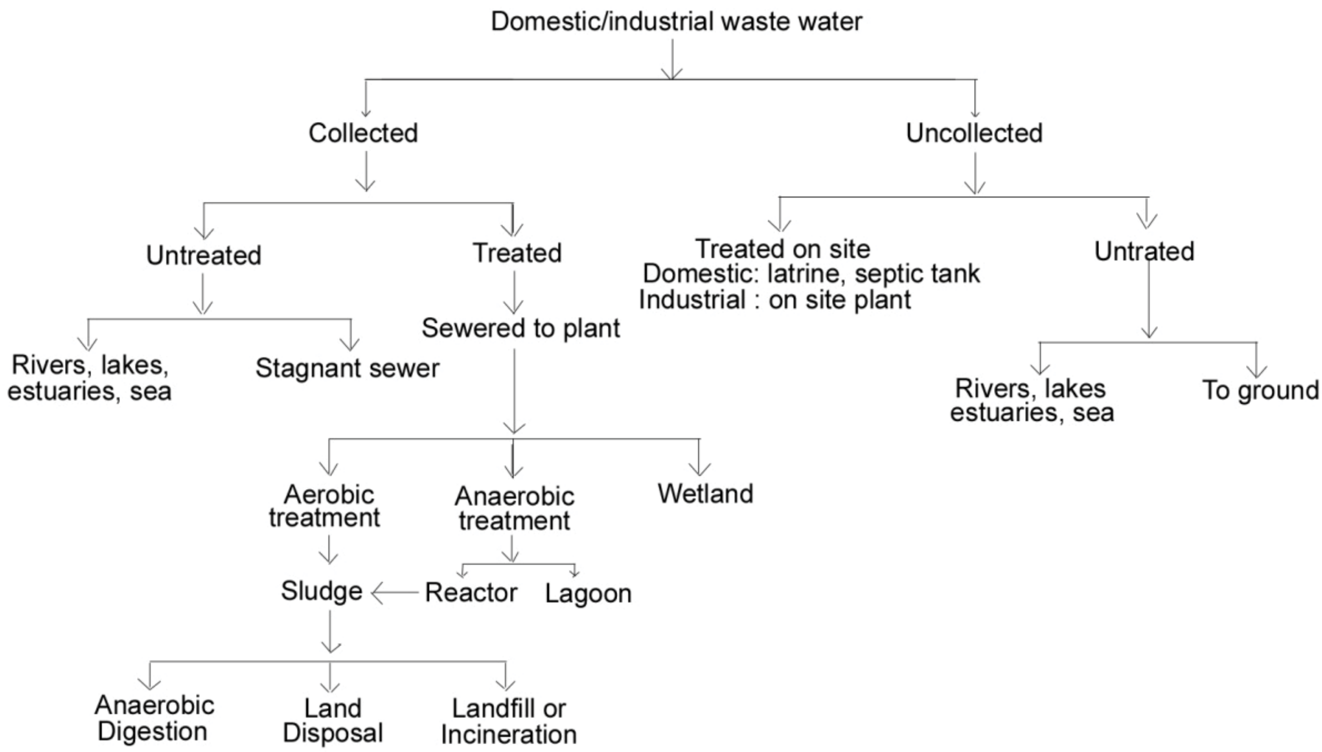

Figure 1: Domestic/industrial wastewater treatment system and discharge scheme.

Wastewater treatment technologies

In waste water treatment technology, various physical, chemical and biological pre-treatment and after treatment can be used to treat raw wastewater. Physico-chemical techniques include membrane filtration, coagulation, flocculation, precipitation, flotation, adsorption, ion exchange, mineralization, advanced oxidation, electrolysis and chemical reduction. Biological treatment systems effectively remove toxic pollutants of large volumes of wastewater at low costs and are preferred alternatives [6]. Biological techniques, including biosorption and bio degradation in aerobic, anaerobic or combined aerobic/anaerobic treatment processes of bacteria, fungi, plants, yeasts, algae and enzymes are known. Generally, the wastewater is highly colored with high biological oxygen demand and chemical oxygen demand and has high conductivity and is alkaline in nature [7]. For this reason, several factors determine the technical and economic feasibility of each removal techniques such as pigment type dyes, wastewater composition, dose and cost of the necessary chemicals, operating costs (energy and materials), environmental fate, and handling costs of generated waste products. Usually, it may not be sufficient to obtain full use of one of the individual processes, because each method has its limitations. The type treatment is choosed based on several factors such as the type of pollutants that should be treated, composition of the wastewater, the cost of the necessary chemicals and operation costs, handling and costs of the waste product generated [8]. Contemporaneous with the in-house multi-dimensional pollution minimization efforts, a number of emerging material recovery/reuse and end-of-pipe wastewater treatment technologies are being projected and explored at different stages of commercialization. Accordingly, despite the fact that virtually all the known physico-chemical and biological techniques have been explored for wastewater treatment, none has emerged as a panacea. Cost-competitive biological options are rather ineffective while physico-chemical processes are restricted in scale of operation and pollution profile of the effluent [9]. Figure 2 depicts a simplified representation of the proposed combinations.

This article gives an inclusive overview of the impending of hybrid technology for treating wastewater. Analogously to the above trends, the combinations were placed in the three broad categories, i.e., a combination of the advanced oxidation process, a combination of physico-chemical treatments between themselves and those with advanced oxidation process, and the one of primary importance, is the combination of biological systems with conventional physico- chemical processes and advanced oxidation process (Figure 3).

The hazardous organic waste that is widely spread in water by industrial and domestic sources is an emerging issue [10]. Advanced Oxidation Processes (AOP) are efficient methods that remove the non degradable organic pollutants by means of biological processes. They involve the production of extremely reactive oxygen species that are able to obliterate a broad choice of organic compounds [11]. AOP are driven by an external energy sources such as electric power, ultraviolet radiation or solar light, so these processes are often more costly than traditional biological wastewater treatment. Furthermore, the AOP can be applied for the disinfection of water, air and for remediation of contaminated soils [12-15]. Table 1 lists the advantages and disadvantages of different individual techniques. It appears that a single, universally applicable end-of-pipe solution is unrealistic, and combination of different techniques is required to devise a technically and economically viable choice. In light of this, the researchers have put forward a wide range of hybrid decolorization techniques.

Process	Advantages	Disadvantages	References
(A) Biological	Cost-competitive option. Direct, disperse and basic dyes have high level of adsorption on to activated sludge	Dyes are generally toxic and very resistant to bio degradation. Acid and reactive dyes are highly water-soluble and have poor adsorption on to sludge.	[16]
(B) Coagulation	Economically feasible; satisfactory removal of disperse, sulphur and vat dyes.	Removal is pH dependent; produces large quantity of sludge. May not remove highly soluble dyes; unsatisfactory result with azo, reactive, acid and basic dyes.	[17-19]
(C) Activated C adsorption	Good removal of wide variety of dyes, namely, azo, reactive and acid dyes; especially suitable for basic dye.	Removal is pH dependent; unsatisfactory result for disperse, sulfur and vat dyes. Regeneration is expensive and involves adsorbent loss; necessitates costly disposal.	[20]
(D) Ion exchange	Adsorbent can be regenerated without loss, dye recovery conceptually possible.	Ion exchange resins are dye-specific; regeneration is expensive; large-scale dye recovery cost-prohibitive.	[21,22]
(E) Chemical oxidation	Initiates and accelerates azo-bond cleavage.	Thermodynamic and kinetic limitations along with secondary pollution are associated with different oxidants. Not applicable for disperse dyes. Negligible mineralization possible, release of aromatic amines and additional contamination with chlorine (in case of NaOCl) is suspected.	[23]
(F) Advanced oxidation processes (AOP)	Generate a large number of highly reactive free radicals and by far surpass the conventional oxidants in decolorization	AOPs in general may produce further undesirable toxic byproducts and complete mineralization may not be possible. Presences of radical scavengers reduce efficiency of the processes some of which are pH dependent. Cost-prohibitive at their present stage of development.	[23,24]
(1) UV/O3	Applied in gaseous state, no alteration of volume. Good removal of almost all types of dyes; especially suitable for reactive dyes. Involves no sludge formation, necessitates short reaction times.	Removal is pH dependent (neutral to slightly alkaline); poor removal of disperse dyes. Problematic handling, impose additional loading of water with ozone. Negligible or no COD removal. High cost of generation coupled with very short half-life and gas-liquid mass transfer limitation	[25-30]
(2) UV/H2O2	Involves no sludge formation, necessitates short reaction times and COD reductionmay be possible to some extent.	Not applicable for all dye types, requires separation of suspended solid and suffers from UV light penetration limitation. Lower pH required to nullify effect of radical scavengers.	[31]
(3) Fenton's reagent	Effective decolorization of both soluble and insoluble dyes; applicable even with high suspended solid concentration. Simple equipment and easy implementation. Reduction of COD (except with reactive dyes) possible.	Effective within narrow pH range of <3.5; and involves sludge generation. Comparatively longer reaction time required	[32]
(4) Photocatalysis	No sludge production, considerable reduction of COD, potential of solar light utilization.	Light penetration limitation, fouling of catalysts, and problem of fine catalyst separation from the treated liquid (slurry reactors)	[33]
(5) Electrochemical	Effective decolorization of soluble/insoluble dyes; reduction of COD possible. Not affected by presence of salt in wastewater.	Sludge production and secondary pollution (from chlorinated organics, heavy metals) are associated with electrocoagulation and indirect oxidation, respectively. Direct anodic oxidation requires further development for industrial acceptance. High cost of electricity is an impediment. Efficiency depends on dye nature.	[34]

Table 1: Advantages and shortcomings of individual dye wastewater treatment techniques.

AOP refer to a set of oxidative water treatments that can be used to treat toxic effluents at industrial level and wastewater treatment plants. AOP are flourishing to transform toxic organic compounds into biodegradable substances. In general AOP are economical to set up but comprise high operating fixed cost due to the input of chemicals and requirement of the power required [35-40]. To limit the costs, AOP are often used as pre-treatment mixed with biologic treatment. Advanced oxidation was recently used as quaternary action or a shining step to remove micro-pollutants from the effluents of municipal wastewater treatment plants and for the disinfection of water. The combination of several AOP is an efficient way to increase the removal of pollutants and in reducing the costs [41-43].

Advanced oxidation process system

Advanced oxidation involves several steps represented schematically in the figure below and explained as follows:

1. Formation of strong oxidants.
2. The reaction of these oxidants with organic substances in water to produce biodegradable intermediates.
3. Further reaction of biodegradable intermediates with oxidants leading to mineralization.

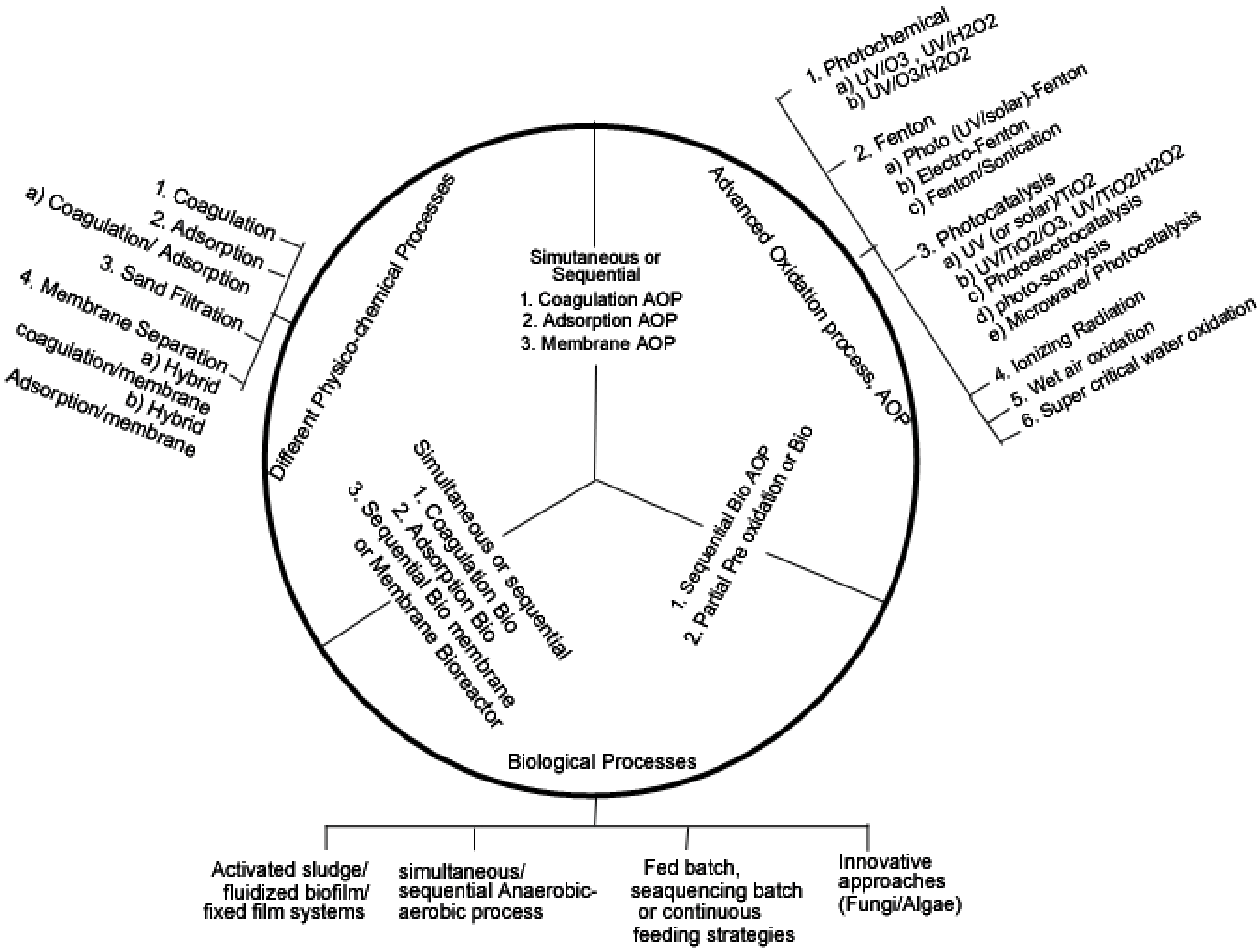

Figure 2: Simplified representation of broad spectrum of combinations proposed in the literature.

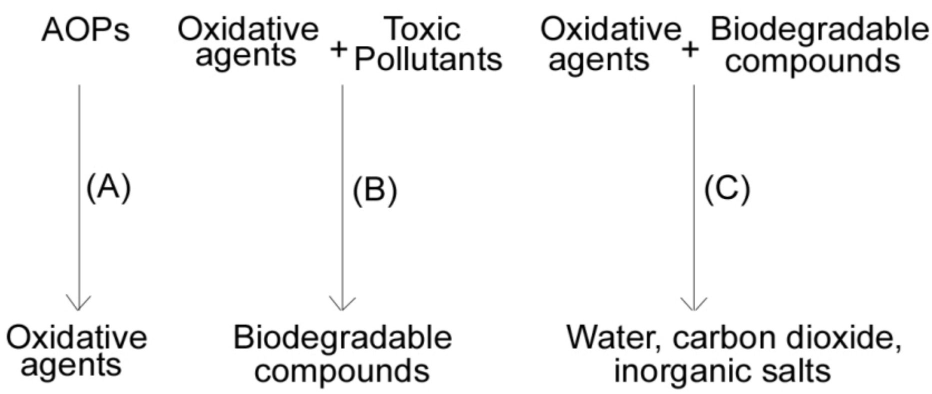

Figure 3: Advanced Oxidation Process Scheme.

Advanced oxidation process combination

AOS have been calculated extensively for wastewater treatment but their commercialization has not yet been realized because of prevailing barriers. These processes are prohibitively expensive and complex at the current level of development. Additional obstacle in the waste water treatment is the existence of relatively high concentration of colorants, and AOS are the only effective ways for wastewater treatment [44-50].

Thus, significant dilution is necessary, as a requirement of the device. The presence of dye additives/impurities such as synthetic precursors, by-products, salts and dispersing agents in a commercial dye bath formulation, cause further reduction in the process efficiency. Although small laboratory investigations reveal encouraging results, such studies are not sufficient to explain the practical feasibility of AOP [51,52].

Photochemical process

The photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of appropriate energy level with the chemical species present in the solution. The UV radiation generated radicals through photochemical degradation of homogeneous oxidizing compounds such as hydrogen peroxide, ozone or Fenton's reagent has been reported to be superior to the sole use of ultraviolet (UV) radiation or the sole use of such oxidants [53-60]. Highly absorbent UV dye wastewater can inhibit the effectiveness of the process by limiting the penetration of UV radiation, which requires the use of high- intensity UV lamps and/or a specially designed reactor. Photocatalytic mechanism occurring at the surface of the semiconductors is the other way of obtaining free radicals.. Titanium dioxide in the anatase form has reasonable photoactivity and is the most commonly used photo catalyst. It also has the advantages of being insoluble, relatively inexpensive, non- toxic, as well as having resistance to photocorrosion and biological immunity [61,62]. The photocatalytic process can be performed by simply using the slurry of fine catalyst particles dispersed in liquid phase in a reactor or by using supported/immobilized catalysts. The limitations of the slurry reactors include the low efficiency of radiation due to the opacity of the suspension, fouling of the surface of the radiation source due to the decomposition of the catalyst and the requirement of ultrafine catalyst particles to be separated from the treated liquid [63-68].

Besides single photocatalysis, there are also reports on the use of photocatalysis in the presence of O_3 or H_2O_2 having improved bleaching and mineralization. Considering the total mineralization of compounds, the photocatalytic ozonation has specific energy consumption much lower than conventional photocatalysis and ozonation. The Fenton's reagent and its alterations, such as the thermal Fenton process or the photo- Fenton reaction using Fe (II)/ Fe (III) oxalate ion, H_2O_2 and UV radiation have established much consideration as a means for the whitening of synthetic dyes [69,70]. In the photo - Fenton technique, H_2O_2 is used swiftly in three synchronized reactions and the shortest action of Fenton, photo - reduction of Fe (III) ions to Fe (II) and H_2O_2 photolysis. Thus, this process produces more hydroxyl radicals compared with the conventional Fenton method or photolysis. Few reports suggest that in case of comparable pollutant removal performance, the Fenton process can be gainful, in conjunction with the use of advanced oxidation alternatives reducing the energy consumption, the consumption of H_2O_2, lower cost of sludge disposal, higher flexibility and lower requirement of maintenance. Fenton reagent requires the use of large amounts of acidic and alkaline chemicals [71,72]. In order to take advantage of Fenton oxidizing agents role in eliminating the separation of iron salts, the usage of H_2O_2/iron powder solution system was recommended. This process can provide better stain removal than the " H_2O_2/Fe^{+2}" due to chemisorptions of iron powder addition to the usual type of reaction (203). Though the Fenton Fenton -type reactions based on different transition metals, was less explored to date, they have been described to be insensitive to pH and effective for the degradation of synthetic dyes. Among the AOP, the photo-Fenton reaction and titanium dioxide (TiO_2) mediated heterogeneous photo catalytic treatment processes are proficient of absorbing the light in the near-UV spectral region for initiating the radical reactions. Their application would virtually eliminate major operating costs when solar radiation is used instead of artificial UV light. The ferrioxalate solution that has long been used as a chemical actinomètre can be used in the process of photo Fenton to derive further benefit by replacing UV light with solar radiation [73-80]. Recently, several attempts have been made to increase the photocatalytic efficiency of TiO_2 that include the deposition of noble metal doping ions, addition of inorganic adsorbent, catalysts of the coupling, the use of nonporous films, and so on. In addition to this, new catalysts, such as metallo porphyrins polymers were reported to be easily excited by violet or visible light, with only 3% usage of the avaialable solar energy for the the commonly used TiO_2 [81].

Combination of electrochemical and photochemical process

In the electrochemical treatment, the oxidation is carried out by means of electrodes, where determined potential difference is applied. Based on this principle, many different processes were developed as direct and indirect electrochemical processes that include cathodic and anodic oxidation, electrocoagulation, electrodialysis, electromembrane, and electrochemical ion exchange. Sometimes the combination of electrochemical technology and photocatalysis has been adopted for avail unique advantages. For example, the chemical synergy process of photocatalysis and electrochemicals can give increased discoloration and the added benefit of the removal of chemical oxygen demand that may be derived from existence of the salt in solution, which otherwise is harmful to perform sole photo catalysis [82-90]. Conversely, electro-Fenton process requires no addition of chemicals other than the catalytic amount of Fe^{+2}, that is produced from H_2O_2 *in situ*, thereby avoiding the transportation of the dangerous oxidant. With high pulsed voltage electrical discharge process, more oxidants such as H_2O_2 give rise to highly reactive free radical species by photo-dissociation of H_2O_2 and thus improves the overall process [91,92].

Sonolysis process

The use of sono chemical methods for treating a variety of chemical contaminants in an aqueous solution have been conducted in many studies. These studies mainly reported the systems and the basic theory of sonochemical reactions for environmental applications. Sonolysis is mainly based on acoustic cavitation including training, growth and implosion of bubbles in a liquid collapse as depicted in Figure 4. For detailed information of cavitation training, the readers are requested to refer to previous references. The positive and negative pressures are exerted on a liquid, by the compression and expansion of ultrasonic wave cycles, respectively [93-100]. When the negative pressure applied on the liquid is sufficiently high, the average distance between the molecules would exceed the critical molecular distance necessary to maintain the intact liquid and the liquid will break down to form cavities in vapor and gas-filled micro bubbles. The gases and vapors are compressed inside the heat generating cavity which ultimately produces a localized hot spot of short duration, creating local pressures and high temperatures [101-103]. Among the sonochimie theories, the hot spot theory is widely accepted to explain the sonochemical reactions in the field of environment, which suggests that the collapse is so rapid and that the compression of the gas and steam inside the bubble is an adiabatic process. Ultrasonic energy affects chemical reactions releasing enormous heat or production of reactive free radicals, there by increasing the mass transfer rate in an aqueous solution through turbulence. Inside the cavitation the breakdown of the water molecules to bubbles forming pyrolysis OH· and H· radicals in the gas phase of the reaction [104-106]. The substrate reacts with either · OH or undergoes pyrolysis. In the interface region, a similar reaction occurs but in an

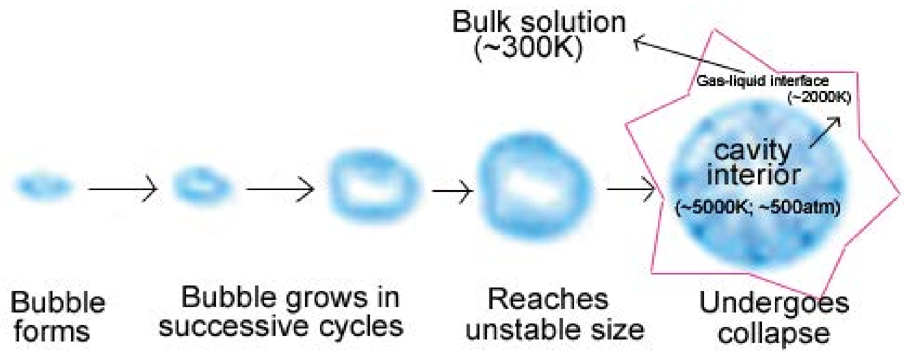

Figure 4: The formation and collapse of a cavitation bubble, and three reaction zones in the cavitation process.

aqueous phase, the · OH radicals recombine to form H_2O_2. In bulk solution, a small number of free radicals produced from the cavities or the interface can move to the liquid phase in the mass, and the reactions are essentially between the substrate and ·OH and H_2O_2 [107].

$$H_2O \rightarrow \cdot OH + \cdot H$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2, \quad k = 5.5 \times 10^9 M^{-1} s^{-1}$$

Physico-chemical process combination with advanced oxidation process

Coagulation based combinations: Many studies have examined different combinations of physicochemical systems for textile processing and dyeing wastewater. The combinations of classical physicochemical and AOP techniques have thus emerged as an attractive option. Flocculation/coagulation precipitation methods have been extensively used for decolorizing dye containing industrial wastewater [107-110]. For pretreatment of raw wastewater before discharging to public capital processing factories, these processes may be satisfactory with respect to the reduction of the chemical oxygen demand, and partial discoloration. Their standalone application in the treatment of textile waste/dye is however relatively ineffective; for example, only 50% of the removal was performed using either alum or ferrous sulfate to a yellow azo dye reagent. In the coagulation process, it is difficult to remove the highly soluble dyes in water, and more importantly, this process produces large amount of sludge. However, the researchers are persistent in their pursuit to minimize the limitations of this technology. For example, polyaluminium ferric chloride, a new type of composite coagulant, was reported to have the advantages of high stability and good coagulating effect of hydrophobic and hydrophilic dyes. The discoloration capacity exceeded that of the poly polyferric sulfate and aluminum chloride. On the other hand, to avoid any problem of the disposal of solid sludge, different innovative approaches have been proposed. These include clotting separate volume low dye bath alum sludge recycling, recovery of chemical coagulant textile sludge, reuse of sludge in textile building materials, and processes such as vermicomposting textile mill sludge, coagulation followed by carbon adsorption. The coagulation followed by adsorption has been reported to produce effluent reuse standard compared with the shoot coagulant consumption by 50%, thereby lowering the formed sludge volume compared to induce coagulation alone [111-115]. Coagulation in combination with AOP, whether sequential or simultaneously, has been reported for dyeing wastewater. For example, simultaneous application of coagulation and Fenton oxidation showed improved performance over one of their autonomous applications. Chemical coagulation of fenton after treatment was found to reduce floc-settling time, improvement in the discoloration and in the reduction of the soluble iron effluent. Conversely photo-Fenton subsequent to coagulation process was reported to finish fading and produce better DCO, with the added benefit of reducing the load on the AOP thus reducing the chemical usage. The studies in the sequential use of coagulation and ozonation revealed the superiority of this arrangement preceded by ozonation coagulation. Reverse multistage coagulation followed by ozonation was shown to be superior to their sequential application of single pass. The advantages of this application in several steps was more convincing if the wastewater is with recalcitrant composition [116-120].

Adsorption: Adsorption techniques are especially used for the bleaching of dyes in industrial effluents. The activated carbon, either in the powder or granular form is the most widely used adsorbent due to its extensive surface micro porous structure, high adsorption capacity and high surface reactivity. It is very effective to adsorb cationic, mordant and acid dyes and to a lesser extent dispersed, direct, vat, pigment and reactive dyes. The use of carbon adsorption for decolorization of the crude wastewater is impractical as a consequence of the competition between the colored molecules, and other organic/ inorganic compounds. Hence, its use is recommended as a polishing step or used at the end of an emergency unit treatment stage to meet the discharge color duration. The weight loss is inevitable during its expensive onsite regeneration and hampers its widespread use. The use of non-conventional, economical sources as precursors for activated carbon has been proposed to achieve the cost-effectiveness in the application. As previously stated, adsorption is a non-destructive method in which there is only the change in the phase of the removed impurities and, therefore impose further problems in the form of sludge [121-124]. The high cost also necessitates the adsorbent regeneration. On the contrary, some catalytic oxidation /reduction systems seem to be more effectively focused on the treatment of the small volume dyes. So it seems attractive to combine other adsorption process in a system where the contaminants are pre-concentrated on the absorbent, and then separated from the water. The thus separated contaminants can subsequently be mineralized (example wet air oxidation) or degraded to a certain extent (example, azo bond reduction with bisulfite mediated borohydride to regenerate the adsorbent and re-use). In this manner, an economic process can be developed linking two processing techniques that can eliminate their inherent disadvantages. The application of partial degradation to regenerate the adsorbent leaves behind a small amount of wastewater to treat. Again, this can be easily taken care of by the application of some AOP. Adsorption simultaneously with ozonation, UV-H_2O_2 or microwave has induced oxidation. The mutual reported improvements such as catalysis of AOP yield by adsorbent and simultaneous regeneration of adsorbent. A rather complicated method involving solvent extraction and catalytic oxidation has been documented in the literature. This method involves dye extraction by means of an economical solvent, followed by recovery with dye chemical stripping [125-127].

Combination with membrane technology: Membrane separation gives the possibilities of either the concentration of the dyes and adjuvants and producing purified water, or the removal of the dye and allowing the re-use of water along with extra chemicals, or even the realization of the recovery of the substantial part of the dye, admixtures and water all together [128]. This recovery/reuse practice reduces many folds the recurring costs for the treatment of waste streams. The fact that the behavior of the paint residual dye ideally identical to that of the fresh dye may restrict recovery and the re-use of specific dye classes. Accordingly, water and/or electrolytic recovery of dye bath effluent have become the focus of contemporary literature [129]. However, the production of concentrated sludge and the occurrence of frequent membrane fouling that involves expensive membrane replacement hinder the widespread use of this technology. Two different trends are so evident among the reported studies that link the membrane separation and other technologies. Some studies focused on the reduction of the membrane concentrated disposal problem, while others concentrated on the full-hybrid systems, which might eliminate the limitations of the membrane technology, and/or that of the counterpart technologies [130,131].

Hybrid processes based on membrane and photocatalysis were reported to eradicate the problem of the ultrafine catalyst to be separated from the treated liquid in the case of slurry reactors. Further they also have the added advantage of the membrane acting as a selective barrier for the species to be degraded. In case of immobilized catalysis, the membrane may play a role in connecting the photocatalyst with photocatalysis and membrane distillation. However it was reported to be more advantageous compared with the pressure-driven membrane process, because it may be associated with significant fouling. It is proposed that the pretreatment of photo- oxidation ($UV/TiO_2/H_2O_2$) before membrane filtration to partially decompose high molecular weight compounds that cause fouling of the membrane. The relatively smaller fragments that were produced were still retainable within the membrane, and unlike the parent compound does not affect the charge of the membrane surface [132]. The membrane contactors encompass mass transfer by diffusion through the pores and offer advantages for higher contact area. They involve lower cost and help in the easy scale-up process without foam formation [133].

Combination with biological treatment

Combination among biological process: A conventional chemical coagulation step that is preceded by or antecedent to biological treatment is applied in the treatment of dye wastewater. This is also combined with municipal wastewater treatment and usually favored wherever applicable [134]. Various biological processes such as activated sludge, liquid biofilm, different solid film systems or combinations thereof have been applied. Although aerobic bacteria mediated co-metabolic reductive cleavage of azo dyes and use of azo compounds as sole source of carbon and energy has been reported, the dyes are generally very resistant to degradation under aerobic conditions. The toxicity of the dye waste water and the factors inhibiting the permeation of the dye by the microbial cell membrane reduces the effectiveness of the biological degradation. A combined treatment of anaerobic-aerobic system of azo dye appears to be attractive as the azo bond reduction can be performed under reducing conditions in anaerobic bioreactors and colorless aromatic amines thus obtained can be mineralized in aerobic conditions [133]. The biotic process, dominates high rate anaerobic bioreactors. The addition of anthraquinone compounds such as redox mediator sulfonate, di-anthraquinone sulfonate were reported to greatly enhance both biotic and abiotic processes. After anaerobic treatment, the post-treatment of the azo dye containing encompasses competition between the biodegradation and auto oxidation of aromatic amines. The biological therapy is a competitive and environmentally friendly alternative [134]. The researchers are therefore persevering their efforts to minimize the inherent limitations of biological dye wastewater treatment. There are several innovative attempts that have been tried and documented in the literature to achieve a better design of the reactor and/or use of the special dye-degrading microorganisms for integrated textile manufacturing wastewater treatment. Some of these innovative efforts include- two stages activated sludge process; high-rate anaerobic systems disconnect the hydraulic retention time of the solids retention time [135].

Hybrid biological process

Physico-chemical and biological treatment: As mentioned above, the literature is replete with examples of using the additional coagulation organic discoloration. The choice between the coagulation - biological or biological-coagulation system depends on the type and dosage of the coagulant, the amount of sludge, and the degree of inhibitory and non-biodegradable substances in the wastewater [136]. Coagulation before biological treatment may be advantageous for the alkaline wastewater. After biological treatment, the ferrous sulfate treatment cannot be used as the pH becomes close to neutral. On the other hand, the dose of coagulants and the amount of the bio-sludge after chemical treatment are smaller compared to those of the coagulation followed biological treatment [137]. Besides coagulation, a variety of other treatments can be combined with a biological treatment. Very often certain physico-chemical process is located before and /or after AOP. The biological method is either applied as a penultimate or the last treatment unit. Given the abundance of the bio resistant toxic substances in wastewater dyes, the physico-chemical pre-treatment and advanced oxidation before biological treatment seems to be a rational choice. The choice between the physico-chemical and oxidative pretreatment depends on the specific wastewater and, usually bright-stream separation would facilitate the application of appropriate treatment or different streams [138].

Biodegradation: The conventional pre or post treatment concepts includes the the design process containing individual components that are independent of each other. In contrast to this, a more innovative "integrated- process" approach was developed which combined the efficacy of the biological and other treatments that are synergistic in their effect [139]. A typical example of this processes is the advanced of an activated sludge treatment where chemical oxidation was specifically designed to partially degrade recalcitrant contaminants to readily biodegradable intermediates. In the recent years, the studies that dealt with the partial pre-oxidation of myriads of dye wastewater reported the involvement of all kinds of PDO. Some of these studies included the partial oxidation ozonation, H_2O_2 photocatalysis, photography -Fenton moist air oxidation combined with photocatalysis and ozonation/H_2O_2, photo-electrochemical process [6] under oxidation, and water and supercritical electron beam bulk of treatment [140]. These studies reported on the improvement of the biodegradability and the reduction of toxicity following PDO treatment without the biological reactor. However, the complete results were not obtained. The combined oxidation and subsequent biodegradation make it necessary to adjust the optimum oxidation treatment point. Further the oxidation cannot lead to significant changes in the molecular weight distribution, but resulted in the increase of thelow molecular weight mineralization substances. Therefore, the rationale is to adopt the shortest possible preoxidizing period and remove the biodegradable fraction using organic profitable process. However, the degree of COD removal obtained from combining with this strategy can be limited in some cases, making the use of an oxidation period [141]. An internal biological process between oxidation and recycling biological step has been recommended to reduce the dose of the chemicals in such circumstances. If there are considerable amount of biodegradable compounds that initially exist in the wastewater, the pre-oxidation step does not lead to a significant improvement in the biodegradability but rather cause unnecessary consumption of chemicals. In such cases the biological pre-treatment is followed by a PDO, and biological polishing step, can be more useful [142].

Adsorption with biodegradation: Conventional biological treatments have limited effectiveness in the treatment of rebellious textiles wastewater that is mostly composed of recalcitrant chemicals. Due to this reason the textile dyes, various adsorbents and chemicals that predominantly include the activated carbon were directly added to the activated sewage systems in some studies [143]. The fact that the additional removal of soluble organic substances (chemical oxygen demand and and total organic carbon), in such a system compared to the conventional system cannot explain the likely contribution of adsorbent as it was predicted that the adsorption isotherms assume a synergistic relationship between the activated carbon and microorganism [144]. Enhanced biodegradation was attributed to the ability of the adsorbent that acts as a modulator by immediately adsorbing the high concentrations of toxic substances, thereby managing the free concentration of toxic substances. This provides an enriched environment for the microbial metabolism that takes place at the liquid-solid surface onto which the microbial cells, enzymes, organic materials and oxygen are adsorbed [145]. The main step in dye removal for activated carbon amended biological process is microbial degradation, which is higher than the adsorption on both activated carbon as well as on biomass [146-155].

Membrane bioreactors: A membrane bioreactor exhibits more improvement over conventional activated sludge treatment, and was shown to be promising in the color treatment of wastewater [156]. For discoloration, a membrane bioreactor for is frequently introduced in conjunction with the charcoal amended digester that involves the current adsorption scheme of treatment. This is preceded by the aerobic membrane bioreactor that comprehends stable discoloration together with the elimination of high total organic carbon. Rarely the membrane bioreactors were used as major treatment process before the polishing of the nano filtration step or in the complicated treatments that include anaerobic/aerobic pretreatment before membrane bioreactor ozonation [157]. The current literature includes an innovative approach of using the membrane separated fungus reactor which helps in the excellent degradation ability of white-mold [158,159].

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