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Original Research

Anaerobic Treatment of Industrial Wastewater by UASB Reactor Integrated with Chemical Oxidation Processes; an Overview

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Abstract

In order to upgrade the quality of anaerobically treated effluent to a level recommended for irrigation, integration of a UASB reactor with UV and AOPs (advanced oxidation processes) (Ozone, H_2O_2/UV, Fenton, and photo-Fenton) could be a better option for almost complete colour, COD removal, and disinfection of pathogens. High efficiency of the UASB can be maintained by proper process conditions, including temperature, sludge age, pH, hydraulic retention time, and gas-liquid-solid separator (GLSS) design. A fraction of the COD and colour is usually non-biodegradable and renders difficulty for anaerobic digestion. AOPs degrade the organic molecules and converting completely the organic compounds to non-toxic components such as CO_2 and/or water. As far as disinfection is concerned, advanced oxidation processes are proved to be extremely effective in killing pathogens (total *coliform*, fecal *coliform*, fecal *streptococci*, *salmonella,* and *E. coli*) due to their strong oxidative characters. Although AOPs effectively accomplish pathogen elimination, re-growth of pathogenic microorganisms can take place in the treated effluent. Re-growth potential of pathogens provides helpful information about the quality of the treated water, which is very important in all possible reuse options. The combined application of AOPs with anaerobic treatment minimizes the chances of regrowth due to irreparable damage to nucleic acid. This review paper focuses primarily on the process conditions and treatment efficiency for UASB treatment systems, and to evaluate the advanced oxidation processes (AOPs) as an option for post treatment.

Keywords: UASB reactor, advanced oxidation processes, UV irradiation, colour removal, disinfection, Pathogen re-growth

Introduction

There are a wide range of treatment technologies. However, anaerobic treatment especially offers very attractive prospects for developing countries because of its several merits such as high efficiency, cost-effective nature and simplicity in construction and operation [1], both in tropical and subtropical regions. Modern anaerobic processes have been successfully applied to the treatment of a large variety of industrial wastewaters [2] because of their several supplementary advantages. Advantages include high nutrient removal and retention of active sludge within the reactor, which enables good treatment performance at high organic loading rates. Natural turbulence caused by the influent flow and biogas production enhances wastewater biomass contact. In addition to the production of high grade biogas as an energy source, less reactor volume and space is required.

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The anaerobic process is performed in high-rate reactors like UASB, which is comprised of a tubular section (UASB column), gas-liquid-solid phase separator (settler), and effluent draw-off facilities. The tubular portion holds sludge biomass and the sludge bed acts as a digestion zone, which is generally in the form of granules generated by the self immobilization of bacteria. Granules differ widely in shape but are normally in spherical form. The presence of the settler on top of the digestion zone enables the system to maintain sludge mass in the UASB reactor, which improves the treatment efficiency of the system.

A disadvantage associated with the biological treatment system is that treated effluent usually needs further treatment in order to remove pathogens and, in some cases, to bring colour and COD levels of the final effluent within permissible limits.

All these features make the anaerobic treatment of wastewaters a very important field of research, where improvements and new developments are needed to overcome the problems. Combined with a proper post-treatment regiment, anaerobic treatment could provide a sustainable and appropriate option not only for developing countries but also for advanced countries. Post treatment can include advanced oxidation processes (AOPs) in addition to conventional methods.

Anaerobic Digestion Process

Anaerobic reactors present a unique ecosystem in which diverse groups of bacteria catalyze the conversion of complex organic compounds to methane and carbon dioxide in a highly controlled and coordinated fashion. Anaerobic degradation of organic matter is a complicated microbial process consisting of several interdependent consecutive and parallel reactions. Several groups of bacteria playing vital roles in anaerobic digestion include:

(i) fermentative bacteria,
(ii) hydrogen-producing acetogenic bacteria,
(iii) hydrogen consuming acetogenic bacteria,
(iv) carbon dioxide-reducing methanogens, and
(v) aceticlastic methanogens [3].

A schematic of anaerobic digestion process is presented in Fig. 1

Step (i) involves the degradation of large, complex, soluble, and insoluble molecules into smaller ones, indicating that proteins are converted via polypeptides to amino acids, carbohydrates are degraded to soluble sugars and lipids are transformed into long-chain fatty acids [4]. In step (ii), syntrophic acetogenic organisms in combination with hydrogen-utilizing methanogens convert the metabolic products from the first group mainly into acetate, hydrogen, and carbon dioxide. These syntrophic acetogenic bacteria can be grown and maintained in co-culture with methanogenic- and sulfate-reducing bacteria, since removal of hydrogen and acetate provide favorable conditions for their growth.

Methanogens utilize simple fermentation products (methanol, methylamines, carbon dioxide, hydrogen, and acetate) and aceticlastic methanogens disproportionate acetate into methane and carbon dioxide in the third and fourth steps. About 70% of the total methane produced in anaerobic digestion originates from acetate, thus acetotrophic methanogens perform important ecophysiological functions of carbon removal. The fifth step represents the completion of methanogenesis wherein unicarbonotrophic methanogens oxidize hydrogen gas and methanol as electron donors and reduce carbon dioxide.

Important Factors Affecting the Anaerobic Process

The anaerobic process appears to be a viable option for the treatment of industrial effluents [5] and domestic wastewater [3] because of its several advantages. Researchers [6]

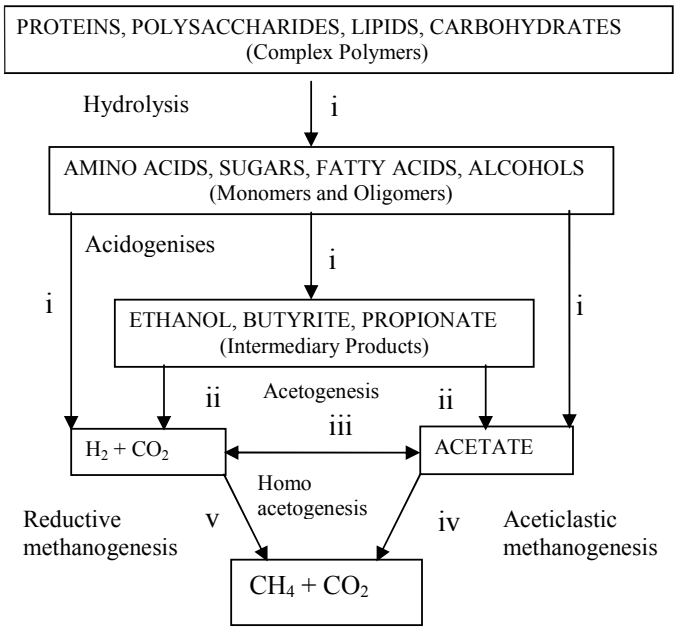

Fig. 1. Schematic presentation of the main steps in anaerobic digestion (adapted from Seghezzo, [3]).

demonstrate the ability of this technology to decolorize and mineralize wastewater to CH_4 without an additional carbon source.

The UASB technology also proved economically more attractive than facultative ponds and oxidation ditches for treating sewage both in tropical and subtropical countries [4, 7, 8]. However, a wide range of factors (process conditions) influence the performance of anaerobic digestion [9]. The important factors are temperature, pH, hydraulic retention time (HRT), organic loading rate (OLR), sludge granulation, phase separator design, seed sludge, sludge aging, degree of mixing, nutrient requirements, ammonia sulfide control, and the presence of toxic compounds in the influent [4].

The Influence of Temperature

The efficiency of the anaerobic process is highly dependent on reactor temperature. In accordance with Arrhenius expression, the temperature not only influences the rate of the process but also the extent of degradation [4, 10]. The rate of degradation of organics is enhanced at elevated temperatures (mesophilic conditions). The mesophilic temperature varies between 30-40ºC. However, the effect of temperature is mainly governed by various physical, chemical, and biological processes taking place in the reactor [10]. Agrawal et al. [2] found a 78% decrease in the gas production rate when the temperature was lowered from 27ºC to 10ºC, while van Lier and Lettinga [11] reported an increase in methane production with a gradual increase in temperature. A sharp drop in methane generation appears as the reactor temperature exceeds 45ºC because of bacterial decay at higher temperatures ranging from 45 to 65ºC.

The effect of temperature on the efficiency of the anaerobic process is governed by the reactor type as well. For example, efficiency of the UASB reactor is badly affected at low temperature, whereas the influence of temperature is not so pronounced in the case of the UASF reactor. A decline in UASB efficiency at low temperature can best be explained due to decreases in biological activity. The effect of temperature is marginal in the case of the UASF reactor because in addition to the biological activity, filtration and adsorption processes also contribute to the treatment. Consequently, its performance appears to be less sensitive to low temperatures [12].

pH

The pH of an anaerobic reactor in the range of 6.3-7.8 appears to be most favorable for methanogenesis [4]. While treating domestic sewage, pH remains in this range without adding any chemical because of buffering capacity of the acid base system in an anaerobic digester. The optimum pH range for all methanogenic bacteria is 6.0 to 8.0, but the most appropriate pH for the group on the whole is close to 7.0. On the other hand, acidogenic bacteria are less sensitive to pH variations so at lower pH acid fermentation may predominate over methanogenic activity [4]. Moreover, at lower pH (<6) methanogenesis of acetate is also inhibited, which results in the degradation of fatty acids (especially propionate). Thus, for the industrial effluents the system must contain adequate buffering capacity to neutralize the production of volatile acids and carbon dioxide.

Hydraulic Retention Time (HRT)

The HRT is defined as the amount of time for which the wastewater is retained in the reactor for digestion (treatment) and is computed by dividing the volume of the reactor by the influent flow rate [13]. The UASB reactor gives high COD removal at very short HRT. However, it is a function of effluent characteristics, which vary from industry to industry. Trnovec and Britz [14] reported COD removal efficiency higher than 90% at an optimum HRT of 10 h during the treatment of a carbohydrate-rich effluent of the canning industry with UASB reactor. Fang [15] investigated the affect of HRT on the acidogenesis of dairy wastewater at 37ºC and retention time ranging from 4 to 24 h, and reported an increase in the acidification (from 28 to 54%) by increasing HRT from 4 to 12 h. Ragen et al. [5] applied a pilot-scale UASB reactor to treat effluent (with an average OLR<6.7 kg COD/ m^3·d) of a sugar factory. The hydraulic retention time ranging between 4-6 h appeared to be optimal, resulting in COD removal of more than 76%. However, they attributed extremely low COD removal efficiency of the system at HRT of 2 h to the higher OLR (with average OLR above 11.5 kg COD/m^3·d).

Sludge Granulation

The success of the UASB reactor lies in the development of a dense sludge bed at the bottom of the reactor, where biological digestion mainly takes place. The sludge bed is basically formed due to the aggregation of suspended solids and bacterial population into flocs and granules, which minimizes washout of the sludge from the system. The granulation of sludge enables the treatment system to show good treatment performance at high organic loading rates. It also leads to the reduction in the reactor size, which renders the treatment system cost effective. Nevertheless, parameters like temperature and upflow velocity effect sludge granulation substantially [16]. Researchers [16] investigated the formation of sludge granulation at ambient temperatures (19-28ºC) and an upflow velocity (V_{up}) of 0.478 m/h. They observed spherical granules after one month of operation. The size of the granules increased up to 8 mm in diameter after a period of 9 months. According to Yasar et al. [17] for the treatment of combined industrial wastewater the steady increase in VSS/TS ratio is associated with the development of sludge granules. Beyond sludge age of 90 days, the increase in VSS/TS ratio is marginal, which leads to the conclusion that proper granulation of seed sludge (dairy plant waste activated sludge) requires a period of three months.

Upflow Velocity

Many investigations in the literature [7, 13, 18] report the influence of upflow velocity on the performance of

upflow reactors. Since upflow velocity influences the settling characteristics of sludge aggregates, it could be a restrictive factor for the design of the reactor depending upon the characteristics of the wastewater [7]. Upflow velocity influences the treatment system in two ways. Firstly, an increase in it can enhance the hydraulic shearing force, which triggers the detachment of the captured solids, resulting in a decline in the performance of the system. Secondly, an increase in the upflow velocity accelerates the collisions between suspended particles and the sludge. Consequently, it increases the efficiency of the system [13]. However, it is desirable that the upflow velocity be high enough in order to:

(i) provide good contact between substrate and biomass, and
(ii) disturb the gas pockets formed in the sludge bed since higher V_{up} facilitates the separation of gas bubbles from the surface of biomass [18].

Upflow velocity also influences the physical characters and specific activity of granules and a correlation exists between upflow velocity and size of the sludge granules. The effect of upflow velocity is more significant in operation of an upflow anaerobic reactor without gas-liquid-solid separator. The increase in upflow velocity demonstrates a significant decline in removal efficiency of the system.

Gas-Liquid-Solid Separator (GLSS) Design

For a well performing biological wastewater treatment system (UASB reactor), it is extremely essential:

(i) to ensure good contact between the incoming substrate and the sludge mass in the system, and
(ii) to maintain a large sludge mass in the system.

In order to qualify these conditions, the treatment system is equipped with a gas-liquid-solid separator (GLSS) in addition to a column and effluent draw-off facilities. The GLSS device also helps to improve the overall treatment efficiency of the reactor by dividing it into a settling zone (upper part) and a digestion zone (lower part). The wastewater is introduced uniformly through the bottom of the reactor; it passes through the sludge bed (digestion zone) and then enters into the settling zone. The enlarged part of the reactor causes substantial decrease in the upflow velocity, which in turn facilitates the flocculation of suspended sludge and enhances its settling. The mass of accumulated sludge on the slopes of phase separator gradually exceeds the frictional force and slides back into the digestion zone and supplements the digestion of the organic matter of incoming wastewater.

Various types (designs) of phase separators have been investigated for treatment efficiency [19]. The introduction of proper phase-separator design into the conventional UASB can significantly improve its treatment efficiency under comparable conditions [19]. According to El-Mitwalli [8], the addition of vertically oriented reticulated polyurethane foam sheets in the upper part of the UASB reactor offers relatively higher efficiency because the presence of foam sheets prevents sludge bed flotation. Cavalcanti [19] demonstrates that a UASB reactor having parallel plates along with a conventional phase separator can give better performance as compared with a reactor equipped with only a conventional phase separator because the addition of plates can enhance the settling of the suspended particles. The addition of gas-liquid-solid separator (GLSS) substantially improves the overall efficiency of the UASB reactor, and due to the proper designing of the phase separator, the overall removal efficiency of the reactor is not declined even at shorter HRT (3 h), and higher upflow velocities (45 cm/h). The contribution of the GLSS portion in overall reactor efficiency predominated up to HRT of 6 h. This could be explained by the fact that with the decrease in HRT, removal efficiency of the reactor portion decreases and in return results in an increase in the load of untreated particles (TSS) in the GLSS, which enabled GLSS to work in full swing furnishing maximum efficiency [17].

Post Treatments

An anaerobic upflow reactor does not prove to be so effective in colour and pathogen removal from treated wastewater within permissible limits. Therefore, post treatment seems to be essential to bring anaerobically treated effluent to the recommended quality. Post treatment techniques include conventional adsorption, stabilization [4, 19], rotating biological contactors, trickling filters, the down-flow hanging spong reactor [2, 20], activated sludge [21], a baffled pond system [21], dissolved air flotation, sequential batch reactors, submerged aerated biofilters, and reed bed systems. In addition to these systems, advanced oxidation processes (AOPs) are the emerging post treatment options. The main advantages of AOPs include a lack of byproducts of environmental concern, high process rate, and efficiency [22]. These treatment processes are considered very promising methods for the remediation of surface water and wastewaters containing non-biodegradable organic pollutants [23]. Post treatment involves the application of UV and AOPs (a schematic of chemical oxidation experimental set-up is presented in Fig. 2) in colour and COD removal and disinfection of wastewater. Post treatment is accomplished by UV and AOPs, including O_3, H_2O_2, UV/H_2O_2, Fe^{+2}/H_2O_2, and $UV/H_2O_2/Fe^{+2}$. According to Yasar et al. [24] all processes show good performance for the removal of colour and COD from the combined industrial biotreated (UASB) effluent. These systems are feasible to quickly remove both the parameters. AOPs (O_3, H_2O_2/UV, and $UV/H_2O_2/Fe^{+2}$) result in over 90% and 80% removal for colour and COD, respectively, UV, and Fe^{+2}/H_2O_2 results in slightly less colour removal of 76% and 68%, respectively, and COD removal 57% and 60%, respectively. Overall it can be said that the photo-Fenton process appears to be the most effective technology, whereas ozonation appears to be similar with proper optimal conditions for pH and temperature.

Application of AOPs in Colour and COD Removal

Ozone

Ozone has proved to be a powerful oxidizing agent and its oxidizing ability is owed to nascent oxygen atoms and hydroxyl radicals. It reacts, directly or indirectly, with complex compounds, breaking them into simpler and smaller molecules. For instance, chromophoric organic compounds (common in textile effluent) with conjugate double bonds are broken into smaller and simpler molecules by ozonation. The ozonation process minimally generates toxic byproducts and its prior application to wastes also enhances their biodegradation [25]. Consequently, no additional disposal problems are associated with the ozone treatment technique. However, process conditions like pH, temperature, initial dye concentration, ozone dose, and exposure time influence the performance of the ozonation process [26, 27].

At lower pH (acidic conditions) ozone exists in molecular state (O_3) and its decomposition into highly reactive species like $HO^{\bullet}$, $HO_2^{\bullet}$, and $HO_3^{\bullet}$ occurs in an alkaline environment [28]. Among these species, $HO^{\bullet}$ is an extremely important oxidant because its rate of attack is 10^6 to 10^9 times faster than that of reaction rate of molecular ozone. It has been demonstrated that ozone decomposition into secondary oxidants enhances at higher pH and the reaction between hydroxide ion and ozone leads to the formation of super-oxide anion radical O_2^- and hydroperoxyl radical $HO_2^{\bullet}$, which through various steps yields $HO^{\bullet}$ radical [26, 29]. It has also been shown that decolorization of dye solution is optimal at initial high pH [25].

The effectiveness of ozone treatment can be influenced by temperature as well. The influence of temperature on ozonation is the net result of two simultaneous effects such as increase in the rate constant of the reaction and the variation of ozone solubility with temperature. Due to an increase in temperature, ozone solubility decreases, which may cause a reduction in the amount of ozone available for the reaction. Consequently, an overall decrease in degradation occurs because of the low rate of reaction between ozone and organics ensues. In the temperature range of 5 to 20ºC, ozone efficiency increases as reaction rate increases with an increase in temperature while solubility is not much effected. However, the removal of COD is not affected significantly up to 40ºC because of compensation due to an increase in reaction rate. On the other hand, a decreasing trend appears beyond 50ºC because of a rapid decrease in solubility, causing depletion of the required supply of ozone [27]. According to Yasar et al. [30], ozonation shows best results for post treatment of anaerobically (UASB) treated effluent for colour and COD removal as compared to the pretreatment of combined industrial wastewater of the same nature. However, the efficiency of the ozonation process increases at elevated pH while temperature shows an adverse effect on removal efficiency as an increase in temperature (>30ºC) results in continuous decrease of colour and COD degradation.

Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is another strong oxidant found to be effective in the degradation of model compounds or in the treatment of real wastewaters requiring less stringent oxidation conditions. Hydrogen peroxide alone produces hydroxyl radicals when it is added to water or wastewater. However, a major problem encountered with its application alone for wastewater treatment is a low degradation rate. Nevertheless, Kos and Perkowski [22] report significant decolorization (up to 66%) of low concentration effluents due to H_2O_2 (depending on dose and exposure time). The dose appears to be important because H_2O_2 itself can act as an effective $OH^{\bullet}$ scavenger when used in excess amounts [31].

UV Light

UV light disrupts chemical bonds by providing necessary energy. When a chemical bond is cleaved by UV irradiation, the remaining fragmented by-products themselves can

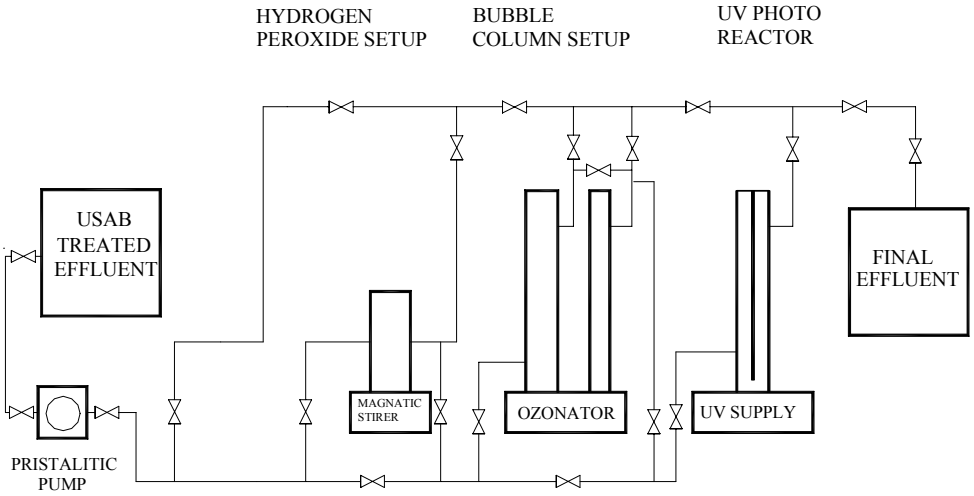

Fig. 2. A schematic of chemical oxidation experimental set-up.

degrade further or become excited and prone to oxidation. High efficiency UV lamps are required for necessary energy. However, the selection of UV lamp pressure and radiation intensity is a function of cost and required efficiency. UV light exposure time has an incremental effect on colour and COD removal. Colour reduction is also a function of initial dye concentration and is not significantly improved even by the use of a high-intensity lamp when dye concentrations are high.

H_2O_2/UV

The use of ultraviolet light in combination with hydrogen peroxide enhances the rate of generation of free radicals $OH^{\bullet}$ significantly. This occurs because UV light supplies energy required for the dissociation of H_2O_2 into hydroxyl radicals. The application of a UV/H_2O_2 system is advantageous in the sense that it can be performed at ambient conditions and produces little sludge.

Photolysis of aqueous hydrogen peroxide has been investigated by many researchers [32]. These investigations demonstrate that the UV/H_2O_2 process provides a powerful means for complete or partial oxidation of organic pollutants in aqueous media and has been found to be very effective in decolorization.

The H_2O_2/UV system also appears to be very effective in treating phenolic wastewater and effluents of oil refineries, shale oil processing units, pharmaceutical plants, and leachate [33].

Fenton and Photo-Fenton Processes

Fenton and photo-Fenton oxidation processes are effective for treating raw, coagulated, and bio-treated textile wastewaters. The photo-catalytic treatment process efficiency is significantly higher than the simple Fenton process for bio-treated wastewater as photo-Fenton provides almost complete colour removal and significant COD reduction [34].

The mechanism of Fenton's oxidation is based on the generation of hydroxyl radicals by the catalytic decomposition of the H_2O_2 in acidic media [35, 36]. Metal catalysts can either be Fe(II)/Fe(III) salts or chloride iron salt, though ferrous iron salt is preferred. In the presence of Fe(II), the peroxide breaks down into $OH^{\bullet}$ and OH^{-} species.The hydroxyl ($OH^{\bullet}$) radicals are very powerful and short-lived oxidant species. The reaction rate is limited by the rate of $OH^{\bullet}$ generation, which is directly related to the concentration of the iron catalyst. Several mechanisms for the reaction of hydroxyl radicals are possible. However, two mechanisms are most effective in the destruction of organic matter. An oxygen addition mechanism involves the addition of hydroxyl radical to the unsaturated compound to form free-radical as given in equation 1.

$$OH^{\bullet} + C_6H_6 \rightarrow C_6H_6\,(OH^{\bullet}) \quad (1)$$

Whereas the hydrogen abstraction mechanism generates an organic free radical and water as shown in equation 2.

$$OH^{\bullet} + CH_3\,OH^{\bullet} \rightarrow CH_2\,OH^{\bullet} + H_2O \quad (2)$$

In the photo-Fenton system, reaction rates are strongly increased by UV irradiation while during simple Fenton reaction, production of hydroxyl radicals ends when all the Fe^{3+} is extinguished [37].

The production of hydroxyl radicals is directly affected by the pH and predominates under acidic conditions. The low activity detected for high pH can be explained by the formation of $Fe(OH)_3$ [38]. Low pH is also essential for keeping ferric ion in solution. At pH less than 3, Fe(III) is in the solution; at pH greater than 3 and less than 5, Fe(III) is out of solution in colloidal form; and above pH5, it precipitates as $Fe_2O_3{\cdot}H_2O$.

Comparison of Electrical Energy Requirements for Chemical Oxidation

In the energy-intensive treatment processes, such as ozone, the Fenton and UV-induced photochemical processes (UV/H_2O_2, photo-Fenton) the key design variables, i.e. energy required by the system and order of magnitude of contaminant concentration removal can be combined into a single function called Electrical Energy per Order of Pollutant Removal. To ease up comparison of reaction efficiencies, a powerful scale-up parameter called EE/O (that is the electrical energy required to remove a pollutant by one order of magnitude in one m^3 of wastewater) can be computed by applying the following empirical relationship after Bolton et al. [39]

$$\mathrm{EE/O\ (kWh/m^3)} = \frac{P \times t \times 1{,}000}{V \times 60 \times \log\left(C_{inf}/C_{eff}\right)} \quad (3)$$

...where P (kW) is the power input, t is the oxidation time (in min.), V is the volume of the effluent sample (in liters) and C_{inf} and C_{eff} are the initial and final concentrations of the contaminant [24, 39, 40]. Energy calculations for the Fenton process is based on power input required by the stirrer while in case of ozonation, it is power required by the ozone generator, and for photochemical processes power input includes UV-lamp and stirring requirements.

Table 1. Comparison of electrical energy requirement by different processes for colour and COD removal [24].

Process	Colour		COD	
	EE/O	Removal (%)	EE/O	Removal (%)
Ozone	8	96	12.5	89
UV	160	79	295	57
UV/H_2O_2	86	91	120	82
Fenton Process	2.6	69	3.4	60
Photo-Fenton Process	6	100	11.8	97

Unit for EE/O is kWh/m^3.

It is apparent from Table 1 that the Fenton process requires less electrical energy for both colour and COD removal, but removal efficiency of the process is not convincing. Thus photo-Fenton proved itself the best option in terms of cost-effective wastewater treatment techniques. Ozone proved to be the second best option in terms of energy consumption and removal efficiency. It is also obvious that COD removal required more electrical energy than colour removal [24, 41].

Disinfection of Wastewater

The main objective of disinfection of bio-treated wastewater with advanced and conventional oxidation processes is to improve the final effluent quality by killing the pathogens including total *coliforms*, fecal *coliforms*, *E. coli*, fecal *streptococci*, and *enterococci*. As these pathogens are found in the gastrointestinal tract of humans and other warm-blooded animals, their presence in wastewater is evidence of contamination from domestic sewage. In addition, total coliform group may also indicate the effectiveness of the disinfectant and the re-growth potential of the damaged pathogens.

It is clear that the disinfection mechanism works in specific ways on biological cells.The disinfection may occur due to:

1. Damage to the cell wall of pathogens resulting in cell destruction.
2. Escape of vital nutrients (N_2, P) due to alteration of the selective permeability of the cell membrane.
3. Alteration of the colloidal nature of the protoplasm because of exposure to heat, radiation, and highly acidic or alkaline environments.
4. Oxidizing and altering the chemical arrangement and inactivation of enzymes.
5. Damage to DNA and RNA in a cell and retarding the organisms to reproduce.

Disinfection of wastewater is accomplished using a variety of oxidants including ozone, per aceticacid (PAA), hydrogen peroxide (H_2O_2), UV irradiation, and advanced oxidation processes (AOPs).

Ozone

Ozone is now commonly used for the disinfection of wastewater because of its very powerful oxidative characteristics owing to the decomposition of O_3 into nascent oxygen (O^-) and/or hydroxyl radicals [28]. It destroys bacteria, viruses, fungi, algae, and protozoa effectively. O_3 is effective in reducing bacterial pathogens (*Aeromonas salmonicida*, *Aeromonas liquifaciens*, *Pseudomonas fluorescens*, and *Yersinia ruckeri*) up to 99%, even in a system where the suspended and dissolved particles were present.

The efficacy of ozone is a function of several factors, including quality and quantity of dissolved and suspended matter in the wastewater, pH, bicarbonate level, total organic carbon content, and temperature. Higher pH could enhance the biocidal affect of ozone. Low alkalinity also enhances the effectiveness of ozone because the presence of bicarbonate and carbonate ions enhances the scavenging of the hydroxyl ions. Other factors include concentration of ozone and necessary contact time. The biocidal effects of ozone are enhanced as the concentration of ozone increases but above a certain value there would be no increase in the biocidal effect. The process optimization is vital because ozone is toxic to humans and residual ozone concentrations should be measured in the treated wastewater.

Per Acetic Acid (PAA)

Among the possible chemical alternatives, per acetic acid is reported to be promising because:

(i) it is neither toxic nor hazardous to handle,
(ii) it does not generate DBPs, and
(iii) it is equally effective in the presence of suspended solid content higher than tolerable limits for other disinfectants [42].

The addition of PAA into water yields acetic acid, hydrogen peroxide, and oxygen. Free radicals formed due to the decomposition of oxygen disrupt sulphydryl and sulfur bonds in proteins and enzymes in biological cells, alter the chemiosmotic function of the cell membrane, and oxidize the enzymes leading to impairment of cellular biochemical pathways. The bactericidal effectiveness of PAA treatment is a function of temperature and pH as well. High temperature enhances its efficacy. However, per aceticacid explodes at temperatures above 110ºC. An acidic environment also appears to be favorable for optimal antimicrobial activity [43]. The optimization of PAA dose is very important as different concentrations are required for biocidal affect of different species of bacteria. *Enterobacteriaceae* require lower doses as compared to *Staphylococcus aureus,* and *Candida parapsilosis*. Concentration has a close relationship with exposure time the effect of contact time is greater at lower dosages. The biocidal effect of PAA also depends on the genetic characteristics of the bacteria. It reacts differently with different bacteria. PAA has a moderate immediate effect on *E. coli* but substantial immediate effect on *Salmonella typhi* [44].

Hydrogen Peroxide (H_2O_2)

The action of H_2O_2 appears to be aggressive against anaerobic and gram-negative bacteria. The antimicrobial action of hydrogen peroxide is not only due to its oxidative properties as a molecule, but also because of other powerful oxidants such as nascent oxygen, superoxide radicals, and the hydroxyl radical. Among these radicals, hydroxyl radical production plays a predominant role in the toxicity of hydrogen peroxide. These reactive species cause irreversible damage to host cell components such as enzymes, membrane constituents, and DNA. According to Anzai et al. [44], hydroxyl radicals enhance the lipid oxidation as well as the ion permeability of membrane. They report a complete membrane breakdown at 17 minutes exposure to hydroxyl radicals.

Another important factor that demonstrates its biocidal effect, is medium of the treatment as liquid phase medium is proved to be efficient. Research studies [45] show excellent disinfection in the liquid phase of H_2O_2 as compared to the vapor phase. However, the disadvantages associated with the H_2O_2 process are a relatively long contact time and high concentrations of hydrogen peroxide.

UV Irradiation

UV technology is not new and its application for disinfection is well established in addition to AOPs. It has been applied with success for decades to disinfect effluents and surface water. UV inactivates microorganisms by damaging their nucleic acids and preventing the microorganisms from replicating. A microorganism that cannot replicate may not be dead but it cannot infect. UV radiation mainly acts physically on the nucleic acids of microorganisms through photochemical reactions, which mainly affect the pyrimidine bases of DNA.

The disinfection of water by UV light is a function of UV intensity, exposure time, and characteristics of the water to be disinfected [46]. Many constituents in water can absorb UV light, hence decreasing the average UV intensity. The most important is the presence of suspended solids, which not only absorb the UV light but also provide a shield to protect microorganisms from UV exposure. It is reported that large particles (about 50 μm diameters) influence the UV treatment substantially.

Kuo et al. [47] found a UV dose of 300 mJ/cm^2 to be sufficient to reduce total coliform concentrations to less than 2.2 MPN per 100 ml while treating the effluent of 53% UV transmittance from a high-purity oxygen-activated sludge plant. The cost of this treatment was estimated to be U.S. \$0.18/m^3 of water, which was comparable to conventional chlorination provided that the wastewater had a UV transmittance of not less than 53%.

Advantages of UV systems are enumerated in many studies [48]. Main advantages include compactness, easy operation, low maintenance, quick treatment, and above all production of no disinfection byproducts. However, a disadvantage of UV disinfection technique is that it does not produce residual protection and bacteria can be reactivated after a few days of disinfection [46].

Application of Combined Systems

The mechanism of action of combined AOPs is not so straightforward. The application of an O_3/UV system enhances the disinfecting characteristics of ozone significantly [49]. However, it is desirable that UV irradiation should follow ozonation because simultaneous application of UV and ozone retards the efficacy of ozone due to the decomposition of ozone to molecular oxygen.

During the treatment of effluent by an H_2O_2/UV system, UV irradiation followed by H_2O_2 produces two hydroxyl radicals that react with organic contaminants or undergo an H_2O_2 decomposition-formation cycle. This decomposition-formation cycle helps maintain nearly constant concentration of H_2O_2 during the treatment process [50]. However, an excessive H_2O_2 dose may hinder the penetration of hydroxyl radicals because of its character to scavenge hydroxyl radicals [46].

Researchers [51] find peroxone (O_3/H_2O_2) to be a far more effective disinfectant than ozone alone. The addition of hydrogen peroxide to ozone initiates the decomposition cycle of ozone and accelerates the generation mechanism of $OH^{\bullet}$ radicals. Glaze et al. [28] attribute disinfection mainly to the ozone decomposition mechanism as compared to H_2O_2. The use of O_3/H_2O_2 as disinfectant is also environmentally friendly because decomposition products of peroxone are non-toxic when introduced to food or the environment [43].

The efficiency of the O_3/H_2O_2 system is also a function of the peroxide:ozone ratio and a ratio above 1:1 would result in a decrease in disinfection rate [28]. H_2O_2/O_3 mass ratio in the range of 0.35-0.45 is considered optimal, whereas a ratio of 0.2 has also been found optimal, for the inactivation of gardia. Combined use of O_3 and H_2O_2 has a demerit as well. Since peroxide greatly decreases the ozone residual concentration, a much higher ozone dose is required to achieve the same residual effect.

Re-Growth of Pathogens

Re-growth is a phenomenon of repair capacity of biocells after some disinfection time. This phenomenon of repairing the damaged ribonucleic acids (DNA/RNA) involves two repair processes such as photoreactivation and dark repair mechanism [46]. The photoreactivation involves the cleaving of the nuclic acid dimers with the enzyme DNA photolyase. The enzyme first adsorbs the dimer and then cleaves it with the assistance of photons in the visible wavelength. The dark repair mechanism involves a multi-enzyme process in the absence of light, whereas an altered strand of DNA can serve as a copy for the damaged strain. This repair mechanism produces an original DNA [46].

Re-growth occurs due to the presence of nutrients required for microbial growth and the ineffectiveness of a disinfectant's residual and corrosion products of the storage or distribution systems. Besides, re-growth of microorganisms also depends on different seasonal variations of the storage or distribution systems. The risk of re-growth is even greater in the case of opportunistic pathogens (*Aeromonas hydrophil*, *Pseudomonas aeruginosa,* and *Salmonella*) after disinfection. There is a relationship between repair mechanisms and UV disinfectant doses. It is suggested that over-treatment (overdosing) could be an option to reduce re-growth [52]. According to Yasar et al. [53] disinfection of anaerobically (UASB) treated effluent can be carried out to eliminate the enteric pathogens by using UV irradiation, peracetic acid, H_2O_2, O_3, and advanced oxidation processes (O_3/H_2O_2, O_3/UV, and H_2O_2/UV). Re-growth potential of these pathogens depends

on time and temperature. Inactivation of pathogens by ozone at the rate of 300 mg/h for 20 minutes approaches 99%. UV irradiation results in 99% pathogen removal at irradiation time of 120 seconds. A dose of 170 mg/L H_2O_2 eliminated more than 99% of pathogens. Samples disinfected with UV, H_2O_2, and O_3 show gradual re-growth with an increase in time and temperature (from 20 to 35ºC). However, disinfection with AOPs prove to be the most effective tool, resulting in reduction of treatment time taken by individual processes. Also, the disinfected samples show minimal re-growth, revealing the superiority of their combined effects.

Conclusions

The following conclusions and suggestions can be drawn from this review paper.

1. The performance of a UASB reactor appears to be temperature-sensitive and under psychrophilic conditions the efficiency of the UASB system declines significantly. Nevertheless, a UASB reactor displays better efficiency at lower hydraulic retention time (3 h), which validates its inherent advantage over other anaerobic processes. The addition of a gas-liquid-solid separator (GLSS) improves the overall efficiency of the UASB reactor substantially.
2. For post treatment in terms of colour and COD removal of UASB-treated effluent, AOPs are highly efficient and feasible for removing both the parameters quickly. In view of the overall performance of the AOPs, it can be concluded that the photo-Fenton is the most effective technology, whereas ozonation appears to be similar under proper optimal conditions like pH and temperature.
3. Disinfection of UASB-treated effluent by UV irradiation, ozone, PAA, hydrogen peroxide, and combined treatments (O_3/H_2O_2, O_3/UV, and H_2O_2/UV) yields high rates of inactivation of pathogens. The optimal pathogen removal by ozonation depends on enhanced liquid-gas contact, resulting in better mass transfer. Hydrogen peroxide independently is the cheapest among the discussed processes. O_3/UV system proves highly effective in the inactivation of pathogens compared to independent application of O_3 and UV. UV efficiency is more pronounced when it follows ozonation.
4. There is comparatively early reactivation of microorganisms in disinfected water treated with O_3, H_2O_2, PAA, and UV. However, water samples disinfected with AOP systems like O_3/H_2O_2, O_3/UV, and H_2O_2/UV show little microbial reactivation, which could be attributed to the fact that the combined application of AOPs ensured nucleic acid damage beyond repair. Temperature appears to be the governing factor in microbial reactivation other than the residual concentration of the disinfectants. Due to the warm enteric nature of the observed microbes the high (%) of re-growth is possible at 35ºC as compared to 20ºC.
5. Electrical energy consumption comparison suggests that Fenton's reagent is an economically viable choice for partial colour and COD removal. However, for best results (more than 90% removal efficiency) the photo-Fenton is the most energy efficient. The electrical energy requirements of the tested processes followed the order UV/Fe/H_2O_2<O_3<UV/H_2O_2<UV.

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