Ozone treatment as an effective advanced oxidation process for the degradation of textile-dye effluents

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Ozone-oxidation or ozonation has tremendous scientific potential in treating wastewater. Some wastewater cannot be degraded by primary or secondary treatments. So the immediate need of tertiary treatment which includes ozonation or other advanced oxidation processes. The scientific endeavour of environmental engineering is surpassing one frontier over another. Research pursuit has proved ozonation to be of higher degradation or higher conversion of wastewater by ozone treatment. The hardship of research in this domain has found to be highly successful. Our research and review will open a new chapter in the knowledge of ozone-oxidation. Our vision is to present ozone-oxidation or other advanced oxidation processes to the scientific community in meticulous detail. Our effort has been tremendously successful and is fully experimentally proved.

Keywords: Ozone, Oxidation, Dye, Textile, Treatment

INTRODUCTION

The ever increasing world population with growing industrial demands has led to a situation where protection of the environment has become a major and critical issue and a crucial factor for several industrial processes, which will have to meet the requirements of the sustainable development of modern society. In order to correlate industrial activities with preservation of the environment (sustainable development), there is a tendency in most countries to adapt rigid environmental legislation where the well-known Green Technology plays a key role. In this context, chemical processes, where the best available technology (BAT) not entailing excessive cost and aspiring to performance without considerable impact, are preferred in substitution of the classical ones.

The environmentally friendly strategy minimises (or even eliminates) the use or generation of hazardous substances in the design, manufacture and application of chemical products. Approaches and principles of Green Chemistry were presented by researchers, who discussed the terms environmentally benign chemical syntheses, alternative pathways to prevent pollution and benign chemistry1. From the above considerations, it is clear that Environmental Chemistry plays a key role in monitoring and controlling the state of the environment, thus facilitating the discovery and development of environmentally attractive technologies and thus, “green products”1.

The objective and vision of this article is to present the role played by environmental and ozone chemistry in achieving environmentally friendly strategies and to discuss the potentialities of ozone application for several types of industrial wastewaters containing recalcitrant pollutants1.

Ozone application and their uses:
The application of ozone in drinking water treatment is widespread throughout the world11. The main reasons for the use of ozone are disinfection and oxidation (eg taste and odour control, decolouration, elimination of micro pollutants etc) or a combination of both. Similar to other disinfectants for water treatment (eg. chlorine and chlorine dioxide), ozone is unstable in water and undergoes reactions with water matrix components. However the unique feature of ozone is its decomposition into OH radicals which are the strongest oxidants in water. Therefore the assessment of ozonation processes always involves the two species-ozone and OH radicals11.

Dyes and their pollution:
Synthetic dyes are extensively used for textile dyeing, paper printing and colour photography and as additives in petroleum products. During the dying process, 10-15% of dye is discharged in the effluent. Approximately a half of all known dyes are azo dyes, making them the largest group of synthetic colourants. Azo dyes and their pigments are versatile and the most common synthetic colorants released into the environment. Approximately 10,000 different dyes and pigments are used for industries and over 7X10⁴ tons of these dyes are annually produced worldwide.

Dyes, their chemistry and their recurrent problem:
Today there are more than 10,000 dyes available commercially, most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin. The extensive use of dyes often poses pollution problems in the form of coloured wastewater discharge into environmental water bodies. Even small quantities of dyes can colour large water bodies, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. In addition, some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals, chlorides, etc, in their structure.

There are many kinds of dyes available in the market. Based on the chromophore group, 20-30 different groups of dyes can be discerned. Anthraquinone, pthalocyanine, triarylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of nitrogen-nitrogen double bonds and associated chromophores, are the largest class of dyes used in textile industry. A wide variety of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes take place inside the azo dyes. Between these, the most used are the reactive azo dyes combined with different types of reactive groups. They differ from all other classes of dyes in that they bind to the textile fibres such as...
of the different AOP-systems, such as, several different contaminated effluents, and the performance promising alternative technology in pollution control for advanced oxidation process in respect of which ozonation is treated by tertiary treatment-ozonation. So the need of sludge process while the tertiary treatment comprises of tertiary. Primary treatment comprises of coagulation and flocculation. Secondary treatment comprises of activated sludge process while the tertiary treatment comprises of ozonation and membrane filtration. Textile effluent dyes cannot be degraded by primary and secondary treatment. So it is treated by tertiary treatment-ozonation. So the need of advanced oxidation process in respect of which ozonation is very powerful.

Advanced oxidation processes, AOP:

Oxidation processes comprising the use of the hydroxyl radical, \( \text{HO}^\cdot \) as the main oxidant constitute the well-known Advanced Oxidation Processes (AOP). AOP are a promising alternative technology in pollution control for several different contaminated effluents, and the performance of the different AOP-systems, such as, \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2 \) (Fenton’s reagent), UV/Ozone, UV/TiO\(_2\) (heterogeneous photocatalysis), etc, has been discussed in the literature by several authors. A recent review dealing with alternative technologies for wastewater treatment involving application of several different AOP systems has been reported by Gogate and Pandit (2004). In the special case of AOP involving ozone application, literature reports have pointed out some considerations involved in wastewater treatment. For example, in the case of ozone-based systems (e.g. \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV} \)) it must be ensured that \( \text{O}_3 \) is not depleted during the course of the reaction, since \( \text{HO}_2'/\text{O}_2' \) radicals liberated in the various peroxyl radical reactions generate further HO radicals by the rapid reaction of \( \text{O}_3' \) with \( \text{O}_3 \). The \( \text{O}_3'/\text{H}_2\text{O}_2 \)-system is one of the most practical since it only involves hydrogen peroxide addition into an ozonated solution. In this case multistage injection systems are another recent invention, reported to yield much better results as compared to conventional operation. Apart from using reactors in series, the addition of hydrogen peroxide or ozone can be adjusted in increasing steps depending on the concentration of the remaining pollutants as well as the oxidation products.

As a rule, AOP efficiencies depend on the chemical nature of the effluent subjected to the treatment, such as, pH, turbidity, chemical oxygen demand (COD) and the presence of radical scavengers.

Ozone Science and Engineering: Strategies and Trends:

Costs associated with ozone production have dropped by 50% in the last decade and, therefore, a great number of new industrial applications has appeared in recent years. Potential markets for ozone technology exist especially in water treatment, surface sterilisation, wood pulp bleaching, materials processing, treatment of textile wastewater, and treatment of cooling water. An important aspect of ozone application in water treatment is its use as disinfectant in purified water loops for the pharmaceutical and electronic industries. Besides, it is worthwhile to mention that ozone application unlike that of chlorine does not leave harmful residues such as haloform after reaction. So, the environmental advantages of ozone over chlorine justify its higher cost of generation for an increasing number of applications.

Ozone is sparingly soluble in water (12 mg dm\(^{-3}\), 25 degree Celsius) and its behaviour in aqueous media can be evaluated by examining \( \text{O}_3 \)-decomposition kinetics. Once ozone enters into water, it becomes highly unstable and rapidly decomposes through a complex series of reactions. According to this mechanism hydroxide ions (\( \text{HO}^- \)) initiate a chain of reactions when ozone enters into water. The hydroxyl radical (HO\(^\cdot\)) is the most important species formed during ozone decomposition. Thus, ozone can react in an aqueous medium directly with substrates, such as molecular-ozone, or indirectly, via radical-intermediates formed during ozone decomposition in aqueous media. Thus, depending on the ozone behaviour in the aqueous medium, the selectivity of ozonation can be high (direct reaction) or low (indirect reaction).

Ozone application in water treatment: Water is the source of life and its availability is decreasing, thus making obvious the need for treatment of water resources. In the industrialised countries improvements in water treatment have led to a near eradication of acute health hazards caused by water-borne diseases. The first experiment on water disinfection via ozonation was carried by De Meritiens in 1886. Since then, there has been a great interest in the use of ozone as a viable alternative to chlorine in water disinfection in order to eliminate the formation of hazardous by-products, such as, trihalomethanes and organochlorine compounds. The production of drinking water requires the removal of numerous compounds (e.g. humic substances and toxic micro pollutants) and ozone acts by oxidising several drinking water contaminants, comprising different organic and inorganic compounds, as well for eliminating pathogenic micro-organisms (e.g. viruses, parasites).

According to the U.S. Environmental Protection Agency (EPA), ozone is the most powerful disinfectant available. The Safe Drinking Water Act of 1996 presents proposed rules for presence of disinfection by-products (DBPs), such as halocetic acids and tri halomethanes, which arise from disinfection of organic pollutants by chlorine and other halogens. Thus the elimination of DBP is the most desirable concern and therefore the use of ozone as an oxidant and disinfectant for the treatment of wastewater is gaining grounds.

Treatment of heavily contaminated effluents:

Textile wastewaters: Textile waste effluents are one of the wastewaters that are very difficult to treat satisfactorily because they are highly variable in composition and contain several different recalcitrant compounds. Wastewaters that are generated at various stages of the dyeing process differ in compositions and temperature. The high pollution load is mainly caused by spent dyeing baths. Their constituents are un-reacted dyeing compounds, dispersing agents (surfactants), salts and organics washed out of the material which undergoes dyeing. Based on the EPA’s toxic release
inventory, approximately 2200 tons of four hazardous dyes are discharged annually into publicly owned treatment works. The classical and versatile methods for treating wastewaters include various combinations of the biological (activated sludge), physical and chemical processes. Dye molecules are highly structured polymers, hence very difficult to breakdown biologically and cannot be treated efficiently by an activated sludge process or any combination of biological, chemical coagulation and physical methods. Besides, the main drawback of these processes is the generation of a large amount of sludge or solid waste, resulting in high operational costs for sludge treatment and disposal.

Different alternative technologies for textile wastewater treatment involving ozone application have been proposed in the literature. Ozone treatment stands above all other processes being totally sound environmentally. Combinations of these alternative technologies with the classical methods already mentioned permit obtaining a very good decolouration and COD reduction of the textile wastewater to meet discharge requirements.

In the special case of ozone application the ozonation efficiency depends on the total organic carbon present in the effluent. For low strength dye waste effluents, ozonation alone is sufficient to totally eliminate the colour and reduce the turbidity. However, for medium and high strength waste effluents, ozonation is found to be sufficient to reduce the colour, but not enough to reduce the turbidity. However, for medium and high strength waste effluents, ozonation is found to be sufficient to reduce the colour, but not enough to reduce the turbidity. Hence, coagulation of the textile effluent using aluminium sulphate or specially designed polymers will be necessary. As reported in literature, ozonation of the wastewater after coagulation-precipitation process, under the same conditions as the raw wastewater ozonation, exhibited more efficient decolouration (>90%) and COD reduction (>30%), while biodegradability was found to increase. After the initial degradation via alternative oxidation processes, the residual organic carbon generated during partial mineralization can be further effectively degraded using the activated sludge process. Thus, the combination of ozonation with proper chemical coagulation and an activated sludge process is a promising alternative technology for dealing with textile industry effluent, which reduces sludge disposal and meet the requirement.

Vision behind ozonation procedure:
Ozone treatment has tremendous potential both in research and in industry. Man’s scientific endeavours are ever-increasing and versatile. The future of research and development in the field of ozonation is wide and bright. It will have no parallels if the right approach is applied. Research is going on in a frantic pace and applications of ozonation in treatment of textile-dye effluents will not be an illusion in future.

Future vision of ozonation and future flow of thoughts:
Ozone—oxidation or other advanced oxidation processes are path breaking and visionary domains of environmental science and technology. Its endeavour is creating scientific wonders. Its application has found to be extremely effective and creating scientific frontiers of science. The future vision of ozonation is exemplary. Research hardship is opening up new innovations and new doors to the world of environmental engineering. Research work in the areas of ozonation of dye wastewater effluents has been found to be very effective and our future vision is to carry out intensively research in the degradation of different types of dyes. Our vision will open up a new dimension in environmental engineering.

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