**OZONE-OXIDATION ASSOCIATED WITH NANOFILTRATION AS A GROUNDBREAKING AND EFFICIENT PROCEDURE IN TREATING DYE EFFLUENTS FROM TEXTILE INDUSTRIES WITH THE HELP OF A BUBBLE COLUMN REACTOR: AN INSIGHTFUL AND FARSIGHTED REVIEW**

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**ABSTRACT**

Our review will describe and delineate in depth the difficulties and hurdles in these scientific processes. Persistent and recalcitrant chemicals in wastewater cannot be destroyed by primary and secondary wastewater treatments. So the urgent need of tertiary treatment processes such as ozonation or ozone-oxidation. Primary wastewater treatment encompasses flocculation and coagulation while secondary wastewater treatment comprises activated sludge process. Tertiary wastewater treatment process encompasses ozonation, membrane filtration and adsorption. The importance and vision of ozonation as an advanced oxidation process is due to the fact that ozonation process is environmental friendly. Our review and overview will delineate the research work done in the area of ozonation, primarily the ozonation of dye effluent in wastewater from textile industries and also nanofiltration of dyes. The ozone-oxidation method is known to be effective for decomposing organic chemicals containing carbon-carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon-nitrogen double bonds, carbon-hydrogen bonds, silicon-hydrogen and carbon-metal bonds. Some visionary and exemplary work has been done in the ozonation of reactive dyes in the wastewater effluent of textile industries. Synthetic dyes released to the environment in the form of effluents by textile, leather and printing industries cause severe ecological and environmental damages. These dyes include several structural varieties of dyes such as acidic, reactive, basic, azo, diazo, anthraquinone based and metal complex dyes. Due to the inhibitory nature of many compounds for biological oxidation, the need for pretreatment by Advanced Oxidation Process(AOP) has become essential. One of the AOP processes is ozonation or ozone-oxidation, which is versatile, wilfull and environmentally powerful. Ozonation of water is a well known visionary technology and the strong oxidative properties of O$_3$ and its ability to effectively oxidise many organic compounds in aqueous solution have been well documented and well researched. In recent years, ozonation is emerging as a potential process for color removal of dyes, since the chromophore groups with conjugated double bonds, which are responsible for color can be broken down by ozone either directly or indirectly forming smaller molecules, thereby decreasing the colour of effluents. Due to its high electrochemical potential (2.08 V), O$_3$ is the strongest oxidant available and applicable as compared to H$_2$O$_2$(1.78 V) and can react with several classes of compounds through direct or indirect reaction. Nanofiltration is very effective and the next generation science and technology. Our aim, objective and vision is to delineate and describe the major research work done in the field of ozonation in order to project it as a powerful advanced oxidation process and also describe significant work done in the field of nanofiltration of dyes. The vision of a scientist is wide and unparalleled. Our research hardship will lead us to new frontiers of science and technology. Nanofiltration and ozone-oxidation will open up new vistas in the areas of environmental science and technology.

**Key Words:** Persistent, Ozonation, Textile, Dyes, Oxidation, Tertiary Treatment, Primary treatment, Azo, Anthraquinone, Nanofiltration
INTRODUCTION

A wide variety of organic compounds discharged and let out into the environment mostly through industrial effluents, result in serious threat for humans and aquatic life due to their toxic nature. There is a continuing and persistent need for the research pursuit of efficient, effective and cost-effective technologies for dangerous and hazardous organic contaminants such as phenol, benzene, polychlorinated biphenyls etc from groundwater and wastewater. Conventional and traditional methods for water remediation/treatment, including bio treatment, carbon adsorption, air stripping, pure ozone oxidation and chlorine treatment, suffer from various limitations. For example, treatment based on aerobic and anaerobic digestion tends to be very large due to the slow rate of the biological reaction. Furthermore, wastewater treatment methods based on physical processes such as reverse osmosis and adsorption on activated carbon are non-destructive and merely transfer the pollutants to the other media, thus causing secondary waste. Chemical methods such as chlorine or pure ozone oxidation have been also shown as limited. Chlorine oxidation produces carcinogenic halogenated hydrocarbons while pure ozone oxidation is limited by high selectivity and slow kinetics.

A number of alternative technologies, so called Advanced Oxidation Processes (AOPs) are considered to be promising methods for the treatment of hazardous toxic organic pollutants in aqueous solutions. AOPs involve the generation of hydroxyl radicals, highly reactive and unselective species, in sufficient quantities to oxidise the majority of organics preset in the effluent water. Common AOPs could be broadly classified into chemical, eg O₃ and/or H₂O₂, photochemical and photo catalytic, eg. UV/oxidant or UV/photo catalyst, mechanical, e.g ultrasonic and electrical eg corona discharge. Treatment of organic compounds by O₃ or H₂O₂ are possible throughout two different pathways, direct and indirect. Direct ozonation involves degradation of organics by ozone molecule under acidic conditions, while the term indirect ozonation consider degradation mechanism of organics throughout hydroxyl radicals and it occurs under basic conditions.

MATERIAL AND METHODS

Review of research work done in the domain of ozonation of dye

It delineated the treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. The degradation of the compounds present in a previously chlorinated wastewater resulting from the production of azoic dyes has been studied in this project. Towards this end, the first step developed was the characterization of the spillage water by GC/MS and GC/FID. Secondly, a combined ozone + Ca (OH)₂ treatment was carried out, determining its efficiency on this wastewater. It dealt with the advanced oxidation process of ozonation of dye and its kinetics. A quantitative estimation of direct ozonation and indirect free radical oxidation of dyes with assorted chromophores was studied through the examination of reaction kinetics in the ozonation procedure. The reaction kinetics of dye ozonation under different conditions was determined by adjusting the ozone doses, dye concentration and reaction pH. According to their research, the ozonation of dyes was found dominant by pseudo-first order reaction and the rate constants decreased as the dye/ozone ratio increased.

They made a quantitative prediction of direct and indirect dye ozonation kinetics. It studied on the treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. Two different oxidation treatments, ozonation and electroflocculation, were experimented on a pilot scale to test their efficiency in removing polluting substances from wastewaters of textile industries. Both pilot plants used reproduced very closely a full-scale treatment in order to obtain indications about the feasibility of a transfer on industrial scale. By means of ozone treatment very high colour removal (95-99%) was achieved and treated waters were reused satisfactorily in dyeing even with light colours. It delineated on the topic of colour removal from a simulated dye wastewater using a two-phase anaerobic packed bed reactor. According to them the treatment alternatives applicable for the removal of colour vary depending upon the type of dye wastewater. A synthetic simulated mixed dye waste (Basuc
Yellow 28, Basic Yellow 21, Basic Red 18.1, Basic Violet Red 16, Basic Red 46, Basic Blue 16, Basic Blue 41) representing a known waste from a fibre production factory, was investigated. The biological process of anaerobic digestion has been recognised as a simple and energy-efficient means of treating and stabilising a wide range of organic industrial wastewaters. Their study sets out to demonstrate the effect of different loading rates, dye concentrations and hydraulic retention times (HRTs) on colour removal efficiency under mesophilic anaerobic conditions. It studied the ozonation of aqueous azo dye in a semi-batch reactor. Results showed that the rate of ozone transfer increased with increases in the initial dye concentration, the applied ozone dose and temperature. A model was developed to predict the enhancement factor of ozone mass transfer. This model which they developed enables the prediction of mass transfer coefficient of ozone from the following parameters: initial dye concentration, applied ozone dose, temperature and concentration of dissolved in the organic-free water. The present model was also valid for reactors of larger sizes. The results of kinetic studies showed that ozonation of the azo dye was a pseudo-first-order reaction with respect of dye. The apparent rate constant increased with the applied ozone dose and temperature. In addition, ozonation reduced chemical oxygen demand and enhanced the biodegradability of the wastewater. In devised a dynamic model of ozone contacting process with oxygen mass transfer in bubble columns. The dynamic process of the dissolution of ozone in a countercurrent bubble column is studied for model establishment. It studied the ozone treatment of textile effluents and dyes projecting the effect of applied ozone dose, pH and dye concentration. The ozonation of wastewater supplied from a treatment plant (Samples A and B) and dye-bath effluent (Sample C) from a dyeing and finishing mill and acid dye solutions in a semi-batch reactor has been examined to explore the impact of ozone dose, pH and initial dye concentration. Results revealed that the apparent rate constants were raised with increases in applied ozone dose and pH, and decreases in initial dye concentration. While the colour removal efficiencies of both wastewater Samples A and C for 15 min ozonation at high ozone dosage were 95 and 97% respectively, these were 81 and 87% respectively at low ozone dosage. It investigated the decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor. Their study comprises decolorization of wastewater containing direct dye (Isma Fast Red 8B) by ozonation and envisioned in an attempt to abate pollution caused by textile dyeing houses and dye-producing plants. The decolorization process of the direct dye was carried out by bubbling ozone at the bottom of a bubble column reactor containing the dye solution. The effect of dye concentration, ozone dose, ozone air flow rate and solution pH on the rate of decolorization was studied. It gave an insight and a detailed description of the influence of parameters like pH and oxidation reduction potential on the ozonation of dyes. It explained the importance of fixed bed on the ozonation of dyes thus delineating the importance of surface area of bed.

RESULTS AND DISCUSSION

Nanofiltration, its vision and insightful aim

Nanofiltration can be positioned between reverse osmosis and ultrafiltration. Nanofiltration is essentially a lower pressure version membrane where the purity of permeate water is less important. This process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness elements such as calcium or magnesium together with bacteria, viruses and colour. Nanofiltration is preferred when permeate with TDS but without colour, COD and hardness is acceptable. Feed water to nanofiltration should be of similar qualities as in case of reverse osmosis. Turbidity and colloids should be low. Disinfection of feed may also be necessary to remove micro-organism. The filtration spectrum indicating size and weight of molecules, operating pressure etc in respect of reverse osmosis, ultrafiltration and nanofiltration is shown in Table 1.
Scientific research advances in the area of nanofiltration of dyes

The textile industry uses enormous quantities of water which in many cases are disposed to the environment with inadequate treatment. The effluent contains high salts and organic concentration and they are therefore difficult to be treated. In this work the effluents from the cotton textile industry was treated by nano-filtration membrane in order to reduce the quantity of the disposed water and at the same time to reuse the treated water\textsuperscript{12}. An excellent performance for the TRISEP(4040-XN-TSF) nano-filtration membrane was found by these researchers. They reduced the total salt concentration by more than 70%.

It integrated nano-filtration and biological processes for textile wastewater treatment\textsuperscript{13}. The implementation of the biological anaerobic-aerobic system in separated reactors to the nano-filtration concentrate treatment was presented. The concentrate was obtained during the nano-filtration of the textile wastewater containing azo-dye Reactive Red 120. The experiments were conducted on the wastewater concentrated from 2 to 10 times. The goal of this research work was to present the implementation of the anaerobic-aerobic system in the separated reactors (two sludge system). A review on textile technology in cotton textile processing and its waste generation and effluent treatment was done\textsuperscript{14}. This review discusses cotton textile processing and methods of treating effluent in the textile industry. Industrial textile processing comprises pre-treatment, dyeing, printing and finishing operations. These production processes not only consume large amounts of energy and water, but they also produce substantial waste products.

This manuscript combines a discussion of waste production from textile processes such as desizing, mercerizing, bleaching, dyeing, finishing and printing with a discussion of advanced methods of effluent treatment such as electro-oxidation, bio-treatment, photochemical and membrane processes.

An efficiency evaluation of textile basic dye removal from water by nano-filtration was done\textsuperscript{15}. The aim of the present research was to study the efficiency of textile dyes removal by a commercial nano-filter NF90(Dow-Film Tec). Dye rejection was studied using basic dye with its relevant additive.

Treatment of textile plant effluent by ultra-filtration and/or nano-filtration for water use was researched by some scientists\textsuperscript{16}. The textile wastewater treatment by membrane processes presents some limitations such as membrane fouling which causes a rapid flux decline. In fact, the membrane processes efficiency can be effected by membrane pore blocking or/and cake formation. In order to limit the effect of membrane fouling caused by plugging particles in textile effluent, a combination between two membrane processes was studied. The ultrafiltration was used as pre-treatment for Nano-Filtration (NF) process.

Research endeavour in the area of review work of nanofiltration and ozonation

It dealt with a review work in the domain of progress in membrane science and technology for seawater desalination\textsuperscript{17}. The research work comprised of the development of membranes and membrane processes for water production in general and seawater desalination in particular. The review highlights some new trends observable in the four areas: membrane development, membrane characterization, membrane transport and membrane system design. It described the review work in the area of solution-diffusion.
model. The solution - diffusion model has emerged over the past 20 years as the most widely accepted explanation in membrane transport. It dealt with the review of ceramic ultrafiltration and nanofiltration membranes for oilfield produced water treatment. Their vision was a mini review. It described the reaction products of ozone in a detailed review. Lot of review work was done in the area of ozonation or ozone-oxidation. One visionary paper was done in the domain of removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes.

Experimentation done in the field of ozonation of dyes

Detailed experiments are done in the field of dye ozonation in a simple bubble column reactor and a fixed bed bubble column reactor. Fixed bed showed increased conversion of dyes than simple dye ozonation. The conversion of dyes also shows dependence on pH and oxidation-reduction potential of the dyes.

Vision of integration of both nanofiltration and ozone-oxidation

Nanofiltration and ozone-oxidation both show higher degree of conversion in the degradation of dyes. So our next vision is to integrate both ozonation and nanofiltration. It can itself create new frontiers in the era of science and technology. Dye degradation studies will witness new vision and new hope in the domain of textile engineering and environmental engineering. Integration of both these processes and subsequent research hardship can usher a new potential and a new domain of science and technology.

Future objectives in the domain of ozonation and nanofiltration

Both nano-filtration and ozonation (advanced oxidation processes) are ground breaking thrust areas of environmental science and environmental engineering. Our future aim is to merge these two processes to increase the dye degradation and removal. Nano-filtration and ozonation of different types of dyes both azo as well as anthraquinone dyes will be our sole future objective and vision. The kinetics of Nano-filtration will be devised, investigated and studied in detail. Waste minimization is of great importance in decreasing pollution load and production costs. From published results it can be deduced that both these processes can increase the dye degradation. It is a hidden area of science and is still immature. It is innovative as well as effective and will open up a new age of dye degradation science and technology.

CONCLUSION

Future vision of nanofiltration and ozonation and future flow of innovative thoughts

Nanofiltration and ozone-oxidation are surpassing one frontier over another in the area of environmental science and technology. A scientist's vision should be innovative and pathbreaking. In that respect, perspectives in these two areas are far reaching. Waste water treatment will usher in a new era if the application areas of nanofiltration and ozonation are effective and efficient. The vision and objective of ozone-oxidation or nanofiltration is to find its application in the far and wide areas of different types of dyes. Intense research is pursued with zeal and intuition in every environmental research institutions throughout the world. The world of unknown opens up a new chapter in the history of applications of environmental engineering. Future flow of thoughts is towards more range of anthraquinone and azo dyes. Innovation has no boundaries. So our vision and objective is to unravel all the hidden domains of environmental engineering science.

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