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# AN OVERVIEW OF OZONATION ASSOCIATED WITH NANOFILTRATION AS AN EFFECTIVE PROCEDURE IN TREATING DYE EFFLUENTS FROM TEXTILE INDUSTRIES WITH THE HELP OF A BUBBLE COLUMN REACTOR

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## ABSTRACT

Recalcitrant chemicals in wastewater cannot be degraded by primary and secondary treatments. So the need of tertiary treatment processes such as ozonation. Primary treatment comprises flocculation and coagulation while secondary treatment comprises activated sludge process or filtration through trickling filters. Tertiary treatment process comprises ozonation, membrane filtration, adsorption and other advanced oxidation processes. The importance of ozonation as an advanced oxidation process is due to the fact that ozonation process is environmental friendly and sound. Our review will delineate the research work done in the area of ozonation and nanofiltration, primarily the ozonation of dye effluent in wastewater from textile industries. The ozone method is known to be effective for decomposing organic chemicals containing carbon-carbon double bonds, olefenic 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 work has been done in the ozonation of reactive dyes in the wastewater effluent of textile industries. Synthetic dyes and pigments released to the environment in the form of effluents by textile, leather and printing industries cause severe ecological damages. These dyes include several structural varieties of dyes such as acidic, reactive, basic, azo, diazo, anthraquinone based and metal complex dyes. Neither simple chemical nor biological treatment alone has proved adequate in decolorization and sufficient depletion of inorganic matter. 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, which is versatile and environmentally powerful. Ozonation of water is a well known 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. Ozone treatment of several types of wastewater has resulted in considerable COD reduction and has been used for treatment of dyes, phenols, pesticides etc. In recent years, ozonation is

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emerging as a potential process for color removal of dyes, since the chromophore groups with conjugated double bonds, which are responsible for colour 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 $H_2O_2$ (1.78 V) and can react with several classes of compounds through direct or indirect reaction. Unlike other oxidising agents such as $Cl_2$, oxidation with $O_3$ leaves no toxic residues that have to be removed or disposed. Studies carried out by several scientists show that ozone generally produces non-toxic end products which are converted to $CO_2$ and $H_2O$ depending on the conditions.Nanofiltration is very effective and the next generation science and technology. Our aim, objective and vision is to delineate 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.

**Key words**: Persistent, Ozonation, Textile, Dyes, Oxidation, Tertiary treatment, Nanofiltration.

## INTRODUCTION

Different types of organic compounds discharged into the environment mostly through industrial effluents, result in serious danger for humans and aquatic life due to their toxic nature. There is a continuing need for the research and development of efficient and cost-effective technologies for dangerous and hazardous organic contaminants such as phenol, benzene, polychlorinated biphenyls etc. from groundwater and wastewater. Conventional methods for water remediation, 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, e. g. $O_3$ and/or $H_2O_2$, photochemical and photocatalytic, e g. UV/oxidant or UV/photo catalyst, mechanical, e g ultrasonic and electrical eg corona discharge. Treatment of organic compounds by $O_3$ or $H_2O_2$ 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.

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

Sarasa et al.[1] 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. Chu et al.[2] 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. Ciardelli et al.[3] studied 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. Talarposhti et al.[4] 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. Wu et al.[5] 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 2002, Chen et al.[6] 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. Sevimli et al.[7] 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. Koch et al.[8] delineated the ozonation of hydrolyzed azo dye reactive yellow 84 (CI).

The combination of chemical and biological water treatment processes is a promising technique to reduce recalcitrant wastewater loads. The yardsticks to the efficiency of such a system is a better understanding of the mechanisms involved during the degradation process. According to a conclusion of their research, for textile mill effluents, ozonation can achieve high colour removal, enhance biodegradability, destroy phenols and reduce the chemical oxygen demand (COD). Their work deals with the degradation of hydrolyzed Reactive Yellow 84 (colour index), a widely used azo dye in textile finishing processes with two monochlorotriazine anchor groups. The ozonation of the hydrolyzed dye in ultra pure water was performed in a laboratory scale cylindrical batch reactor. Rittman et al.[9] did pilot studies and interpreted models from the treatment of a coloured groundwater by ozone-biofiltration. Pilot studies investigated the fates of colour, dissolved organic carbon (DOC), and biodegradable organic matter (BOM) by the tandem of ozone plus bio-filtration for treating a source water having significant colour (50 cu) and DOC 93.2 mg/L). Transferred ozone doses were from 1.0 to 1.8 g $O_3$/g C. Rapid bio-filters used sand, anthracite or granular activated carbon as media with empty-bed contact time (EBCT) up to 9 minutes. The pilot studies demonstrated that ozonation plus bio filtration removed most colour and substantial DOC and increasing the transferred ozone dose enhanced the removals. A. H. Konsowa[10] 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.

## Scientific research pursuit 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[11]. 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%.

Pazdizor et al.[12] integrated nano-filtration and biological processes for textile wastewater treatment. 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 by Babu et al.[13] 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 by Torabion et al.[14] 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[15]. 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[16]. 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[17,18].

## 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[19,20]. Fixed bed showed increased conversion of dyes. The conversion of dyes also shows dependence on pH and oxidation-reduction potential of the dyes.

## Future objectives and future vision

Both nano-filtration and ozonation (advanced oxidation processes) are ground breaking associated with visionary thrust areas of environmental science and environmental engineering. Our future vision and objective is to merge these two processes to increase the dye degradation. Nano-filtration of different types of dyes both azo as well as anthraquinone dyes will be our sole future objective. 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 an unknown and latent area of science. It is innovative as well as effective and will open up a new era of optimism in dye degradation science and technology.

## Vision of ozonation and nanofiltration

Both ozonation and nanofiltration are far reaching domains of environmental engineering. Continuous research pursuit has brought them to the forefront of scientific community. It can creat wonders in the field of textile-dye wastewater treatment. It is a burning problem for textile industries. Man's as well as scientist's vision is expanded and envisioned by the wonders of the science of environmental engineering. Both the processes have shown to have higher conversion values by research pursuits. Research hardship will open up a new and innovative area of science and engineering.

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