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COLOUR REMOVAL TECHNOLOGY USING OZONE IN TEXTILE INDUSTRIAL WASTEWATER EFFLUENT: AN OVERVIEW

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ABSTRACT
The elimination of pollutants from waste water is a serious challenge that needs to be addressed. The conventional treatment process has limitation of not completely removing colour from wastewater. Oxidation with ozone proves to be one of the most efficient methods of treatment of colored aqueous effluent from textile industries. The study highlights the importance of ozone in colour removal technology. Ozone is one of the most powerful and commercially available oxidants and is commonly used for municipal water and wastewater treatment. In addition to its oxidizing capabilities, it is an environmentally friendly method of treatment. Pollutants, colored substances, odors and microorganisms are directly destroyed by oxidation, without creating harmful chlorinated by-products or significant residues. The overview revealed that ozone reacts quickly with a large number of compounds and these compounds are attacked either directly by the ozone molecule or indirectly by the intermediately occurring hydroxyl radicals.
Keywords: Ozone; textile, colour, wastewater, effluent

INTRODUCTION
In recent years the treatment of coloured aqueous effluent streams from industry has attracted the attention of environmentalists and entrepreneurs. Coloured wastewater not only affects the aesthetic merit and water transparency of receiving water bodies, but there are also environmental concerns about the possible toxicity and carcinogenicity of some organic dye. Various techniques for removing dyes from the wastewater have been developed, including flocculation, coagulation, adsorption, reverse osmosis, and chemical oxidation (Park et al. 2001). Although these techniques have colour removal capabilities, their popularity in application is limited by disadvantages such as significant sludge production, adsorbent regeneration, membrane fouling, and high cost. The public demand for colour-free waste discharge to receiving water body and the tougher colour standards have made decolourization of a variety of industrial wastes a top priority. Unfortunately, with the complicated colour-causing compounds, the decolourization of these wastes is a difficult and challenging task. At present, large amounts of highly colour wastewater are discharged from textile, printing, paper, and leather industries in which they use many kinds of artificial composite dyes. These dye-containing industrial wastewaters discharged into nearby streams and river especially in developing countries which constitutes one of the major sources of water pollution. Colour waters are objectionable on aesthetic grounds for drinking and other agricultural purposes. Colour affects the nature of the water, inhibits sunlight penetration into the stream, and reduces the photosynthetic action. In addition, some dyes are either toxic or mutagenic and carcinogenic and these wastes must be treated prior to discharge in order to comply with the environmental protection laws for the receiving waters.
In the past years, several investigations have been carried out to explore the treatment operations of colour wastewater, such as biological treatment. However, the conventional biological treatment processes frequently used to treat textile effluents are generally efficient for biochemical oxygen demand (BOD) and suspended solids (SS) removal, and are largely ineffective for removing colour from the waste

water , due to most dyes are stable to light and oxidation. Thus, treated waste effluents may contain appreciable amounts of colour when discharged. The treatment technologies recommended meeting colour removal requirements are physical–chemical treatment operations, including adsorption, chlorination and chemical precipitation. Each has its merits and limitations in application. In the decolourisation process by chemical precipitation, the coagulant is used and produces flocs together with dye stuffs. The flocs are then separated from the aqueous solution by means of physical sedimentation. The well-known conventional coagulants such as alum, PAC, $FeSO_4$ and lime are widely used in the industrial wastewater treatment. In recent years, the study on magnesium salts ($MgCl_2$) has been used on the removal of colour from textile waste effluents. Comparing with those conventional chemical coagulants, the $MgCl_2$ has shown to be an effective alternative and can enhance removal efficiency of impurities or pollutants in the treatment of wastewater. In addition, one of the most attractive characteristics of $MgCl_2$ is recycled through the process. This recoverability may significantly reduce the chemical costs and especially may reduce the pollution. The adsorption process is another attractive alternative treatment process if the adsorbent is inexpensive and readily available. Activate carbon is the most powerful and common adsorbent and has been used successfully. But the high cost in the preparation of activated carbon restricts its use in the industrial wastewater treatment.

In recent years, many studies have been conducted on the non-conventional and economic adsorbents, especially those researches on making use of industrial solid waste (Pena et al 2003; Park et al. 2001). Using an industrial solid waste for the treatment of wastewaters from another industry could be helpful not only to the economy, but also to solve the solid waste disposal problem. Red mud is a solid waste residue formed after the caustic digestion of bauxite ores during the production of aluminium. For every ton of aluminium produced, approximately one to two tons (dry weight) of bauxite residues are generated. Each year, about 90 million tons of red mud is produced globally and nearly 20 million tons of red muds are created annually in China. Red mud is a highly alkaline waste material with pH 10–12.5 (Paraskara et al 1998). Due to the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment and proper disposal of waste. In the past years, several investigations have been carried out to explore the applicability of red mud for dye removal from wastewater. Utilization of industrial wastes for another waste treatment produces many benefits in terms of economy and environment.

The major pollutants in textile wastewater are higher suspended solids, total organic compound (TOC), colour, and other soluble substances. The release of these coloured wastewaters into the environment is a considerable source of non-aesthetic pollution and eutrophication parathion of crystal. Investigated foam separation of the reactive dyestuffs from simulated and industrial textile effluents. The residual dye content could be lower than the limit of 300 American Dyestuff Manufacturer's Institute units (ADMI). Although the previous studies demonstrated that foam separation could remove dyes effectively, most focused on ideal single dye solutions or laboratory simulated wastewater. There were few reports on the use of this technique for the removal of dyes from actual textile wastewater. Consequently, it is worthwhile to assess whether foam separation is useful to treat genuine process-generated effluent. Foam separation, however, cannot be used directly to remove dyes from wastewater because textile wastewater alone cannot produce stable foam when aerated. Direct dyes can be classified as anionic dyes. They carry negative charges in aqueous solutions due to the presence of sulfonate ($SO3^-$) groups. Therefore, CTAB was chosen as a surfactant in order to produce stable foam and to promote the formation of dye–surfactant complexes by electrostatic interactions.

In recent years, the colour of the effluent discharged into receiving waters has become a serious environmental problem. The discharge of woolen, carpet, pulp, paper and textile effluents often imparts colour to the receiving waters for miles downstream from the source. The colour is aesthetically objectionable and it also reduces light penetration into water decreasing the efficiency of photosynthesis in aquatic plants, thereby, having adverse impact on their growth. In addition, some of the dyes might be toxic to some organisms. The effect of various operating parameters such as adsorbent dose, concentration of dye, pH, temperature, particle size, adsorption dynamics and thermodynamic parameters were studied for various dyes. Characterization of the adsorbent by scanning electron micrographic method was also undertaken. The micrograph of the Neem sawdust represents typical lateral rack type of structure giving rise to the formation of different steps on the surface which will provide more surface area for adsorption. The step and lateral racks are very distinct in the micrographs.

Ozone and Colour Removal Technology

Many wastewater and textile processors are gradually substituting chlorine with ozone. Ozone is a powerful oxidizing mean and safer in use in comparison with other oxidizing agent. Water is shown coluor when visible radiation is absorbed from dissolved materials, or when light is reflected on suspended solids (Heerbest 1994). These two sources of colour are the base for the distinction between the pseudo and true colour. The pseudo colour is due to absorption as well as light reflection. The true colour depends exclusively from the kind and quantity of the dissolved substances. Particles with a size of 400-800 nm that means within the wave length of visible light are responsible for light reflection. It is possible with filtering (membrane 0.45 μm) the phenomenon of reflection to be eliminated. It must also be noted that the difference between the pseudo and true colour is related to water's turbidity.

The units Pt–Co (USA), or mg Pt-Co / l (Europe) are defined as colour measurement units. These units are considered equivalent. The acceptable limits of colour values for the disposal of treated wastewater ranges from 50-100 units Pt-Co, depending on the nature of the receiver (river, sea, lake etc) True colour is created by the presence of compounds that absorb visible light in wavelengths of 400-800 nm, or from compounds that fluoresce in the 200-400 nm spectrum. These are compounds of poly-aromatic structure, substituted aromatic structure, polygenic, concentrated hetero-circular molecules or perplex ions. It should be noted that π bonds absorb into the UV (‹200nm) spectrum and the existence of conjugate bonds (polygene) is necessary for the absorption in visible light spectrum. Most compounds responsible for colour creation contain one or more aromatic rings and start absorbing colour at 250 nm. The synthetic colour carriers come mainly from industrial plants as dye-houses, clothing industries with washing-machines, food and beverage industries, and slaughter houses. Wastewater is processed with ozone after its exit from the chemical or/and biological treatment plant and the usual dosage varies from 50-150 mg/l, according to the wastewater origin, its temperature, and the degree of its previous process.

Ozone-wastewater contact system

The contact system consists of a three-chamber tank, height of 0.5meter with splits that guide the wastewater to a vertical labyrinthine flow (Fig. 1). Ozone is supplied to the tanks through diffusers made of a special porous material of high resistance. These diffusers have the ability to create multi-numbered and very thin ozone bubbles, with a diameter of 220μm. With their appropriate geometric installation in the bottom of the contact tank and better distribution also increase in the liquid-gas contact surface to its maximum is achieved.

The diffuser is used due to the high rate of transport (70%) and its trivial energy consumption. In a tank of three-chambers, diffusers are installed in depth of 5 meters and succeed a transport rate more than 75%. The wastewater must have a hydraulic retention time greater than 45 minutes.

Fig. 1 Three Chanber tank with ozone supplied to the tank

Colour Removal Quality of Ozone

The quality of the ozone treatment effluent in terms of colour removal depends on the colour values of the feed, the ozone dose, waste water type, temperature of the waste water (Jeris et al. 1975). The best results concerning colour removal are achieved if the wastewater has been previously treated in order to lower the values of the other characteristics so that the ozone oxidizing effect is "consumed" only or at least at a maximum proportion in colour removal. Additionally the temperature must be below 30-deg C in order to achieve the best physical conditions for its solubility. The above remark certainly concerns the practical usage of ozone technology in wastewater treatment, as it indicates that the increase of the ozone dosage could give good results even in unprocessed wastewater as long as it has been efficiently cooled.

Wastewater colour removal requires an ozone dosage which in most cases fluctuates from 50 to 100 mg/l, for colour reduction of 85-92%. This dosage succeeds simultaneously a COD reduction about 40%, while small increases of BOD in the area of 3-7% have been noticed. The ozone treatment installation represents a significant construction and purchase cost. On the other hand a conventional treatment scheme using chemical coagulants for colour removal has high operational costs (cost of the coagulants themselves and cost for the produced sludge management requirements). In general and for the same effluent quality, the investment of an ozone installation can be paid off in 3-5 years, depending on the size and other specific details of each case.

The textile industry is one of the most complicated industries among manufacturing industry. Wastewater treatment is one of the major problems faced by textile manufacturers. A detailed study of the textile processes will reveal that there are many complicated processes and chemicals used throughout the production. In the case of manufacturing of woven polyester and cotton blended fabric, the textile main processes starts from fiber production in the case of synthetic fibre followed by spinning to convert the fiber to yarns. Yarns are then strengthened with sizing chemicals like starch, polyvinyl alcohol and wax so that they can withstand vigorous movements when the yarns are weaved into fabric in high speed weaving looms. After weaving, weaved fabric must be pre treated before they can be dyed, printed and finished. During pre treatment there are various chemicals being used. Fabric is desired either with enzyme or oxidative chemicals and scoured using sodium hydroxide and detergents. Bleaching is done normally by using hydrogen peroxide to remove the natural colour of the fabric white. Fabric is then mercerized using high Concentration sodium hydroxide to stabilize the fabric. During dyeing and printing, many types of dyes are used e.g. disperse, reactive, vat etc. Fabric is finally finished to give the last touch and intended properties by using resins, softeners and other finishing agents e.g. fluorocarbon, silicones etc The combination of the processes and products make the wastewater from textile plant contains many type of pollutants. The dyeing and finishing operations are such that the dyestuffs, chemicals and textile auxiliaries used can vary from day to day and sometimes even within several times a day.

Characterization of textile wastewater

The characteristics of the textile effluent may contain organic load due to the presence of grease, dirt and/or sizing agents, nutrients from dye bath additives and residual dyes. These different components explain the values of total chemical oxygen (COD) demand and biochemical oxygen demands (BOD_5) to about 1185 and 900 mg/L, respectively. The influent used to feed bioreactors presented low COD and BOD_5 values due to the dilution results from different washings. Alkali or acids from the bleaching, desiring, scouring and mercerizing steps result in an extreme pH of 11–12 plus a high salt content of 2.84 g l^{-1}. The influent presented a basic pH of 9.6; this is not suitable for the biological activity of microorganisms. For those reasons, the influent pH was adjusted daily at 7.5 corresponding to the optimal pH for a maximal biological activity. This influent presented a blue colour, with maximal absorbance spectra of 0.98 obtained at the wavelength of 620 nm. The values of CODs, which are very close to total COD and to the COD/BOD5 ratio of 1.31, confirmed that this influent is easily biodegradable and presents approximately the same ratio (1.35).

Colour Removal from Textile and other Industrial Wastewater using Ozone

Ozone has been used for successful removal of colour from textile wastewater streams in plants around the world as well as in other industrial wastewater processes. In wastewater treatment, ozone is often used in conjunction with biological treatment systems such as activated sludge. Organic dyes are mostly refractory due to their large molecular size and they can be poorly removed by adsorption on activated sludge. In some cases ozone has been used before the biological process, but mainly after biological treatment. If the wastewater is hardly biodegradable or toxic to activated sludge pre-treatment is an option.

Ozone can be used prior to a biological process because it has a tendency to convert organic molecules into smaller more biodegradable species. This can enhance the efficiency of the biological process. In addition, ozone treatment of wastewater increases the oxygen content of the water (unconverted oxygen and ozone that decomposes back to oxygen that was mixed with the water) which results in improvement in aerobic processes. This benefit is well known in the literature it is difficult to practically apply since the amount of improvement is difficult to predict and pilot studies involving ozone and biological processes are difficult to carry out. In textile wastewater processes, 20-30% improvement in the action of the biological system has been observed.

The effect of ozone on improving biodegradability and reducing toxicity is worth noting in terms of the effect of the treated water on the receiving stream. Where the treated water is tested for toxicity, the impact of the treatment process on this parameter must be considered. Destroying one organic molecule, but creating more toxic ones in a treatment process has been observed, for example the chlorination of MTBE without any additional agents or treatment processes can result in a more toxic wastewater. Another consideration is the presence of surfactants and the need to remove these compounds from the water. In some locales surfactant concentrations are tightly controlled and must be kept under 1pm. This creates an additional demand for oxidant. Some textile waste waters contain the colour and surfactants. Ozone is effective in removing the colour from all dyes used in textile processing. The amount of ozone can vary depending on a number of factors: how much colour was removed in the biological process, the type of dye used, where ozone is applied in the process, knowing the proper amount of ozone required to meet the colour removal objective for the receiving water body is critical to the economics of the ozone system. In general it is not easy to predict the amount of ozone required, so in virtually all cases where specific previous experience is not available, pilot testing is employed. Tosik (2) has shown that about 1 mg/l of ozone dye is required to achieve 95% colour removal, although this ratio varies by dye type. The ratio increases to about 1.5 for 100% removal. Reaction times were on the order of 10 minutes. In the textile industry a typical dosage might be 15 mg/l post biological treatment, but the levels could easily reach 25 mg/l. It is important to note that the ozone dose only needs to make the dye compound un-coloured and not necessarily completely mineralize the material.

Fig. 2a Ozone System Design 1

Fig. 2b Ozone System Design 2

Most industrial ozone generators convert oxygen to ozone using the corona (silent) discharge method. The oxygen can come from dry air, oxygen concentrated from air or LOX. The use of oxygen in an ozone system is dictated primarily by the local economics. The use of oxygen reduces the size of the ozone generator for a given amount of production, lowers the energy requirement and reduces energy employed in mixing the ozone with water if a venture style injector is used. This is offset by the cost of LOX, including the LOX storage and evaporation equipment, or the additional compressed air required for the concentration process. As the size of the units increase, oxygen tends to be favored. Oxygen is also favored by high energy costs, but is disfavored when the cost of LOX is high. An air fed ozone system for a textile wastewater application would include the following components: an air compressor, an air dryer, an ozone generator, an ozone water mixing system and an ozone destruct unit. The use of an air fed system in this example would probably be the worst case for ozone. If the equivalent electrolytic system cannot compete his type of ozone system, it is probably not economical in general. The use of dry air is critically important to the successful operation of an ozone generator. Most modern air fed ozone systems employ high pressure air driers which employs the pressure swing adsorption (PSA) method. This eliminates themed for a refrigeration unit as well as a heated desiccant dryer, but increases the pressure required from the Compressor to around 100 psi. Ozone makes up a small percentage of the final gas mixed with the water (2-3% in the case of air and 6-10% in the case of oxygen). A venture or fine bubble diffusers can be used to mix the gas with the water in order to dissolve the ozone. This excess gas must be disengaged from the water.

The use of a venturi type injection system requires a booster pump. Fine bubble diffusers are normally deployed on the bottom of the contact vessel. This can be cheaper since it would eliminate the booster pump and substitute less expensive diffusers for the venturi. The dissolved ozone must be allowed to remain in contact with the water for a certain period of time so the reaction can go to completion. This time is probably on the order of 10-20 minutes. To achieve this retention time some form of tank or contact vessel is required. This tank can also be employed to allow the gas and liquid disengage. We have taken this approach in costing out the example system below. The gas liquid mixture will enter the tank and the gas will be disengaged from the liquid in the tank since the transfer efficiency for ozone into water commercially varies from 80-95%, a portion of the ozone is found in the vent gas. In some locales, this must be decomposed. An ozone destroyer is employed for this process. It would pull air off the top of the contact vessel Ozone systems of the type discussed above have fairly low installed cost factors since most of the equipment is factory tested and skid mounted. Power, air, water and ozone lines are connected. Typically, the ozone generator and electronics would be housed indoors. The equipment operates in a temperature range of 40-95 ^{0}F.

CONCLUSIONS

The experimental results from a study on the removal of colour from an industrial discharge have been reported. Carbon adsorption, ion exchange, ultraviolet light in combination with hydrogen peroxide, and ozone were all bench top tested on a representative sample of the waste stream. Carbon adsorption and ozone were the only viable technologies that successfully decolorized the sample. Ozone was selected for pilot scale testing because the initial cost analysis indicated that ozonation was less expensive than carbon adsorption. Adjustment of the waste stream pH entering the ozone pilot system did not affect the ozone demand. COD did not significantly decrease in the ozonated samples and respirometer results indicate that ozonated samples are not toxic to the ASP treatment process. Testing indicated that the initial colour strength of individual wash waters had little effect on the ozone demand at the selected colour reduction limits. Decolourization was more efficient at greater dilutions as compared to more concentrated dilutions.

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