Oxidative Decomposition of Pulp and Paper Industry Effluents: A Kinetic Study

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Abstract
Increasing attention, interest and demand by public for a cleaner environment have been a global concern now-a-days. Besides municipal discharges, industrial point sources make substantial contribution to the pollution of river waters releasing a wide range of organic contaminants. Pulp and paper industries are water intensive industries, releasing a lot of pollutants to water bodies with significant colour load. Although many process modification technologies and /or end-of-pipe treatment methods have been implemented out to satisfy the pollution discharge limit, still there is a search of proper technology for colour reduction in industrial scale. The oxidation of pollutants from pulp and paper industry post oxygen stage effluents has been done by ozonation to reduce the colour load. The kinetics of decolourization has been studied. The ozonation reactions follow a first order disappearance of colour and the first order rate constant increases with increase in ozone concentration. Ozonation in presence of catalytic amount of Fe^{3+} & TiO_2 enhanced the colour reduction efficiency significantly. It is found that the ozonation of intermediate stage effluents having high colour load is more effective towards ozonation.

Keywords: - *Effluent, Colour, Kinetics, Ozone, Lignin, Extractives, B.O.D & C.O.D*

I. INTRODUCTION

The removal of colour from pulp and paper industry waste water has been receiving increasing attentions in recent years. The interest has been prompted by public demands for a cleaner environment [1]. In the pulp and paper industry effluent, the principal colour bodies include tannins, humic acids and humates from the decomposition of lignin [2]. These lignin bodies are highly coloured and quite resistant to biological attack resulting in their long persistence to the environment. Colour interferes with aquatic life by limiting light transmittance, also contribute taste problem and increasing stability of some bivalent metal ions by chelating colour bodies present in the effluent which may also serve as a potential bacterial nutrient. As a rule, colour bodies are resistant to removal by conventional methods of effluent treatments. The primary sedimentation clarifiers followed by biological methods(Aerated lagoons or activated sludge treatment) are effective only in reducing biological oxygen demand(BOD), chemical oxygen demand(COD), total organic carbon(TOC), suspended solids but not the colour [3]. The pulp and paper industry effluent mainly contains lignin and degraded lignin organic compounds. These compounds mainly removed in pulping and bleaching process. Due to presence these compounds pulp and paper industry effluents are visually dark in colour [4-5]. The lignin compound contains number of chromophoric groups which generally absorbs U.V light through their functional groups having excess electrons such as $-C=C-$,$-C \equiv C -$, six member aromatic rings, nitro, sulphur and oxygen containing groups. These compounds absorb light in visible range and generate colour in the effluent. *Gierer et al.*(1997) proposed a reaction mechanism which involves the phenolate anions, formed under the alkaline conditions of the process, being converted into phenoxy radicals followed by the formation of hydro peroxides and the eventual degradation of aromatic rings to muconic acids [6]. Further developments in this area have been associated with structural studies of lignin isolated from oxygen delignified pulp using the effluent liquor. *Kaneko et. al.* (1983) reported on degradation of lignin with & reactivity of lignin model compound with ozone. In order to elucidate the reactivity of different types of lignin-structural units toward ozone, they apply ozone in various lignin model compounds [7]. *Rajeswari et al.*[2009] reported on TiO_2 based heterogeneous photocatylic treatment of pesticide carbendazim combined with ozonation for carbendazim degradation [8]. *Parveen Kumar et al.* (2011) worked on the advanced photo catalytic oxidation of the pulp and paper industry effluent (primary clarified and bio treated) with UV/TiO_2 and $UV/TiO_2/H_2O_2$ treatment processes for environmental load reduction [9]. *Thiruvenkatachari et. al.* (2008) reported that titanium dioxide exposed to sunlight becomes photoactive, the surface of the catalysts generates free electrons, and valance band holes form. Water encounters the valance holes and the water oxidizes to form hydroxyl radicals [10]. *Konstantinou et al.* (2004) reported that oxygen from the air and dissolved in the water can accept the free electrons on the surface of photoactivated TiO_2 generating the radical anion, O^{2-}. The anions can further oxidize the organic compounds [11]. *Daneshvar et. al.* (2003) reported that many of the reactions occurring on the surface of titanium dioxide lead to the breakdown of the dyes making it an efficient photo catalyst [12]. *Pekakis et.al.*(2006) reported on the

oxidative degradation of an textile dye house wastewater was investigated by means of photocatalysis in the presence of TiO_2 [13]. The UV-induced photo catalytic oxidation over TiO_2 suspensions was capable of decolourizing the effluent completely, as well as reducing chemical oxygen demand [14].

II. MATERIALS AND METHODS

The reagents used are of anal-R grade and are recrystallised or redistilled before use. For Ozone determination, the iodometric method as described in standard method has been followed. The sample is collected in a 250 ml volumetric flask containing 10 ml of 0.1 N H_2SO_4 and 20 ml of 20 % KI solution. A blank is also set up and the titrations are carried out using 0.005N sodium thio-sulphate solution. Ozonation was carried out in a bubble reactor at room temperature. Treatability tests were conducted using a conical flask of one litre capacity. The reactor was a fine-bubble diffuser. The gas flow rate was kept constant. Ozone was produced from pure oxygen (stored in tank) using a Aquazone ozonator (model-CD500, Aquazone systems & engineering Ahmadabad, India) and was injected inside the reactor with the bulb having small holes (bubble diffuser).The diffuser is a spherical stone, with dimensions of 2 cm. The ozone concentration in the gas phase was measured with an ozone monitor where displayed the volumetric or weight-based concentration of ozone in the mixed gases, and stored in memory of the measurements performed. Valves were used to direct the gas stream from the diffusers to the ozone monitor for inflow ozone concentration measurements. By reversing valve positions, the gas stream went to the diffusers within the reactor. The post oxygen stage coloured effluents of pulp and paper industry is taken for the present study. The ozone concentration applied has been calculated from the graph of standard concentration at different flow rate. The kinetic runs are performed by following the disappearance of colour in the effluent at different reaction time after passing the ozone at fixed flow rate. The reactions are quenched by putting ice. The reduction in colour (in Platinum Cobalt Unit) concentration are determined spectro-photometrically at 465 nm after centrifuging the solution. Kinetic experiments are carried out by passing the O_3 at a fixed flow rate into a reaction flask of one litter capacity with 500 ml of effluent after adjusting the pH to 9.5.The amount of O_3 passing to the solution was calculated.

III. RESULTS & DISCUSSION

Colour reduction rate on ozone treatment

Kinetic experiments were performed by passing laboratory generated ozone gas in the colour effluent by maintaining the initial conditions. [Colour] = 2000 PCU, [O_3] at a rate of 2.64g/hr and pH =9.5, by passing excess of O_3 over colour. The unreacted O_3 after the completion of reaction was estimated. In the run, readings were taken after long intervals until 100 % of completion of the reaction. Then the oxidant concentration consumed or involved i.e. [O_3], for the completion of the reaction with respect to known concentration of the colour was calculated, from which the stoichiometric ratio of [Colour] to [O_3] was found out for the overall reaction. The rate of reaction is observed from the graph [Percentage(%) of colour reduction vs. Time] which is presented below. In the graph, the colour reduction percentage gradually increases by the increasing of reaction time with certain interval then remains constant, which indicates the reaction follows first order rate law. Again it is clear from the graph that by the application of catalytic amount of Fe^{3+}, or TiO_2, the rate of colour reduction increases significantly which is shown in figure-1.
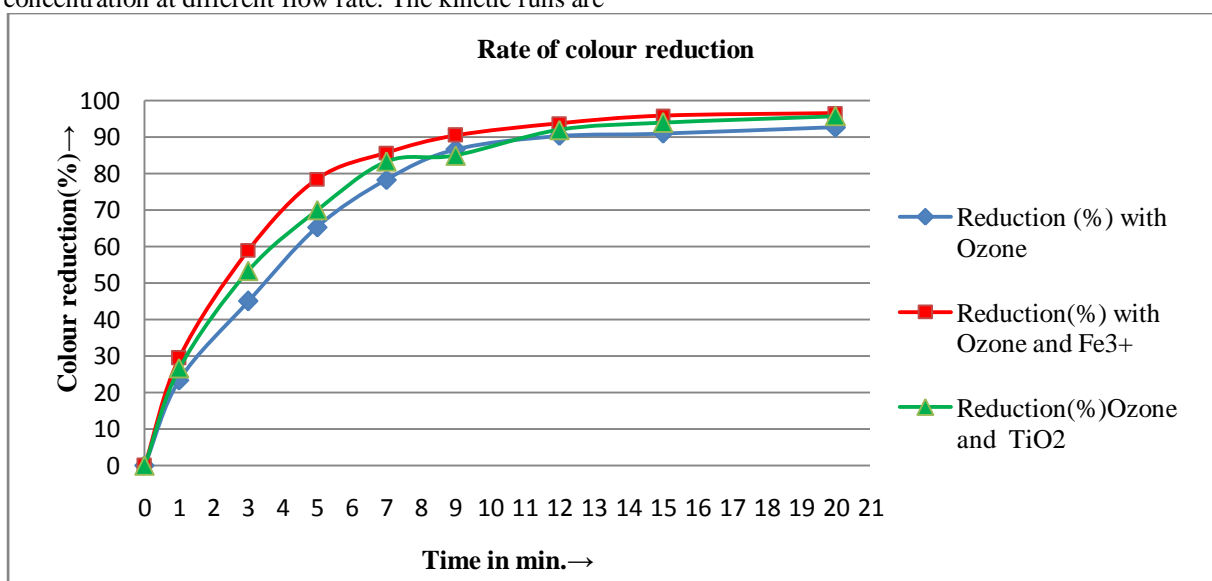

Figure-1: Rate of Change of colour from pulp and paper industry PO-stage effluent on ozone treatment with or without catalyst

From the study, it is clear that the rate of colour reduction effeciency depends upon the concentration of ozone and pH i.e. the $[H^+]$ and the initial colour concentration.

$$- \frac{d[C_R]}{dt} \propto [O_3][H^+][I_C]$$

Where,

C_R = Colour reduction percentage.
$[O_3]$= Ozone concentration
$[H^+]$= Hydrogen ion concentration
I_C =Initial colour of effluent

The initial colour concentration of the effluent plays an important role for colour reduction by ozonation. With the application of ozone as a oxidant only, it is observed that when initial colour of the effluent is more then 2000PCU, the rate of colour removal efficiency is high. Simerlarly when the initial colour dose is less then 2000PCU the rate of colour reduction efficiency again increases which is shown in figure-2. This may be due to presence of more degradation of organic colour material when the colour of the effluent is high or low.
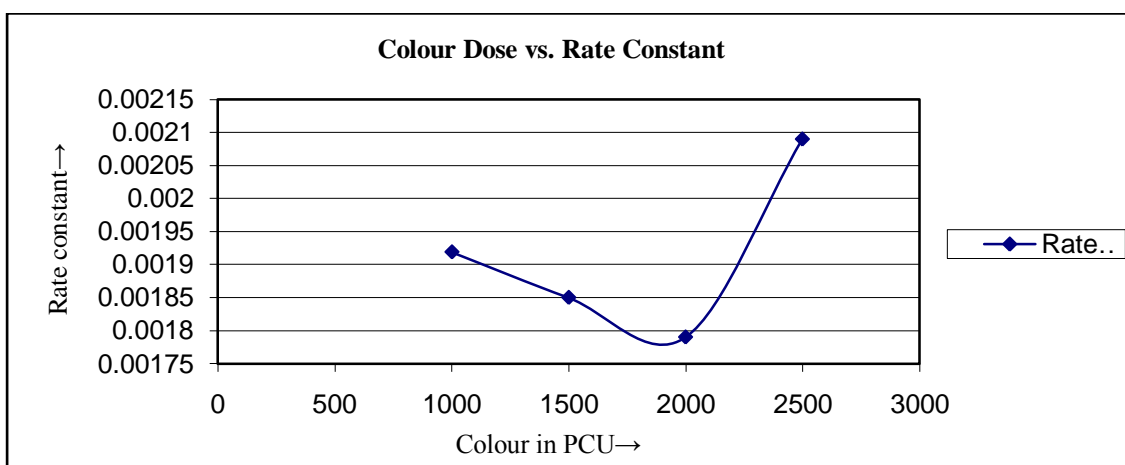

Figure-2: Effect of initial colour to the Rate to the pulp and paper industry PO-stage effluent on ozonation

The colour reduction efficiency is more at higher pH i.e. when greater than 10.0, this may be due to the reaction of almost all organic and inorganic compounds with molecular ozone and oxygen radicals, including the hydroxyl radical. Again at lower pH i.e. less than 5.0 the colour reduction efficiency increases. At neutral pH the colour reduction percentage by ozonation is less which is clearly identified from figure-3.
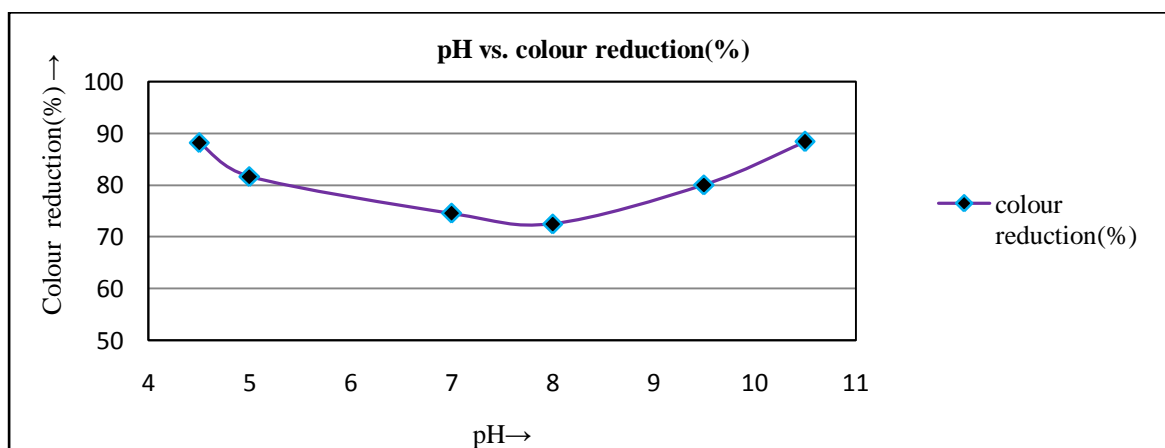

Figure-3: Effect of changing of pH to colour reduction percentage on ozonztion to pulp and paper industry PO-stage effluent

Ozone is a powerful oxidizing chemical so with the increase in ozone dose the colour reduction efficiency increases, which is shown in figure-4. The lignin related aromatic organic compounds degraded easily by ozone. The advanced oxidation processes exploit the high energy of hydroxyl radicals(OH ·), which attack most of the organic molecules, aromatic rings, polyphenols, halogenated compounds, resin acids and unsaturated fatty acids.
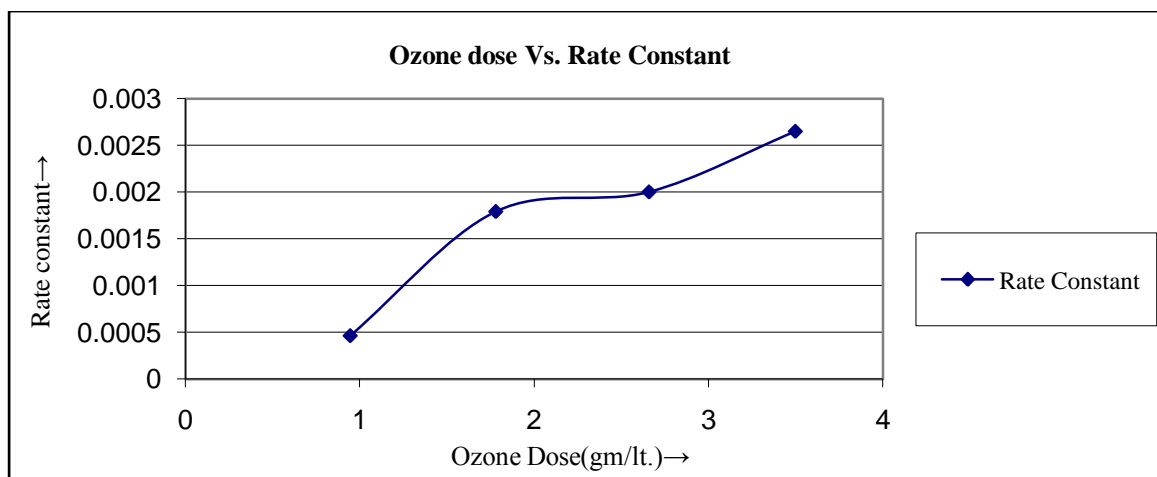
Figure-4: Effect of changing of rate of colour reduction on ozone dose to pulp and paper industry PO-stage effluent

IV. CONCLUSION

The overall studies based on oxidative decomposition of the colour effluents of pulp and paper industry with ozonation and catalytic ozonation and its kinetic study reveals the followings:

- The colour of pulp mill effluents is mainly due to degraded lignin based chromophoric compounds.
- The rate of ozonation reaction follows first order kinetics.
- Colour reduction (%) and the first order rate constant by ozonation are maximum in acidic pH in between 4.0 to 5.0 and alkaline pH (above 10.0). In neutral pH, it is not effective significantly.
- With the application of catalytic amount of Fe^{3+} salt at acidic pH (4.0 to 5.0), the colour reduction efficiency is outstanding.
- Application of catalyst TiO_2 also gives better result for colour reduction during ozonation.

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