Ozone for Color and COD Removal of Raw and Anaerobically Biotreated Combined Industrial Wastewater

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Abstract

Ozonation was carried out for decolorization and COD removal of raw and anaerobically treated UASB (upflow anaerobic sludge blanket) combined industrial (mainly textile) effluent in a lab-scale bubble column reactor. Ozonation of anaerobic bioprocess effluent at a dose of 300 mg/h for 10 min resulted in 81% color and 75% COD removal (100 mgO$_3$/80 mg COD) while for raw wastewater 25 min ozonation furnished 51% color and 67% COD removal (250 mgO$_3$/345 mg COD). Optimal process conditions for biotreated effluent (pH = 8 and temperature = 25°C) resulted in 100% color and 96% COD removal for 10 min ozonation (100 mgO$_3$/104 mg COD). Electrical energy comparison demonstrated that post ozonation required less electrical energy, 16 and 2.9 times as compared to pre ozonation.

Keywords: ozonation, biotreated, energy requirement, effluent, pre and post

Introduction

Selection of an appropriate and cost-effective treatment technique for the removal of contaminants has always been a major concern. Although upflow anaerobic sludge blanket (UASB) reactors have been proven to be viable options for the treatment of combined and even complexed industrial effluent [1, 2], a fraction of color and COD imparted by different dyeing and finishing processes is usually non-biodegradable and renders it difficult for anaerobic digestion to bring final color and COD levels of effluent within permissible limits. To overcome these limitations anaerobic wastewater treatment is added with pre/post treatment arrangement, which involves a variety of techniques ranging from simple physical processes adsorption and flocculation [3] to emerging advanced oxidation processes (AOPs). The main advantages of AOPs include the lack of byproducts of environmental concern, high process rate, efficiency and enhanced biodegradation [4, 5]. Among AOPs ozone has proved a powerful oxidizing agent and its oxidizing ability is owed to nascent oxygen atoms and hydroxyl radicals [6]. It reacts, directly or indirectly, with complex compounds, breaking them into simpler and smaller molecules [7]. For instance, chromophoric organic compounds (common in textile effluent) with conjugate double bonds are broken into smaller and simple molecules by ozonation. The ozonation process minimally generates toxic byproducts [8] and its prior application to wastes also enhances their biodegradation by converting the more slowly biodegradable COD into simpler compounds or by reducing the amount of inert organic matter [9]. Post-ozonation, on the other hand, may have a polishing effect on effluent quality. It is therefore important to set the basis for the selection of the appropriate location for ozone application. The right choice between pre- or post-ozonation alternatives is significant for the optimum use of the chemical oxidation potential provided, both for overall COD and

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color removal, and for reduction of soluble non-biodegradable COD fractions.

Process conditions like pH and temperature influence the performance of the ozonation process [10, 11]. At lower pH (acidic conditions) ozone exists in molecular state (O_3) and its decomposition into highly reactive species like $HO^{\cdot}$, $HO_2^{\cdot}$ and $HO_3^{\cdot}$ occurs in an alkaline environment [12, 13]. Among these species, $HO^{\cdot}$ is an extremely important oxidant because its rate of attack is 10^6 to 10^9 times faster than that of the reaction rate of molecular ozone [14]. It has been demonstrated that ozone decomposition into secondary oxidants enhances at higher pH and the reaction between hydroxide ion and ozone leads to the formation of super-oxide anion radical O_2^{-} and hydroperoxyl radical $HO_2^{\cdot}$, which through various steps yields $HO^{\cdot}$ radical [10, 15].

The effectiveness of ozone treatment can be influenced by temperature as well. The influence of temperature on ozonation is a net result of two simultaneous effects such as increase in the rate constant of the reaction and the variation of ozone solubility with temperature. Due to an increase in the temperature, ozone solubility decreases, thereby a reduction in the amount of ozone available for the reaction, which may result in an overall decrease in degradation [16, 17]. The difference in solubility inhibits reactions between ozone and organics. In the temperature range from 5 to 20°C ozone efficiency increases as reaction rate increases with an increase in temperature, while solubility is not much effected. However, the removal of COD is not effected significantly up to 40°C due to compensation of increase in reaction rate with the decrease in solubility of ozone. On the other hand a decreasing trend appears beyond 50°C as the decrease in solubility overcomes the increase in reaction rate [11, 18, 19].

The aim of this study was to investigate the possibilities of using ozone for the treatment of combined industrial effluent and inline with UASB as a post treatment option.

Experimental Procedure

Wastewater Characteristics

Wastewater used in this study was obtained from the combined industrial effluent drain carrying the effluents of more than one hundred textile units along with five dairy, two sugar and three flour mills. Integrated samples were prepared by mixing water samples taken along the width of the drain at varying depths. Wastewater was characterized in terms of color, COD, chloride and pH of influent and effluent in accordance with Standard Methods for the Examination of Water and Wastewater [20]. Color was measured as absorbance values (optical density) at wavelength of 465 nm [21]. To avoid interference from suspended matter with the result for color measurement the wastewater sample was centrifuged before examination [20]. The wastewater characteristics are given in Table 1.

Biological Treatment Setup

A bench scale anaerobic experimental setup was used for the biological treatment (Figure 1a). The experimental assembly was divided into four parts: (1) UASB reactor, (2) feed tank, (3) gas collection arrangement, and (4) effluent collection tank. The UASB reactor was made of Perspex tubular circular column (tubing) with an inside diameter of 7 cm and length of 120 cm. In order to enhance the capturing of suspended particles an enlarged

Table 1. Characterization of wastewater and UASB-treated effluent used in the study.

Parameter	Unit	Wastewater	UASB effluent
pH	-	7.9[a] (0.08)	7.2 (0.05)
Colour	Absorbance	0.65[a] (0.02)	0.085 (0.001)
COD	mg/L	515[a] (29.4)	108 (7)
Chloride	mg/L	144[a] (17.6)	57 (3.3)

Values in parenthesis represent standard deviation and [a] is mean of five values.
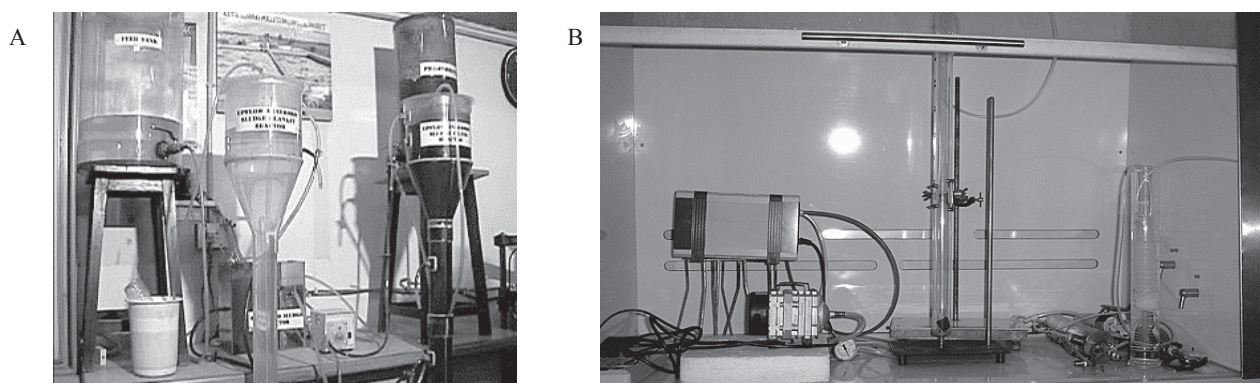

Fig. 1. A. Anaerobic wastewater treatment system; B. Experimental set up for ozonation.

portion, termed as gas-liquid-solid Separator (GLSS), was added at the top of the column, giving the reactor a total height of 160 cm. Wastewater was introduced to the reactor for treatment at an HRT of 6 hrs and at 30°C. The characteristics of the UASB-treated effluent are given in Table 1. This effluent was further used for the post treatment.

Application of Ozone

Ozonation was carried out in bubble column reactor with an internal diameter of 3.3 cm. Ozone generator (JQ-6M PURETECH) was employed to produce ozone from air and was bubbled at the bottom of the reactor by means of a diffuser at a rate of 300 mg/h (Figure 1b). Ozone dose varied from 25 to 125 mg. The effect of pH (7 to 11) and temperature (25 to 60°C) was also studied at constant ozone dose of 100 mg for raw wastewater and 50 mg for biotreated effluent. All the experiments were carried out in batch mode on a sample volume of 500 ml.
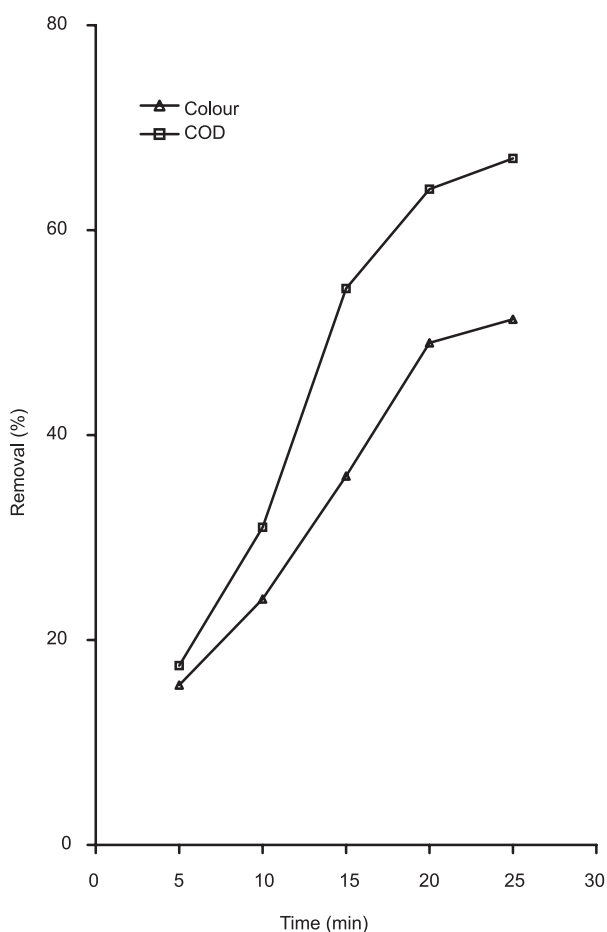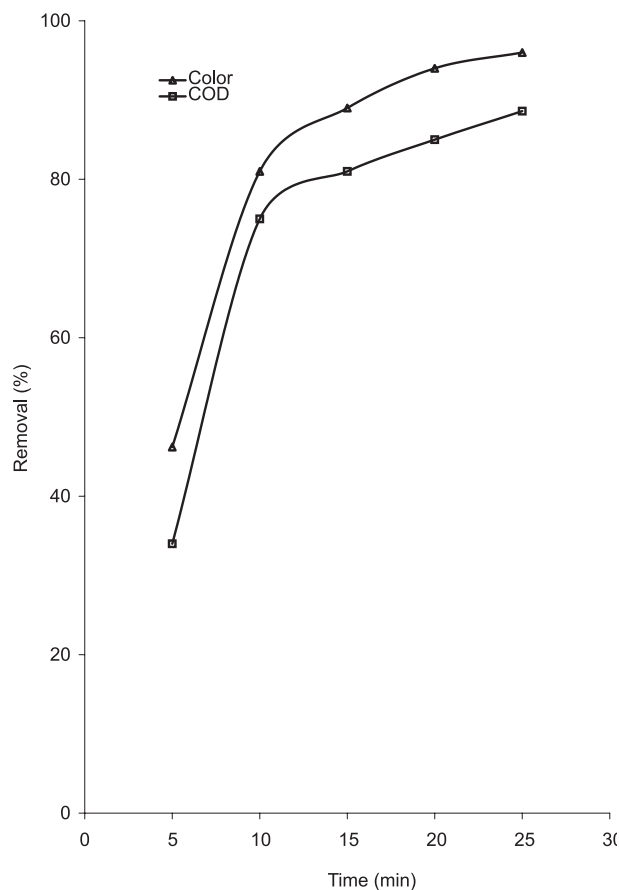

Fig. 3. Effect of ozone dose for color and COD removal of biotreated treated effluent (pH = 7.2 and ozone dose = 300 mg/h, Color $_{influent}$ = 0.085 absorbance, COD $_{influent}$ = 108 mg/L).

Calculations of Energy Requirements

Operating costs are directly affected by treatment performances of the applied processes. To ease up comparison of reaction efficiencies, powerful scale-up parameters called EE/O (that is the electrical energy required to remove a pollutant by one order of magnitude in one m³ of wastewater) values have been calculated by applying the following empirical formula:

$$EE/O\left(kWh/m^3\right) = \frac{P \cdot t \cdot 1000}{V \cdot 60 \cdot \log\left(C_{inf}/C_{eff}\right)} \tag{1}$$

where P (kW) is the power input, t is the oxidation time (in min), V is the volume of the effluent sample (in liter) and C_{inf} and C_{eff} are the initial and final concentrations of the contaminant [22-24].

Results and Discussion

Color and COD removals were increased with an increase in ozone dose. Figs. 2 and 3 shows the effect of ozonation on color and COD removal of raw
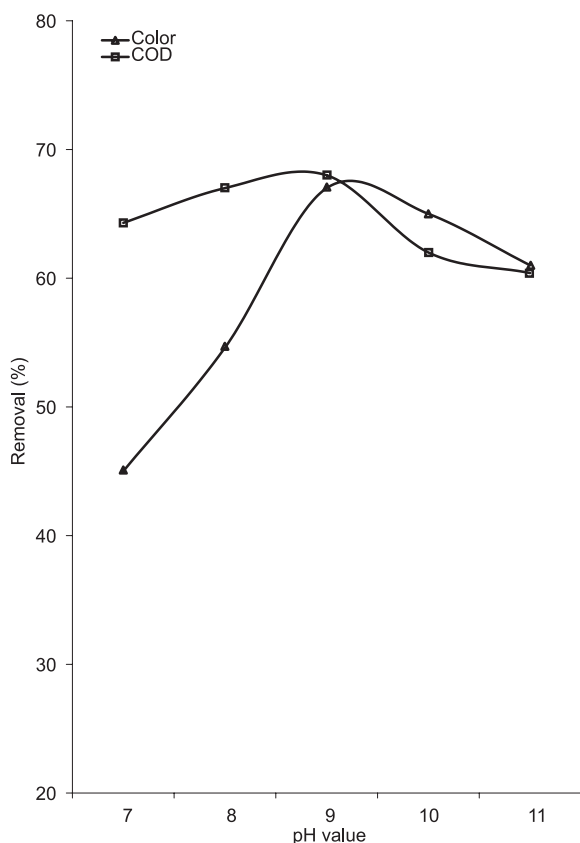

Fig. 2. Effect of ozone dose on the color and COD removal of raw wastewater (pH = 7.9 and Ozone dose = 300 mg/h, Color $_{influent}$ = 0.65 absorbance, COD $_{influent}$ = 515 mg/L).

Fig. 4. Effect of pH on the efficiency of ozone (100 mg) for color and COD removal of raw wastewater (Color $_{influent}$ = 0.65 absorbance, COD $_{influent}$ = 515 mg/L).

obtained for pH 9 (Fig. 4). While 94% color and 92% COD removal was achieved at pH 8 for biotreated effluent (Fig. 5). However, decreasing trend in removal efficiencies with a further increase in pH (> 9) was observed. This could possibly be associated with the organic compounds present in the wastewater that were more susceptible to oxidation at pH 8 to 9 [26]. Decreasing tendency in color removal at higher pH (> 9) can be explained by the fact that dye molecules with greater affinity towards ozone are selectively oxidized in preference to other dyes in the solution increasing the recalcitrant fraction of the waste stream which remains untreated and responsible for decrease in color removal [27]. A decrease in COD removal at high pH is due to the fact that ozone initially converts the suspended solids into dissolved solids and subsequent ozonation destructs high suspended solids into very small molecules, which enhance COD level in the ozonated wastewater [25]. It should also be noted that if the operating pH is above the p*K* value of the pollutant, i.e. the pollutant is not in molecular state, not much enhancement in the rates of degradation will be observed as reported by Beltran et al. [28].
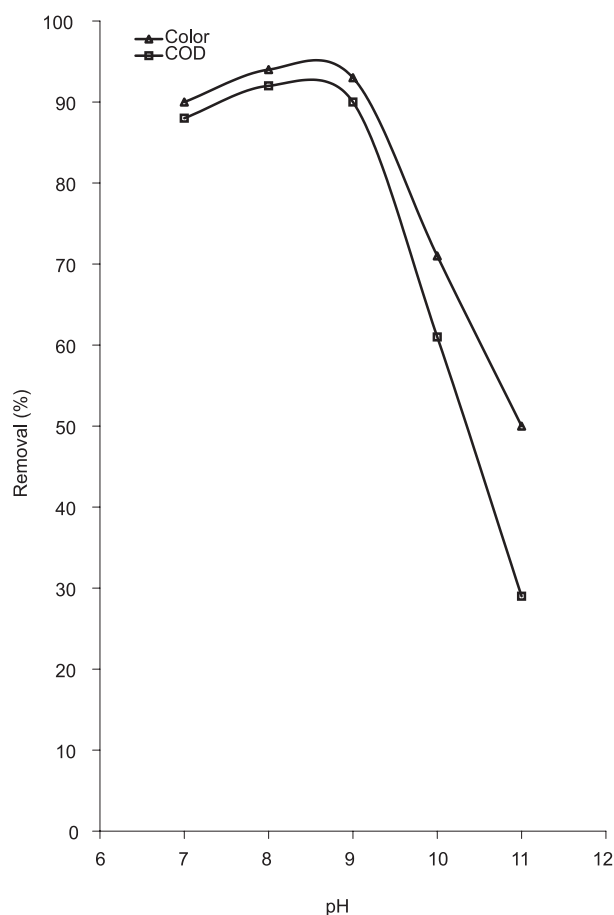
wastewater and UASB-treated effluents. Introduction of raw effluent to ozone dose of 125 mg (25 min) resulted in color and COD removal (%) of 51.3 and 67, respectively. On the other hand an increase in ozonation dose from 25 to 125 mg resulted in the increase in color removal efficiency of 46 to 96% for UASB effluent. While for COD this increase was 34 to 88.6%. Results reveal that UASB effluent was more susceptible to ozone for decolorization as compared to raw wastewater. This may be attributed to the difference in the concentration and nature of the organic matter. In the case of UASB-treated effluent the remaining compounds were in the simple form due to the anaerobic digestion (hydrolysis and acetogenesis). In comparison, the organic matter in raw wastewater was present in suspended, dissolved and more complex form [25].

Effect of pH on Ozonation

Reaction pH is an important operating parameter which influences the performance of the ozonation process significantly [14]. Ozonation at elevated pH is a promising technique for rapid decolorization and COD removal. Ozonation of raw and bio-treated wastewater was carried out at pH range 7 to11. For raw wastewater optimal color and COD removal of 67 and 68% was

Fig. 5. Effect of pH on ozonation (50 mg) of biotreated wastewater for color and COD removal (Color $_{influent}$ = 0.085 absorbance, COD $_{influent}$ = 108 mg/L).

Effect of Temperature

Temperature also has a notable effect on the efficiency of ozone for color and COD removal. Another reason for ozone efficiency evaluation at elevated temperatures was the fact that textile effluents are typically discharged at elevated temperatures. Temperature for the raw and biotreated wastewater was maintained from 25 to 60°C. Complete decolorization and 96% COD removal was obtained at 25°C for biotreated wastewater. While for raw wastewater maximum color removal of 58% was achieved at 30°C. Both color and COD removal gradually decreased with an increase in temperature from 30 to 60°C for raw as well as biotreated wastewater (Figs. 6, 7). This was the result of the two simultaneous effects, increase in the rate constant of the reaction and the indirect effect through the variation of ozone solubility with temperature. Due to an increase in temperature, ozone solubility decreases, thereby reducing the amount of ozone available for the reaction, which may result in decreased degradation [16, 24]. Results obtained are supported by literature [11, 18].
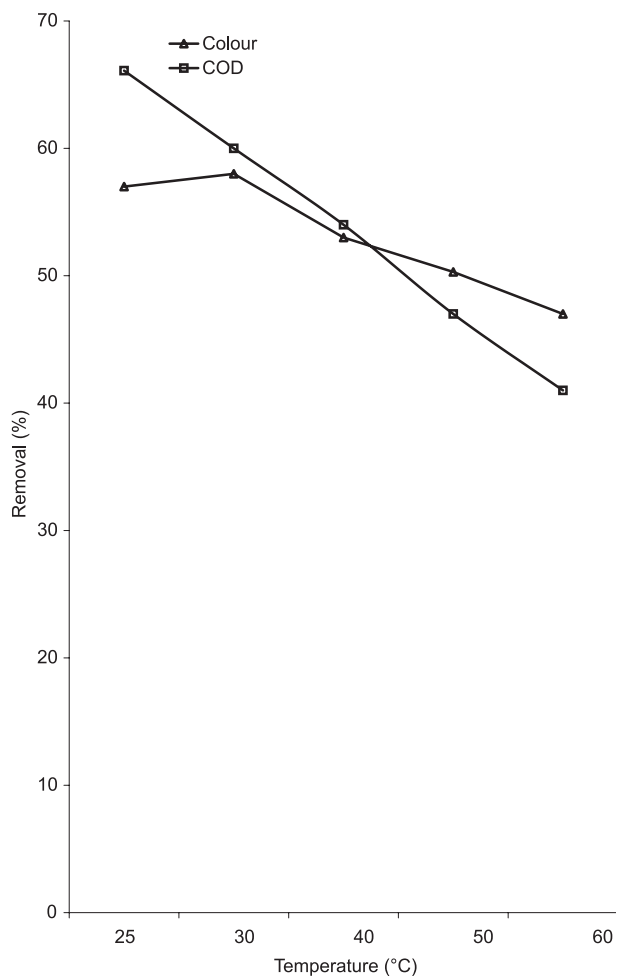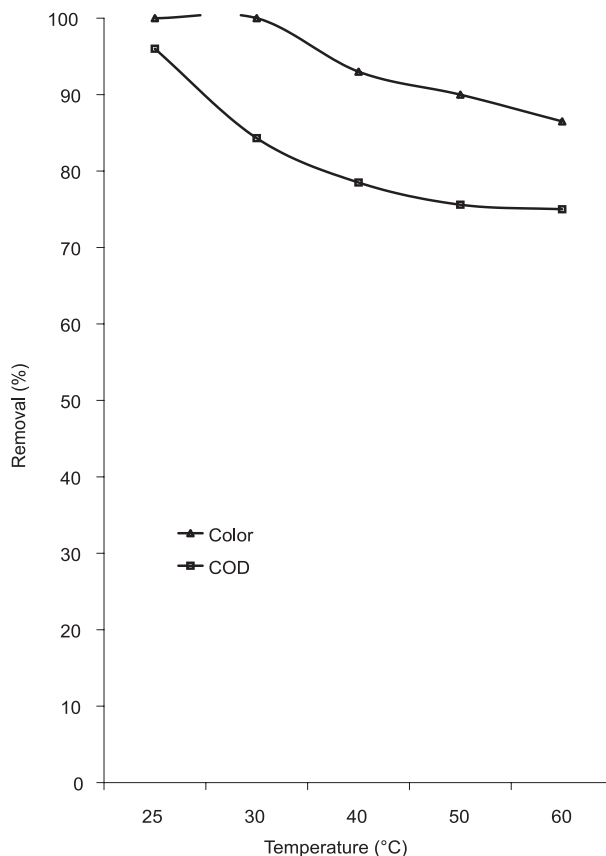

Fig. 7. Effect of temperature on ozonation (50 mg) of biotreated wastewater for color and COD Removal (Color $_{influent}$ = 0.085 absorbance, COD $_{influent}$ = 108 mg/L).

Comparison of Electrical Energy Requirements for Biotreated Wastewater

In energy intense treatment processes such as ozone, the key design variables, i.e. energy required by the system and order of magnitude of contaminant concentration removal can be combined into a single function called Electrical Energy per Order of Pollutant Removal (EE/O). The EE/O is a powerful scale-up parameter and a measure of the treatment rates obtained in a fixed volume of contaminated water as a function of the applied specific energy [22]. Electrical energy consumption for pre and post ozonation processes at optimal conditions for their maximum removal efficiency of color and COD was 20.8 kWh/m³, 20.4 kWh/m³ for pre ozonation and 1.3 kWh/m³, 7 kWh/m³, respectively for post ozonation. Results clearly reveal that post ozonation required less electrical energy for both color and COD removal as compared to pre ozonation that require 16 and 2.9 times more energy for color and COD than post ozonation of anaerobically treated effluent.

Fig. 6. Effect of temperature on the efficiency of ozone (100 mg) for color and COD removal of raw wastewater (Color $_{influent}$ = 0.65 absorbance, COD $_{influent}$ = 515 mg/L).

Conclusions

Ozonation showed best results for post treatment of anaerobically treated effluent for color and COD removal as

compared to the pretreatment of combined industrial wastewater of the same nature. However, efficiency of the ozonation process was further increased at elevated pH. Optimal results for raw and biotreated wastewaters were observed at pH 9 and 8, respectively. Temperature showed an adverse effect on the removal efficiency as an increase in temperature (> 30°C) resulted in continuous decrease of color and COD degradation. Electrical energy comparison demonstrates that post ozonation is a more cost-effective and feasible option.

Acknowledgements

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