Chemical Oxidation Process For The Treatment Of Antibiotic Wastewater

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Abstract

There is growing concern from the scientific community that pharmaceutical compounds are not treated sufficiently by current wastewater treatment methods and therefore trace amounts of such compounds are being identified in surface water, ground water and sewage effluents. Advanced oxidation processes (AOPs) are now being proposed for the specific treatment of industrial wastewaters and wastewaters containing pharmaceutical products. The AOP treatment for the antibiotic wastewater was researched following an anaerobic digestion. Various combinations of AOPs were considered using ozone (O_3), hydrogen peroxide (H_2O_2), ultra-violet (UV) and Fenton's reagent. Chemical oxygen demand (COD), total organic carbon (TOC) and sulphate analysis were carried out to evaluate the efficiency of the AOPs. Results showed that the UV/H_2O_2 and UV/H_2O_2/O_3 AOPs were considered to be most effective for this particular wastewater. A 70% COD removal and a 56% TOC removal were recorded for the UV/H_2O_2 processes, a 66% COD removal and a 56.6% TOC removal were recorded for the UV/H_2O_2/O_3 processes. Sulphate concentrations increased during all AOPs due to oxidation of hydrogen sulphide (H_2S).

Key words: Advanced oxidation process, antibiotic wastewater, chemical oxidation, sulphate

Introduction

Extensive research in to the occurrence and fate of pharmaceuticals in the environment has been carried out in recent years[1]. The aim of the majority of this work is to identify particularly persistent substances, the quantities they occur in surface waters and wastewater effluents and the eventual long-term effects they may have in the aquatic environment[2-4]. To complete this research the long and complicated life-cycle of these products had to be fully examined in order to understand the magnitude of the effects and propose ideas to minimise these adversities. This 'cradle to grave' strategy has resulted in vast amounts of data and several proposals for future improvements in manufacturing processes and the treatment of wastewaters resulting from these processes[5]. Only a small minority of these proposals, however, have actually been put in to practice.

The presence of trace concentrations of pharmaceuticals in surface water, groundwater and wastewater has been recorded in recent years with such frequency that it has become a matter of some environmental concern[6]. Various different compounds have been found in varying concentrations including; antibiotics, beta-blockers, anti-ulcer drugs, analgesics and anti-inflammatory[7]. Birth control pills and caffeine have also been found in trace concentrations[8]. Neither the extent of the exposure of drugs to the environment nor the proportion of subsequent effects is known presently.

Most drugs are designed to be persistent and can therefore affect the biological systems resulting in the easy penetration of bio membranes and persistent biodegradation in order to be effective as possible. Environmental engineers are developing methods of reducing pharmaceutical concentrations through improved wastewater treatment methods and improvements in the biodegradability of pharmaceutical wastewater effluents[2].

There are various methods that have been proposed to treat wastewater containing pharmaceutical drug extracts or drinking water supplies that may contain trace quantities of such contaminants[9]. These methods include membrane filtration, granular activated carbon (GAC) and various "in series" methods using combinations of floatation and filtration. Although these methods have been successful in some cases for some pharmaceuticals, there is great interest in a new theory utilising advanced oxidation processes (AOPs) as either a pre-treatment or co-treatment stage of the wastewater treatment process[10]. This method has not only been highly successful in reducing contaminant concentrations, it has also been deemed suitable for treatment of high strength industrial wastewaters containing particularly persistent compounds.

The AOPs use a combination of strong oxidising agents such as O_3, H_2O_2, UV and Fenton's reagent[11]. When used individually or in combination (e.g. O_3 with H_2O_2) they can provide an efficient alternative for treatment of pharmaceutical wastewater[12]. This particular study examines pharmaceutical wastewater from the production of an antibiotic. Various AOPs were applied to the wastewater in order to determine significant effects of each individual or combined process. The evaluation of these processes took in to account overall efficiencies of the processes and also economic measures and practical measures for applying such treatment methods in practice.

The aim of this research was to investigate treatment methods for the antibiotic wastewater using (O_3), hydrogen peroxide (H_2O_2), ultra-violet (UV) and Fenton's reagent.

Material and Methods

The apparatus for O_3, UV, H_2O_2 and Fenton's reagent were set-up according to the following specifications: O_3 generator Model BA-023 UK, measured using Standard Method 2350E 'O_3 /Demand Requirement - Semi Batch Method', O_3 output was set at 1.6% with flow rate of 1 $Lmin^{-1}$ at 200V; Fenton's reagent: Ferrous Sulphate ($FeSO_4$) – 6% solution, H_2O_2 – 30 % solution; H_2O_2: 30% w/v; UV: Pond-Clear UV6 Model UK with 6W bulb and 254nm.

The antibiotic wastewater was taken from an effluent anaerobic reactor treating real pharmaceutical wastewater and contains the following characteristics: COD, 1931 mgL^{-1}; TOC, 148.6 $mg.L^{-1}$; sulphate, 102.2 mgL^{-1} and pH, 8.2. Around 500ml samples of wastewater used in each experimental run and subjected to 3 h reaction period. Control sample (time zero) was also examined. "Free pH" used in each case and all experiments were repeated 3-fold and average values taken.

All chemical analysis was performed according to standard methods[13]: COD using Standard Method 5220C Closed Reflux Titrimetric Method, total organic carbon (TOC) using Standard Method 5310A and sulphate analysis by Dionex DX-100 Ion Chromatograph. Duplicate readings taken for each sample and then averaged. Statistical analysis using standard deviations of the means for each AOP were calculated to assess any significant differences in the data. T-testing carried out on 0 – 60 mgL^{-1} O_3/H_2O_2 and a 2-sample t-test was used to evaluate any significant difference between 6 - 20 mgL^{-1} H_2O_2/UV.

Results and discussion

Ozone/Hydrogen Peroxide

COD Removal

The results show a general pattern of increasing COD removal with increased H_2O_2 dose (Figure 1). T-tests show there is a significant difference between samples with initial and H_2O_2 added. It is evident, however, that an optimum dose exists which needs further examination when combining H_2O_2 and O_3 with UV. The results appear to show that at concentrations of 6 and 20 mgL^{-1}, percentage reduction of COD is highest at values of 50% for each. However, the standard deviations, calculated from the means of these experiment show that there is no significant difference between the COD removal efficiency for 6 to 20 mgL^{-1} of H_2O_2. Therefore, H_2O_2 concentrations of 6 and 20 mgL^{-1} were both further examined when considering UV combined AOPs to investigate which concentration is most effective; the upper limit or the lower limit.

At H_2O_2 doses of 60 mgL^{-1} a marked increase of 53% is witnessed (not shown on Figure 1) denoting an inhibitory effect. This is caused by the H_2O_2 accumulating in water and acting as a radical scavenger hence suppressing the removal of COD[14]. The increase in removal efficiency between the initial (zero) H_2O_2 dose and 2 – 30 mgL^{-1} doses proves that O_3 as an individual AOP is not as efficient as when combined with other oxidants. The formation of hydroxyl radicals will be greatly accelerated by the addition of H_2O_2 until a maximum (optimal) is met. The overall process of radical oxidation is much faster than direct oxidation by O_3 which has a much lower oxidation potential. The lowest COD value achieved here is 960 mgL^{-1}. This is still a high value if this AOP is to be considered the final method of treatment.

Figure 1

TOC Reduction

TOC removal efficiency (Figure 2) steadily increased with increased H_2O_2 dose and few inhibitory effects were witnessed as in the case of COD, the highest removal efficiency being 31.8% at 60 mgL^{-1} of H_2O_2. The lower percentage removal may be due to certain resistant organic compounds which may not be oxidised during TOC analysis and therefore any data recorded is a slight underestimate. The TOC removal efficiency for O_3 as a single AOP was 7.6% and it is therefore evident that the addition of H_2O_2 increases efficiency in this case. T-tests indicate that there is a significant difference between sample means demonstrating that TOC values decrease with increased H_2O_2 concentrations.

Figure 2

Sulphate Analysis

The wastewater examined had a low original content of sulphate at 102.2 mgL^{-1}. The odour of the untreated wastewater was particularly strong. It had undergone anaerobic digestion previously and so it was evident that the anaerobic micro-organisms had reduced any sulphate to sulphide meaning a strong hydrogen sulphide odour/gaseous emission. The AOP results in an increased level of sulphate, with a maximum 45% increase at 60 mgL^{-1}. Levels of 159.9 to 184.5 mgL^{-1} were recorded after 3 h contact time (Figure 3).

Figure 3

Ozone/Hydrogen Peroxide/UV

Having found two possible optimum concentrations of H_2O_2 when combined with O_3 (6 and 20 mgL^{-1}), it is possible to investigate the efficacy of this system and examine whether the addition of UV can have a positive effect on COD and TOC reduction and further investigate sulphate increase data. Figure 4 shows the comparative COD data and by calculating the COD removal efficiency for each sample and taking the mean, the effect UV has as an AOP can be seen more clearly.

The results show clearly that UV with 6 mgL^{-1} H_2O_2 produces the greatest COD reduction overall at 70% (Figure 5). Second to this is the UV, H_2O_2 6 mgL^{-1} and O_3 system at 66%. It is evident from the graph that the lower dose of H_2O_2 (6 mgL^{-1}) has a more positive effect on the efficiency of the AOP than the higher dose (20 mgL^{-1}). This implies that an optimum dose also exists when H_2O_2 is combined with UV. Statistically, no significant difference was apparent between the means of samples UV/H_2O_2 6 mgL^{-1} and UV/H_2O_2 20 mgL^{-1}. It is apparent, however, due to the nature of the data set that a difference does exist if the small % differences between all samples investigated are taken in to account.

Generally, the COD removal efficiency is much higher with the addition of UV than with H_2O_2 and O_3 alone. It is apparent that if COD values of lower than 1000 mgL^{-1} are required, UV must be applied to ensure effective COD removal for this particular wastewater. However, the key is accelerating the formation of the hydroxyl radicals. UV/H_2O_2/O_3 is the strongest form of oxidation although for this particular wastewater, UV and H_2O_2 is sufficient to increase the efficacy of the AOP. The final COD values recorded in this case range from 580 to 700 mgL^{-1}. Longer contact times of the wastewater effluent with UV should allow for COD values to be recorded at <500 mgL^{-1}.

Figure 4
Figure 5

Total Organic Carbon

Figure 6 shows the pattern of TOC decrease over time and the averaged values of TOC removal efficiency show more clearly the effect UV has on TOC reduction. Figure 7 shows that under UV and a H_2O_2 dose of 6 mgL^{-1}, a 56.0% TOC removal can be achieved. This is slightly increased to 56.6% with additional O_3 treatment. T-tests show a significant difference between samples UV/H_2O_2 6 mgL^{-1} and UV/H_2O_2 20 mgL^{-1}. Once more the TOC removal efficiency overall are higher than with only the H_2O_2 and O_3 combination processes. TOC values of less than 70 mgL^{-1} are recorded via O_3/H_2O_2/UV combined AOPs. These levels may be lowered with longer reaction times with UV and O_3.

Figure 6
Figure 7

Sulphate Analysis

Figure 8 shows that the greatest increase (%) in sulphate is produced when UV, H_2O_2 and O_3 are combined (with 6 mgL^{-1} of H_2O_2); an increase of 44% is witnessed. The COD and TOC values indicate that increase levels of oxidation are achieved by the addition of UV. This is evident by comparing the UV-combined AOP sulphate results with the O_3/H_2O_2 AOP sulphate results where slightly higher figures are witnessed under UV treatment than O_3/H_2O_2. Interestingly, UV as a single treatment does not increase sulphate levels as significantly as with other AOPs.

Figure 8

Fenton's Reagent

Due to time constraints, the Fenton's reagent reaction was applied to the wastewater and stirred continuously for three hours; ideally longer reaction times are required with the end-point of the reaction signified by a distinct colour change[15]. The reaction was duplicated for purposes of accuracy. A third experiment could not be undertaken at this stage. Fenton's reagent has shown the ability to reduce COD levels to 890 mgL^{-1}; a 54% decrease. The most efficient O_3/H_2O_2 combined AOP achieved a 50% COD removal and the most efficient UV - combined AOP achieved a 70% removal. The efficacy of the Fenton's system is therefore slightly better than O_3/H_2O_2 systems for this particular wastewater. Further research on Fenton's reagent would allow for reaction times to be further investigated and dose requirements ($FeSO_4$, H_2O_2) to be experimented with, in order to find optimal levels. From the above results it can be concluded that the four most efficient AOPs were as follows: O_3/H_2O_2 6 mgL^{-1}, UV/ H_2O_2 6 mgL^{-1}, UV/O_3/H_2O_2 6 mgL^{-1} and Fenton's reagent (Table 1). Figure 9 shows that overall, considering COD removal, TOC removal and sulphate increase, the AOP that is deemed to be most efficient is UV, O_3 and H_2O_2 6 mgL^{-1}, followed closely by UV and

H_2O_2 6 mgL^{-1} alone. This is shown by an even distribution within the bars.

Table 1
Figure 9

General discussion

The COD values overall show the amount of oxygen consumed in the oxidation of organic and oxidizable inorganic materials in the wastewater. Although large COD removal efficiency were achieved, the high initial COD value (1931 mgL^{-1}) means that the lowest COD value achieved via AOPs in this case, is only 560 mgL^{-1}. This is still high if AOPs were applied post-anaerobic digestion as the final stage of the wastewater treatment process. The most efficient system proved to be UV combined with 6 mgL^{-1} of H_2O_2. The least efficient system was O_3 alone and O_3 with 2 mgL^{-1} of H_2O_2. As mentioned previously, an increase dose of 60 mgL^{-1} H_2O_2 exerted an inhibitory effect on the AOP. There is a theory that O_3 AOPs alone will be equally as efficient as combined systems. This is due to the hypothesis that O_3 can breakdown the organic waste which will yield H_2O_2 and therefore ozonation can take place without the extra addition of H_2O_2. The results here show that O_3 alone is not as effective without H_2O_2, for this particular wastewater. It is possible that O_3 ability to yield its own H_2O_2 is at a much slower rate than if H_2O_2 is added artificially to the system. Overall, the increase in COD removal indicates an increase in the biodegradability of the antibiotic wastewater but it is evident that either: longer reactions times are required to further remove COD or further treatment of the wastewater is required following the AOP to further decrease the COD levels of the water e.g. flocculation.

The TOC percentage removals quantify the proportion of organic material that has been oxidised during the AOP. The largest TOC removal efficiency was reported during the O_3/H_2O_2/UV APOs, where a 56.6% removal was recorded. This particular AOP has been proven to be particularly intense in the treatment of various different industrial wastewaters. The efficacy of the AOP is largely dependent on the type of wastewater being treated. In this case, it is evident, that due to the initial strength of the wastewater (i.e. high TOC and COD levels), high strength or highly intense treatments are required if TOC levels are to be removed to a suitable standard. During treatment with O_3 and low concentrations of H_2O_2, the TOC content of the samples was not reduced by any significant amount; only 8.1% with O_3 and H_2O_2 2 mgL^{-1}. An increase in H_2O_2 concentration did increase TOC removal but it wasn’t until the introduction of UV that any significant changes in the wastewater samples were witnessed.

In the post-anaerobic digestion, sulphur is mainly present as sulphide and sulphites. During AOPs the sulphur is converted to sulphates and it was observed an overall increase in sulphate concentration. The general pattern being; the more powerful the oxidation, the higher the concentration of sulphate. In this case the most powerful AOPs are UV/H_2O_2 and UV/O_3/H_2O_2 which result in a sulphate concentration increase of 56 and 56.6%, respectively. This also explains the reduction in odour due to the mineralization of hydrogen sulphide to sulphate under aerobic/O_2 rich conditions experienced during AOPs.

Conclusions

The treatment of the antibiotic wastewater with various different AOP combinations proved to be successful in the removal of COD and TOC. An increase in sulphate concentrations was also witnessed. H_2O_2 concentrations were experimented with for the O_3/H_2O_2 combined AOP. It was obvious from the COD data that an optimal dose > 60 mgL^{-1} existed and 6 mgL^{-1} of H_2O_2 produced the most efficient COD and TOC removals overall. Although O_3 is able to produce H_2O_2 alone by the breakdown of organic matter, it was concluded that the addition of H_2O_2 artificially to the system greatly accelerated the formation of the hydroxyl radicals necessary for the efficacy of the system and allowed shorter contact times.

UV proved to be the most effective AOP when combined with the optimum dose of H_2O_2 (6 mgL^{-1}) and O_3/H_2O_2 together. The UV/H_2O_2 system proved to be most efficient with a 70% COD removal and 56% TOC removal. COD levels of below 700 mgL^{-1} were achieved and TOC levels of below 70 mgL^{-1} were achieved. Fenton’s reagent proved to have some positive effect on the biodegradability of the antibiotic wastewater although it is evident that further experimentation is required concerning reaction times and dosing requirements (H_2O_2 and $FeSO_4$). It was however one of the most successful AOPs and avoids the extra costs required for generation of UV and O_3. COD removals of 54% and TOC removals of 26% were recorded.

Sulphate concentrations increased during all AOPs. The strong smell of the wastewater effluent demonstrated a large concentration of hydrogen sulphide present after the application of anaerobic digestion. Odour was reduced considerably through advanced oxidation as the hydrogen sulphide was converted to sulphate. This was supported by the data recording a considerable increase in sulphate concentration for each AOP.

Acknowledgments

The authors thank University of Newcastle, UK and Universiti Teknologi Malaysia for funding and facilitating this project.

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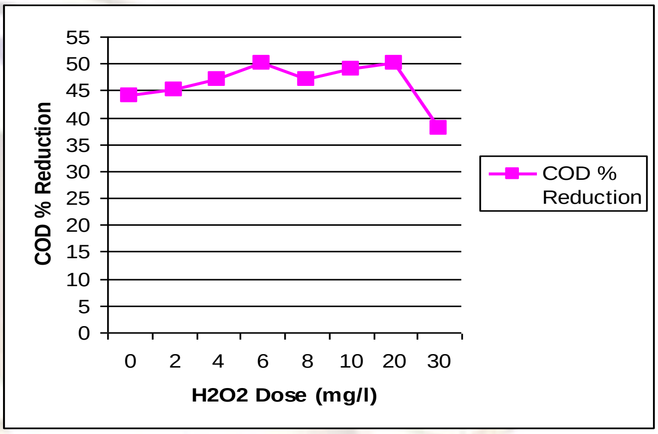

Figure 1: COD reduction for O_3 and varied concentrations of H_2O_2

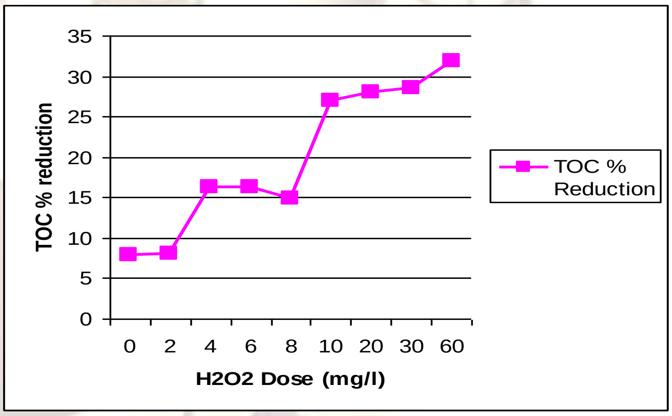

Figure 2: TOC reduction for O_3 and varied doses of H_2O_2

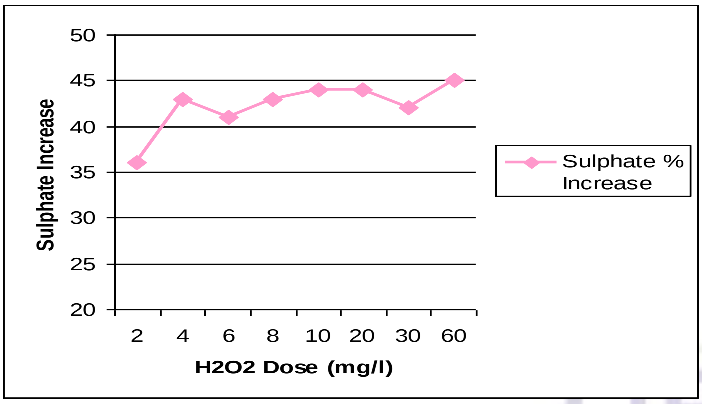

Figure 3: Sulphate profile for O_3 and varied concentrations of H_2O_2

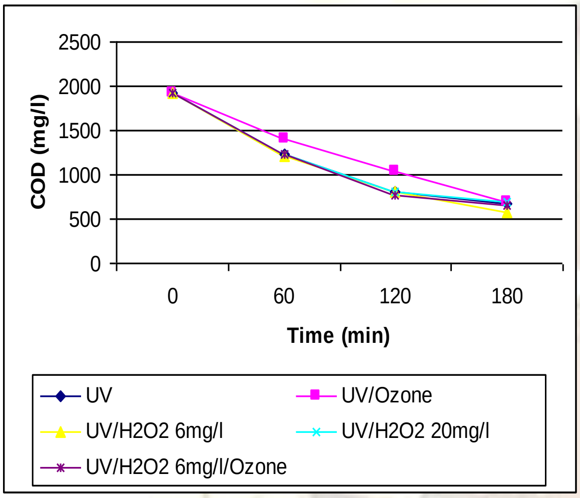

Figure 4: COD profile for UV combined AOPs

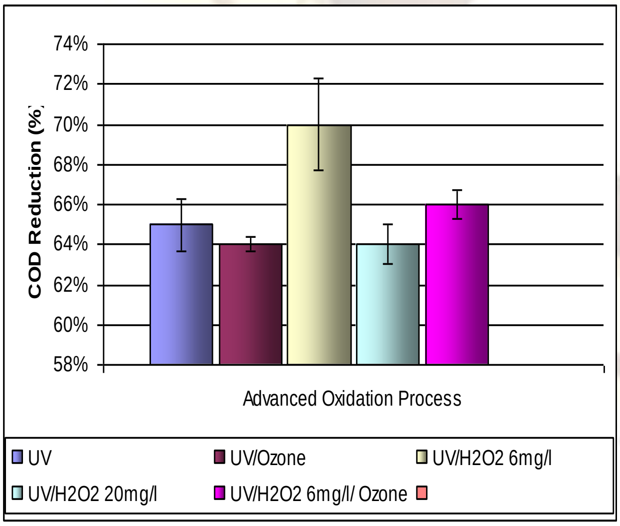

Figure 5: COD reduction profile for UV combined AOPs

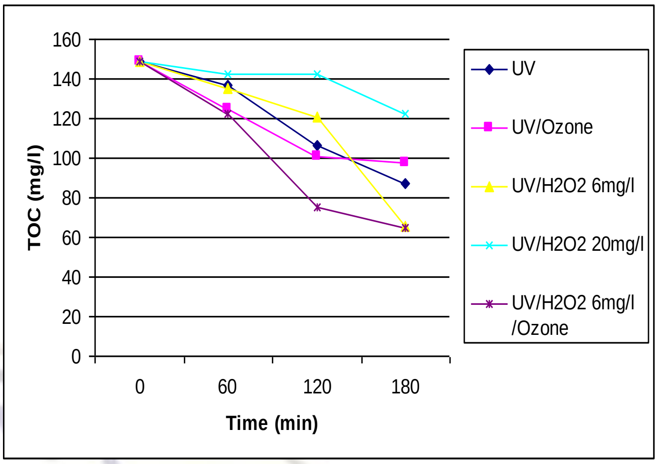

Figure 6: TOC profile for UV combined AOPs

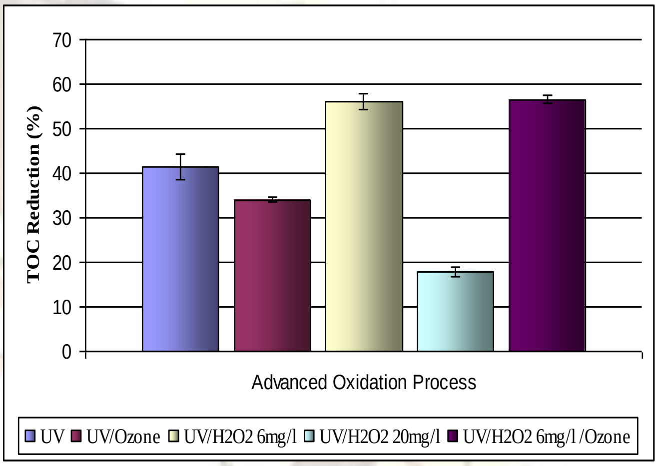

Figure 7: TOC reduction profile for UV combined AOPs

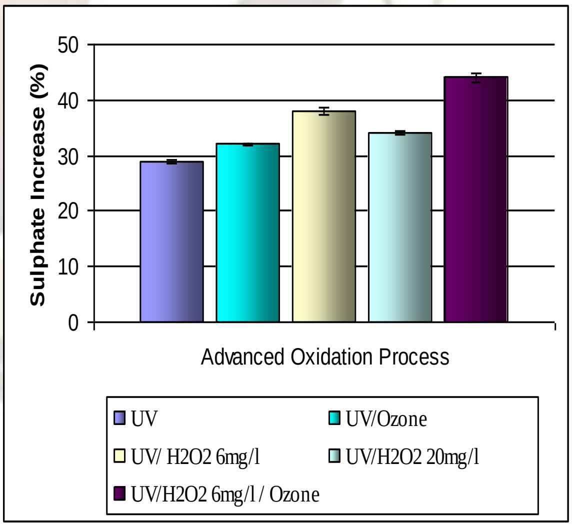

Figure 8: Sulphate profile for UV combined AOPs

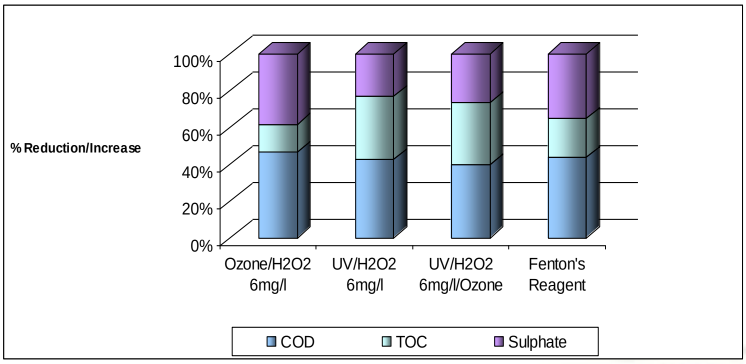

Figure 9: Comparative profile for the four most effective AOPs

Table 1: Comparative data for four of the most efficient AOPs

AOP	COD Removal (%)	TOC Removal (%)	Sulphate Increase (%)
O_3/H_2O_2 6 mgL^{-1}	50	16.2	41
UV/H_2O_2 6 mgL^{-1}	70	56	38
$UV/O_3/H_2O_2$ 6 mgL^{-1}	66	56.6	44
Fenton’s reagent	54	26	43