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Pre-ozonation of aqueous azo dye (Acid Red-151) followed by activated sludge process

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Abstract

In this study, the efficiency of the integrated process was investigated in which the pre-ozonation step was followed by activated sludge process (ASP) in treating the aqueous Acid Red-151 (AR 151) solutions. The percent dye removal in the integrated process was found to be 47% for a pre-ozonation time of 30 min, instead of 25% in the singly ASP without pre-ozonation. The treatment efficiency of this process could be higher if the pre-ozonation time of 120 min yielding maximum enhancement of biodegradability at a peak value of BOD_5/COD ratio were used before the biological treatment process.

Keywords: Activated sludge process; Pre-ozonation; Acid Red-151; AR 151 ozonation; Enhancement of biodegradability; Integrated process of chemical and biological oxidations

1. Introduction

Wastewaters from textile industry are toxic, mostly non-biodegradable and also resistant to destruction by physico-chemical treatment methods [2,3]. Moreover, strong color of textile wastewaters is reported to have inhibitory effects on microbial populations and their activities in the aquatic environment. Chemical oxidation processes are good alternatives in enhancing the biodegradability of wastewaters for their further treatment in a biological process [1,4–6].

Ozonation is capable of decomposing the highly structured dye molecules into smaller ones, which can easily be biodegraded in an activated sludge process [2]. Also, ozonation process was found to be very effective in decolorization of textile wastewaters by many researchers [7–9]. Ozonation was not economically feasible to oxidize many compounds completely to CO_2 and H_2O. On the other hand, partial oxidation by ozone was suggested by several researchers [5,6]; because partial oxidation of these compounds yielded biodegradable products, which were subsequently treated by conventional biological processes. Arslan-Alaton [10] investigated the pre-ozonation of 14 different reactive dyestuff hydrolysates at alkaline pH to assess possible relationships between ozone transfer efficiency, first order decolorization kinetics, release of initially complexed heavy metals and relative changes in the biodegradability of the partially oxidized dye waste samples. Pre-ozonation studies to enhance the biodegradation of dichlorodiethyl ether (DCDE) and of the aqueous solutions of 2,4-dichlorophenol were reported by Kaludjerski and Gurol [11] and by Contreras et al. [12], respectively. Shiyun et al. [13] studied the ozonation of naphthalene sulfonic acids in aqueous solutions; elimination of COD, TOC, and increase of the biodegradability were reported.

Activated sludge process (ASP) is one of the most widely used biological processes in wastewater treatment. Activated sludge contains different types of microorganisms (MOs) that utilize organic substances as food supply and convert them into biological cells. However, non-biodegradable substances (dyes) in textile wastewaters (WWs) are toxic to ASP. Although it was generally assumed that azo dyes can be degraded only anaerobically, recent studies showed that some dyes were less recalcitrant in aerobic environment than others [14]. Azoreductase enzyme from *Caulobacter subvibrioides* strain C7-D was investigated, the effect of dye concentration on enzymatic activity was evaluated [15]. Eleven azo dyes were used to check for inducibility of azoreductase activity. It was found that azoreductase acted specifically on certain azo compounds, the reduction efficiency being dependent on the structural features of the substrates. Electron withdrawing sulfo (SO^{3-}) groups on the phenyl group

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Nomenclature

ASP	activated sludge process
ASR	activated sludge reactor
BOD_5	biological oxygen demand (mg O_2/L)
C_{dye}	dye concentration (mg/L)
$C_{dye,i}$	initial dye concentration (mg/L)
COD	chemical oxygen demand (mg O_2/L)
GAC	granular activated carbon
MLSS	mixed liquor suspended solid concentration (mg/L)
MO	microorganism (plural: MOs)
OTASP	once-thro activated sludge process
PACT	powdered activated carbon treatment
S	substrate concentration (mg COD/L)
t	time (min)
TOC	total organic carbon (mg C/L)
WW	wastewater (plural: WWs)
X	biomass concentration (mg MLSS/L)

appeared to accelerate the reaction for Acid Red-151 (AR 151), while due to their dual role, of being charged groups in proximity to the azo group, they hindered the enzymatic activity. Since AR 151 has two azo bonds which were reduced at different concentrations resulting in two distinct peaks in velocity versus concentration plot. The concentrations at these peaks were 3 and 20 μM [15]. Kumar et al. [16] investigated the decolorization, biodegradation and detoxification of Direct Black-38, a benzidine based azo dye, by a mixed microbial culture isolated from an aerobic bioreactor treating textile wastewater. The studies revealed a biotransformation of Direct Black-38 into benzidine and 4-aminobiphenyl followed by complete decolorization and biodegradation of these toxic intermediates by the culture. From cytotoxicity studies, it was concluded that detoxification of the dye took place after degradation of the toxic intermediates by the culture; pre-ozonation was not used in this contribution. Ledakowicz et al. [17] reported that even very long contact time of activated sludge with the dyestuff solution (10 days) did not result in complete decolorization. On the other hand, ozonation, well known as an effective decolorization method, did not decrease the COD to a great extent for which a biological process following chemical oxidation was advised. Interestingly, the experimental value of yield coefficient of microbial growth (Y) remained practically constant at 0.5 for the biodegradation of the un-ozonated as well as the pre-ozonated textile wastewater. Forgacs et al. [18] reported in their review paper that 11 azo dyes, out of 18 dyes studied, passed through the ASP practically untreated, Acid Red-151 being one of them. Only three of them (Acid Orange 7, Acid Orange 8 and Acid Red 88) were biodegraded [19]. Therefore, ASP by itself was not sufficient in the treatment of textile effluents. An integrated process of pre-ozonation and subsequent treatment of generated biodegradable products by ASP would be more efficient and economical. It was reported that in some cases, the intermediate oxidation products formed during pre-ozonation might be more toxic to the MOs than the original dye molecules in the un-ozonated wastewater [5]; this point showed the necessity of acclimating the seed bacteria to the pre-ozonated wastewater before feeding it into ASP. The individual and integrated processes of biological and chemical oxidations of olive oil wastewaters were performed by Benitez et al. [4]. For individual ozonation process, the conversion of chemical oxygen demand (COD) ranged between 17 and 28% depending on the operating conditions, also average reduction of aromatics was proposed as 76%. They examined the integrated process separately, and obtained total COD conversion of 84.6% for the process of pre-ozonation followed by aerobic degradation. Ozone pre-treatment enhanced the subsequent aerobic process, probably by removing some inhibitory compounds. In another study [6], ozonation of pulp mill effluent prior to activated sludge treatment was investigated; for this, parallel biological reactors were used to compare the results of the pre-ozonated and un-ozonated wastewaters. They observed 60% reduction in COD and more than 80% reduction in BOD with whole mill effluent by ASP only. These removal percentages increased up to 85 and 91% with pre-ozonated effluent for COD and BOD, respectively. In the study by Costa and Marquez [20], textile dye removal from a dyeing wastewater was investigated in an activated sludge lab plant with powdered activated carbon treatment (PACT). Quantitatively, the amount of dye (Acid Orange 7) degraded by MOs per biomass unit was found to be about 100 times higher than the dye adsorbed on activated carbon per adsorbent mass unit, and this was about 10 times higher than the amount of dye adsorbed on biomass per biomass unit. Therefore, they assumed basically a biological process in their modeling study, because 99% of the dye removal was due to microbial degradation. On the other hand, it was proven in the sole adsorption studies that granular activated carbon could bind acid dyes and the kinetics of adsorption was elucidated by Walker and Weatherley [21,22]. As it can be deduced from the literature results that further studies are needed for the dye AR 151; therefore, the objective of this study was to investigate the treatment of aqueous solutions of an azo dye, namely, Acid Red-151, by the integrated process of pre-ozonation followed by ASP.

2. Experimental

2.1. Experimental strategy

Experiments were carried out in three main parts:

(i) continuous pre-ozonation of AR 151 solutions to investigate the decolorization, COD removal and the enhancement of biodegradability during 180 min of ozonation time [1];
(ii) batch ozonation of AR 151 solution under previously determined controlled conditions [23] to prepare the stock of pre-ozonated dye solution to be fed into the OTASP;
(iii) treatment of pre-ozonated and un-ozonated AR 151 solutions in OTASP.

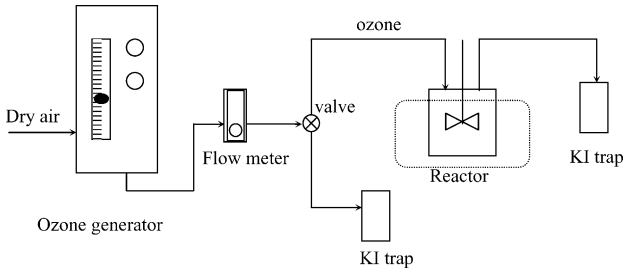

Fig. 1. Set-up for pre-ozonation experiments.

2.1.1. Set-up for pre-ozonation of AR 151 and summary of the results obtained in this part

Experimental set-up is shown in Fig. 1. This part of the study was previously reported by the authors [1]; therefore, it will be briefly mentioned here. Aqueous AR 151 solutions, at different initial dye concentrations of 100, 250, 500 and 1000 mg/L, were ozonated for 180 min at constant pH (7) and temperature (25 °C). The chemical structure of AR 151 is given in Fig. 2. The resulting data of the dye, dissolved (residual) ozone, consumed ozone, color, COD and 5-day biological oxygen demand (BOD_5) values at different times of ozonation were plotted [1]. The peak value of the BOD_5/COD ratio (indicating the peak enhancement of biodegradability) occurred at an ozonation time of 120 min always; it did not change with the initial dye concentration; however, the magnitudes of these peaks varied in the range of 0.028–0.35 for the studied initial dye concentrations being in the range of 1000–100 mg/L, respectively. The effect of pre-ozonation on biodegradability, decolorization and COD removal is discussed shortly in the following section of the paper.

2.1.2. Batch ozonation experiments prior to OTASP

This part of the experimental work was undertaken to prepare the feed solution of ozonated aqueous azo dye (AR 151) for OTASP under controlled conditions, since the optimum COD removal conditions had been determined as $C_{dye,i} = 20$ mg/L, pH 2.5 and $T = 25$ °C in the same set-up [23].

In each run, 1 L of distilled water at a constant pH of 2.5 was ozonated in a reactor until the maximum attainable ozone concentration (that is 0.04 mmol/L) in water was achieved. At that moment, a sample was withdrawn from the reactor into the Indigo reagent plus pH 2 buffer solution for the determination of initial dissolved ozone concentration [23]. Then, inlet ozone-gas flow to the reactor was stopped, and immediately, 20 mg AR 151 dissolved in water was added into the reactor, and 30 min of ozonation was allowed. At the end of this time, two samples were withdrawn for measuring the final dye and ozone concentrations in the solution. Before transferring the contents of the reactor into a glass container of 10 L volume, the remaining

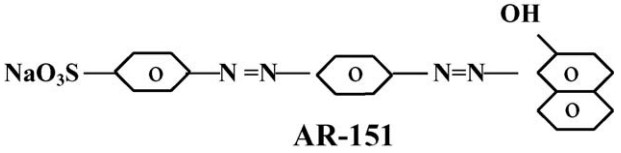

Fig. 2. Chemical formula of Acid Red-151 (AR 151).

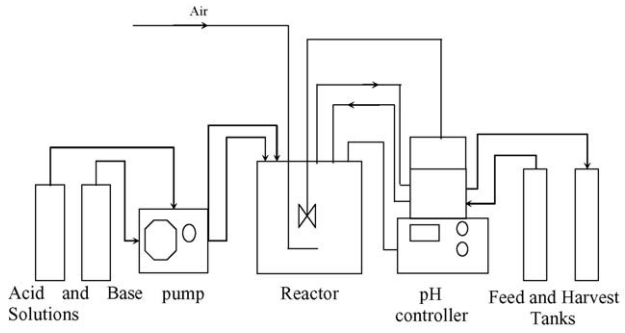

Fig. 3. Experimental set-up for once-thro activated sludge process.

dissolved ozone (if exists) was stripped from the pre-ozonated dye solution by nitrogen gas for 20 min. This way, the possible interference of any dissolved ozone in the feed into OTASP was eliminated. By ozonating 20 mg/L AR 151 solutions in several batches as explained above, a stock of pre-ozonated solution at a final AR 151 concentration of 6.2 mg/L was prepared. Lastly, the pH of the stock solution was adjusted to 7 using KH_2PO_4–NaOH buffer solution; because a neutral pH was necessary in the activated sludge reactor (ASR) for a successful biological process.

2.1.3. Set-up for once-thro activated sludge process (OTASP)

In the set-up of OTASP as given in Fig. 3, a continuously stirred glass tank reactor with a working liquid volume of 2 L was used. The pH of the medium was kept constant in the range of 6–8 by a pH controller; two peristaltic pumps (Cole Parmer) were used to feed 0.1N H_2SO_4 or 0.1N NaOH automatically to the reactor when the pH exceeded the limits. Aeration was provided by a compressor. The influent to the reactor was fed and the effluent from the reactor was withdrawn by peristaltic pumps. The reactor was well mixed by a magnetic stirrer at 500 rpm.

2.2. Acclimation of microorganisms to AR 151 and experiments in OTASP

Two hundred and twenty five milliliter of fresh seed MOs, obtained from Ankara Metropolitan Water and Sewage Works (Ankara Su Kanalizasyon İdaresi-ASKİ), was placed into a 2 L Erlenmeyer flask; then sufficient amount of synthetic wastewater (WW) with a composition given in Table 1 was added into this flask to make the total volume 1500 mL. Aeration and mixing was provided for 48 h for the growth of healthy microorganisms. Afterwards, 2.25, 5.51 and 6.16 mg of Acid Red-151 were added into the flask sequentially, at 48 h intervals using a fill and draw procedure. During the acclimation procedure, turbidity measurements were performed by a Hach Dr/2010 spectrophotometer at 860 nm, and the turbidity values were recorded in Formazin Attenuation Units (FAU). A gradual increase in the turbidity of the samples from the flask, during the fill and draw procedure, was considered as a proof of the successful acclimation of the MOs in the medium.

Acclimated MOs were placed into the activated sludge reactor and the volume was completed to 2 L by adding 500 mL of

Table 1
Synthetic wastewater composition

Constituents	Concentration (mg/L)
Proteose-peptone	1221.7
NaCl	407.4
K_2HPO_4	44.6
Na_2SO_4	44.6
$CaCl_2{\cdot}2H_2O$	3.7
$FeCl_2{\cdot}2H_2O$	3.7
$MgCl_2{\cdot}6H_2O$	3.7
$CuSO_4$	0.076
$MnSO_4$	0.057
$CoSO_4$	0.049
$ZnSO_4$	0.046
NaOH	0.008

synthetic WW. The reactor was operated batch wise for 72 h to allow the growth of MOs. Then, the continuous process was started by feeding the ASR with a mixture of synthetic WW (Table 1), and the pre-ozonated AR 151 stock solution (at an effluent dye concentration of 6.2 mg/L from the pre-ozonation step). The volume percent of the synthetic WW in the feed stream into the OTASP was almost 30%, corresponding to a volume ratio of 2/7, to provide the necessary nutrients for MOs. The inlet and outlet flow rates were adjusted in order to obtain a hydraulic residence time (HRT) of 50 h. Samples taken from the effluent of the ASR were used in the measurements of substrate (COD), dye and biomass (mg MLSS/L) concentrations and turbidity. In analyzing a sample, after measuring its turbidity, it was centrifuged and its supernatant was used in the measurements of substrate and dye concentrations. The run was continued until the steady state was reached. Biomass concentration was used as an indicator of the steady-state condition in these experiments. When it remained constant with respect to time, the steady state values of all the parameters were recorded and the process was stopped.

OTASP experiment was repeated by using un-ozonated AR 151 solution as the feed to the process at the same initial dye concentration. For this purpose, un-ozonated AR 151 solution at a start-up concentration of 20 mg/L was diluted almost four times to provide a feed into the OTASP at almost the same inlet dye concentration of the pre-ozonated feed. By dilution, the toxicity of the un-ozonated dyeing wastewater was reduced. Thus, it would be possible to compare the ASP treatment efficiencies between the runs with the pre-ozonated and the un-ozonated feed solutions of AR 151.

2.3. Analytical methods

Dye concentrations in the solution were determined spectrophotometrically in the visible region at 512 nm corresponding to maximum absorbance wavelength of AR 151 by using a Hitachi UV–vis double beam U-3010 spectrophotometer. Due to the generation of colorless oxidation products, no interference at 512 nm wavelength was detected; therefore the absorbance measurements were found to be reliable. Also Demirev and Nenov [24] reported that the oxalic acid was the final by-product of ozonation of both of the two azo dyes, namely, Schwarz GRS and Orange Acid 8. The peak of oxalic acid was observed at a wavelength of 250 nm. Based on the literature information [25] concerning the ozonation by-products of similar dyes, Demirev and Nenov [24] could not detect benzenesulfonate, formaldehyde, acetaldehyde, formic acid and acetic acid after an intensive search they carried out by means of gas chromatograph and liquid chromatograph techniques. Therefore, it can be assumed in this research too that no interference between the ozonation by-products and the original dye (AR 151) at 512 nm was probable. With the same instrument, the residual ozone concentrations in water were determined by Indigo method [26] at 600 nm. COD analysis was performed using a thermoreactor (WTW-3000) and Hach DR-2010 spectrophotometer according to the Standard Methods [27]. Also for color and turbidity measurements, Hach DR-2010 spectrophotometer was used. A gravimetric procedure was used for the MLSS analysis [27].

3. Results and discussion

3.1. Effect of pre-ozonation on biodegradability, decolorization, and COD removal

The amount of ozone consumed leading to the maximum BOD_5/TOC value varied with the target compounds, lying between 2.3 and 3.8 mg per mg of initial TOC for nitrophenols, and between 1.3 and 1.7 mg for synthetic dyes [5]; the time value leading to maximum biodegradability was reported for each specific dye type. For example, it was found as 1.5–2 h for organics, 1.5 h for Orange-II and 4–5 h for Congo Red [5].

In the present case, the amount of ozone consumed for achieving the maximum BOD_5/COD ratio for AR 151, varied between 0.0006 and 0.0017 mg ozone per mg COD for the dye concentrations in the range of 100–1000 mg/L. Since the system was a continuous ozonation one, therefore the ozone concentration was not limited in the reaction medium; as a result, increasing the ozone dosage in the inlet gas stream would not be expected to change the time required for the achievement of the maximum BOD_5/COD ratio. The obtained pre-ozonation time of 2 h yielding the peak value of the BOD_5/COD ratio for AR 151 solutions was in the same order of magnitude and in agreement with the reported values in the literature [5]. Representative figures for the variations of biodegradability, dye concentration (decolorization), and COD with the pre-ozonation time are given in Figs. 4–6, respectively, for the aqueous solutions of AR 151 containing different inlet dye concentrations (in the range of 100–1000 mg/L).

3.2. Effect of pre-ozonation on the treatment efficiency of OTASP

In an ASP without recycle (OTASP), it is usually difficult to maintain a high biomass concentration in the reactor, which will provide a more efficient treatment for the wastewater. In such a system, the washout time is greater than that of the one with a recycle [28]. Therefore, in the present activated sludge system, 50 h of hydraulic residence time was chosen compared to the

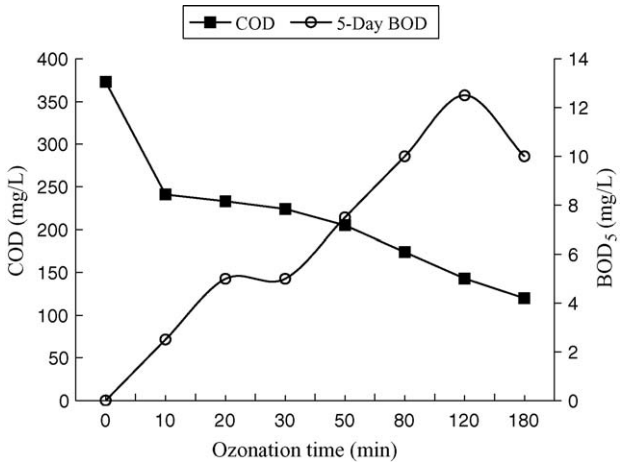

Fig. 4. COD and BOD_5 variations with ozonation time for an initial 250 mg/L AR 151 solution during continuous ozonation.

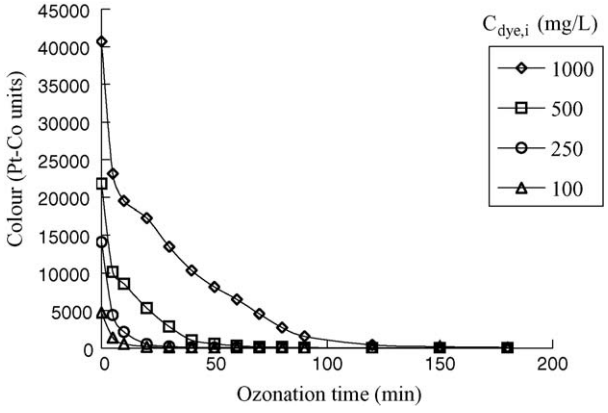

Fig. 5. Decolorization data during continuous ozonation of AR 151 solutions at different $C_{dye,i.}$

conventional value of 3–5 h to prevent the washout condition. Since the HRT is equal to the sludge age (or approximately, the mean cell residence time) in OTASP, 50 h (almost 2 days) of sludge age is still not a high value compared to the sludge ages,

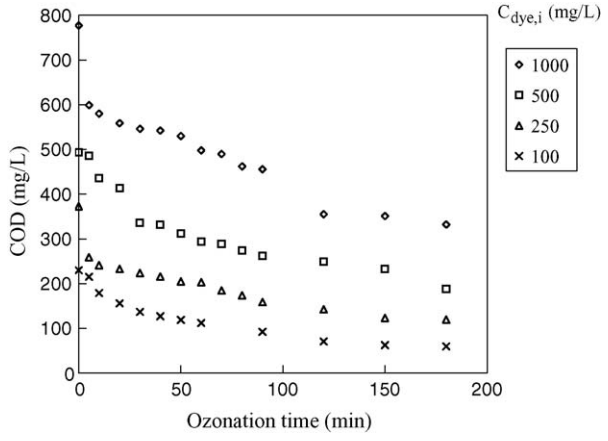

Fig. 6. COD vs. ozonation time in continuous ozonation of AR 151 solutions at different $C_{dye,i.}$

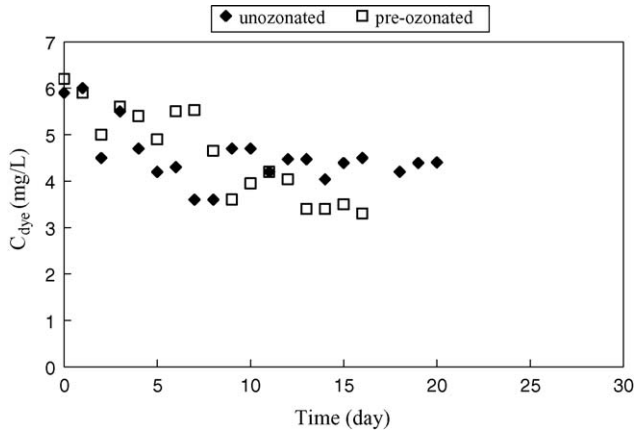

Fig. 7. Unsteady-state data of the dye concentrations for the feeds of un-ozonated ($C_{dye,i}$ = 5.9 mg/L) and pre-ozonated AR 151 solutions ($C_{dye,i}$ = 6.2 mg/L) in OTASP.

in the range of 10–15 days, in a conventional ASP. Thus, the endogenous phase of "microorganism growth curve" in which death of cells occurs, is not favored to a high extent [28].

The unsteady-state data showing the variations of substrate, biomass, and the dye concentrations with respect to time until they become almost constant at the steady-state condition are given in Figs. 7–9, for the pre-ozonated and the un-ozonated AR 151 feed solutions into the OTASP. As can be seen in Fig. 7, the percent dye removals obtained are 47 and 25% for the former and the latter cases, respectively. The positive effect of ozonation in enhancing the biodegradability is obviously seen from the higher treatment efficiency of 47% in the OTASP with the pre-ozonated feed. Considering the overall treatment efficiency (based on dye concentration) with respect to the inlet dye concentration of 20 mg/L to the pre-ozonation step, it is not possible to make any comparison between the integrated process and

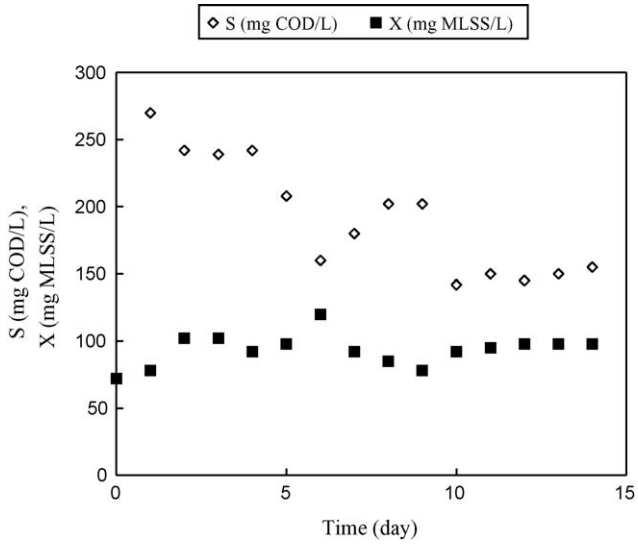

Fig. 8. Unsteady-state data for the feed of pre-ozonated AR 151 solution into OTASP with operating conditions of COD_i = 438 mg/L, $C_{dye,i}$ = 6.2 mg/L, HRT = 50 h, pH 7.

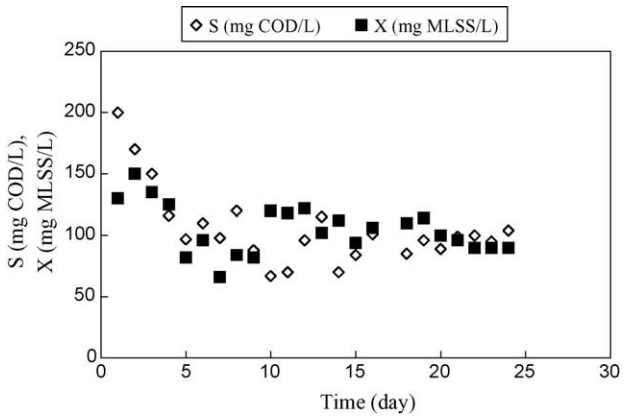

Fig. 9. Unsteady-state data for the feed of un-ozonated AR 151 solution into OTASP with operating conditions of $COD_i = 381$ mg/L, $C_{dye,i} = 5.9$ mg/L, HRT = 50 h, pH 7.

the sole OTASP. It can be said that the sole OTASP has the disadvantage from the start due to the need for dilution of the un-ozonated original AR 151 dye solution from 20 to 5.9 mg/L, to reduce its toxic effect on the MOs. Because four times dilution is equivalent to an increase in the OTASP capacity by a factor of 4; thus in turn the total cost (fixed + operating costs) will be much higher in the sole OTASP than that of the integrated process of chemical and biological oxidations. Under these circumstances, pre-ozonation of the dye solutions for a longer period of time (120 min in this case) in order to enhance the biodegradability to a sufficient level, will be worthwhile to consider for achieving higher treatment efficiency in the integrated process, most probably at the lower overall cost. It was measured that the contribution of even 1221.7 mg/L proteose peptone to the absorbance at 512 nm was 0.01 which was about 9% of the absorbence measured for the approximate outlet dye concentration of 3 mg/L from the OTASP, and about 5% of the absorbance value corresponding to 6 mg/L dye concentration, which was the approximate value for the inlet dye concentration to the OTASP. Actually, the concentration of the proteose pepton in the feed mixture of synthetic WW with the dye solution is much lower than 1221.7 mg/L, therefore the percentage error can be expected even smaller than 5% on the average. Therefore, the measured dye concentrations can be accepted as quite accurate in terms of the measured absorbance values, and it can be assumed that the contribution of proteose pepton to the absorbance is negligible. Considering the effect of adsorption on the dye removal, according to the results reported by Costa and Marquez [20], quantitatively the amount of an acid dye degraded by MOs per biomass unit was found to be about 100 times higher than the dye adsorbed on the powdered activated carbon per adsorbent mass unit, and this was about 10 times higher than the amount of dye adsorbed on biomass per biomass unit. Therefore, they assumed basically a biological process in their modeling study, because 99% of the dye removal was due to microbial degradation. Therefore, the effect of adsorption seems to be negligible compared to the dye degradation by the culture.

The treatment efficiencies of the pre-ozonated and un-ozonated feed cases based on the overall substrate concentration (total effluent COD due to synthetic wastewater, original dye and reaction by-products), can also be compared. As it can be observed from Figs. 8 and 9, the initial substrate concentration in the pre-ozonated WW is higher than that in the un-ozonated WW for almost the same inlet dye (AR 151) concentration of around 6 mg/L. This could be attributed to the additional COD due to the accumulation of the main ozonation by-product, namely, oxalic acid, which was resistant to further oxidation, as concluded by Demirev and Nenov [24]. As a result, the inlet COD of 438 mg O_2/L was reduced to 150 mg O_2/L for the pre-ozonated WW, and it was reduced from 381 to 104 mg O_2/L for the un-ozonated WW, the treatment efficiencies being 66 and 73%, respectively. The lower treatment efficiency obtained with the pre-ozonated WW might be due to the ozonation by-product of oxalic acid being more resistant to the biological degradation. However, the steady-state condition was reached at a shorter time (14 days) in the case of pre-ozonated feed to the OTASP due to the acclimation of MOs than that reached in the case of un-ozonated feed which took more than 25 days. This also showed that if the feed were pre-ozonated for a time period of 120 min for the achivement of the maximum biodegradability before feeding to the OTASP, then the treatment efficiency would be expected to be much higher. But here the disadvantage of four times dilution of the un-ozonated wastewater to bring the two types of WWs to almost the same initial dye concentration should not be forgotten. As a conclusion, pre-ozonation before the ASP still seems to be a more advantageous process due to the achievement of almost 100% decolorization and the higher treatment efficiency based on the original dye concentration at a lower cost, especially if the pre-ozonation time of the feed to ASP is sufficient to achieve the peak enhancement of the biodegradability.

4. Conclusions

The effect of pre-ozonation on the decolorization and the efficiency of the combined chemical and biological oxidation process (or integrated process) in the treatment of aqueous azo dye (AR 151 as the model compound) solutions were investigated. It can be concluded that even the acclimation of seed microorganisms to the pre-ozonated dye effluents may be necessary; because in some cases, ozonation by-products of the dye effluent may be more resistant to the biological treatment than the original dye [5]. Otherwise, the time duration of pre-ozonation applied to the wastewater must be sufficient to provide an optimum BOD_5/COD ratio which may be considered as a degree of biodegradability [1].

In this study, the efficiency of the biological treatment process with the pre-ozonated feed was found as 47%, which was almost two times higher than that of un-ozonated feed case. But, it can still be improved by increasing the pre-ozonation time from 30 to 120 min at which the optimum BOD_5/COD ratio occurs in the continuous ozonation of the aqueous Acid Red-151 solutions [1]. Besides, it should be noted here that pre-ozonation time yielding an optimum ratio of BOD_5/COD should be determined by preliminary tests for each type of wastewater before the integrated process, because this time was only dependent on the type of wastewater [5].

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