Improvement of the Wastewater Biodegradability by Means of Photocatalytic and Wet Oxidation Processes in the Presence of Hydrogen Peroxide

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In this study, the effectiveness of photocatalytic oxidation (PO) and wet oxidation (WO) processes as a pre-treatment step on improvement of biodegradability and colour removal of mixture of raw domestic and pre-treated industrial wastewaters, have been evaluated. More oxygen was obtained by H_2O_2 (as an oxidant in WO and PO processes) than stoichiometric demand. PO of the wastewater was carried out by illumination of the wastewater with UV lamp (at room temperature, atmospheric pressure, 16.5 h reaction time) and WO of the wastewater was carried out by means of thermal oxidation at autoclave conditions (at 118–120 °C, 1.9–2 bar, 3 h reaction time). 1 g L^{-1} TiO_2 in PO process and 0.2 mg L^{-1} Cu^{++} in WO process were used as catalyst. The results obtained from experiments were not compared with each other due to the difference between the quality and quantity of the used catalyst and the consumed energy. Colour removal efficiency was 33 % for WO process and 77.6 % for PO process. By applying WO process, 72.7 % increase in the reaction rate coefficient describing the degradability of organic compounds in wastewater was obtained, but this value was 34.5 % in PO process.

Keywords:
Wet oxidation, photocatalytic oxidation, biodegradability, colour removal, $\zeta_{BOD_5}/_{COD}$, reaction rate coefficient, wastewater

Introduction

The advanced oxidation processes, such as wet oxidation (WO) and photocatalytic oxidation (PO), can be used to oxidize a persistent organic compound to a harmless inorganic, such as CO_2, H_2O and mineral acids, that can be converted to biodegradable intermediates. Chemical oxidation methods generally aim to complete mineralization, but they are not cost-effective, due to the oxidized end-products which are refractory to total oxidation. An alternative method to complete oxidation is the use of a chemical oxidation pre-treatment step to convert bio-recalcitrant organics to biodegradable intermediates, and later to biogas, biomass, and water by biological oxidation. Chemical oxidation breaks bio-recalcitrant organics into smaller intermediate compounds that enter cells and are more biodegradable than the original molecules. The rate of biological oxidation increases with decreasing molecular size. Conversely, total chemical oxidation of these intermediates to CO_2 and H_2O is difficult and require severe oxidative conditions, since the rate of chemical C-C bond scission decreases with decreasing molecular size. Coupling chemical pre-oxidation with biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared with the efficiency of each individual stage.[1]

Researchers showed that processes, such as wet oxidation[2–8] and photocatalytic oxidation,[9–13] have been proposed for the enhancement of the biological treatment efficiency.

The aim of this study is to investigate the effect of photocatalytic oxidation and wet oxidation processes as a pre-treatment step in the improvement of biodegradability of mixture of raw domestic and pre-treated industrial wastewaters.

Investigated wastewater was consisted of raw domestic wastewater and pretreated industrial wastewaters of various sectors such as tire, drug, chemistry, yeast industries. This wastewater mixture is not treated effectively in biological system. The characterization and biological treatability of this wastewater mixture was studied previously by *Arslan* and *Ayberk*.[14] The major fraction of chemical oxygen demand (COD) in this wastewater is slowly biodegradable organic matter. Hence, chemical pre-treatment is required prior to biological system for increasing the rate of hydrolysis period.

Materials and methods

The wastewater was obtained from the inlet of the biological treatment unit of the integrated raw

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domestic and pre-treated industrial wastewaters treatment plant. In the experiments, TiO_2 (Degussa P25, presented by Degussa) and $Cu(NO_3)_2$ (purchased from Merck) were used as catalyst and H_2O_2 (w = 30 % purchased from Riedel deHäen) was used as oxidant. All the other chemicals were of analytical purity. Prior to all experiments, wastewaters were separated by filtration with Millipore AP 40 filter papers of 0.45 μm pore diameter.

Experimental procedure

In WO process, the wastewater was exposed to thermal oxidation at autoclave conditions. In PO process, the wastewater was illuminated by two lamps (Philips®-TUV model) with a power of 15 W used as a source of radiation in the UVC domain. Lamps used as light sources have qualification of monochromatic ($\lambda \approx 253$ nm). Experiments were performed in complete mixed batch reactors. In open vessel the distance between water surface and the lamps was approximately 10 cm and the radiation was straight up to the water surface. The conditions of WO and PO processes were summarized in Table 1.

More oxygen than stoichiometric demand was supplied in the experiments, because pre-studies brought up the necessity of high amount of oxidant in order to obtain appropriate/enough colour removal without changing the other process conditions such as temperature, pH, pressure and amount of catalyst. Turbidity plays a significant role in PO efficiency as particles absorb reactive light. Turbidity increased from 69.6 FAU to 296 x 100 FAU with additional TiO_2. Increase at turbidity value absorption of light increased by particles 30.5 %. Before further investigations to be separated of TiO_2 from photooxidated wastewater was centrifuged at n = 5000 rpm for 10 min. The efficiency of colour removal by WO and PO processes was evaluated by scanning absorbance-wavelength for raw and treated wastewaters. The improvement on biodegradability of PO and WO processes was evaluated by examining with the biological oxygen demand (BOD) analyzer of the series summarized in Table 2. The BOD analyzer similiar to oxitop

Table 1 – *The conditions of WO and PO processes*

Quantities	WO process	PO process
temperature	118–120 ºC	room temperature
pressure	1.9–2 bar	atmospheric pressure
water volume	2 L	2 L
catalyst	0.002 g L^{-1} Cu^{++}	1 g L^{-1} TiO_2
reaction time (hour)	3	16.5
oxidant (H_2O_2)	6.1 mL*	4 mL**

* 10.5 times of stoichiometric O_2 demand
** 6.9 times of stoichiometric O_2 demand

Table 2 – *Series used in BOD Tests*

Series	Content
Blank (WO)	(2 mg L^{-1} Cu^{++} *+ nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with distilled water
Raw (WO)	(2 mg L^{-1} Cu^{++} *+ nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with raw wastewater
WO	(2 mg L^{-1} Cu^{++} *+ nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with treated wastewater in WO process
Blank (PO)	(nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with distilled water
Raw (PO)	(nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with raw wastewater
PO	(nutrient**+ATH***+4 mg L^{-1} biomass****) made up to the last volume with treated wastewater in PO process

Note:
* $Cu(NO_3)_2$ salt was used
** Addition of nutrient was done according to ISO 7393
*** ATH (*N*-Allylthiure) was used as a nitrification inhibitor
**** Activated sludge observed from integrated treatment plant was washed out 3 times with distilled water, than centrifuged at 5000 min^{-1} for a period of 10 min and separated completely from its upper supernatant. The solid content of activated sludge was 13520 mg L^{-1}. In BOD test bottles, dry biomass concentration was adjusted as 4 mg L^{-1}.

system expressed by *Reuschenbach* et al.[15] offers an individual number of reactors consisting of glass bottles with a carbondioxide trap (NaOH) in the headspace. The volume of the test mixture is 428 mL. The bottles are furnished with a magnetic stirrer and sealed with a cap containing an electronic pressure indicator. The test was run for 21 days at 20 °C with continuous shaking. The decrease in headspace pressure in the closed test vessel is continuously recorded as BOD.

In WO process the homogenous Cu-Catalyst added in wastewater could not be removed before the biodegradability test. The concentration of Cu^{++} was kept at a nontoxic level to activated sludge microorganisms. The interference effect of Cu^{++} was considered by adding the same amount of Cu^{++} in blank (WO) and raw (WO). The series of blank were prepared to determine the effect of factors which were sourced externally on BOD values. The effect of pre-treatment processes on the biodegradability of wastewaters was evaluated by comparing the results of the raw and treated series.

Analysis

CADAS 200 spectrophotometer was used to scan and measure the absorbance and turbidity of raw and treated wastewater. BOD was determined with Lovibond BOD-sensor, which operates according to the principle of manometric measurement by using a pressure sensor calibrated according to ISO 7393 (accuracy 2.5 % = 1 digit). COD was analyzed by the closed reflux dichromate method using a COD reactor, Hach Company (USA) and spectrophotometer DR/2000, Hach Company (USA). Before the BOD and COD analysis, residue H_2O_2 was removed. For this purpose, MnO_2 was added until dissolved oxygen (DO) has reached a proper level of $\gamma_{DO} \cong 7$ mg L^{-1}. DO was analyzed by using WTW OXI 3000 oxygenmeter.

Results and discussion

In the literature, there exist lots of studies discussing the degradation of some compounds qualified as pollutant by WO and PO processes. In this study, by applying these processes to the mixture consisting of pre-treated industrial and raw domestic wastewater, the effects on improvement of biodegradability and colour removal were evaluated. The organic matter has been degraded by the consuming energy in the presence of oxidants and catalysts in both of the processes. In WO process, the consumed energy is heat energy and type of oxidation is thermal oxidation. Although in PO process, acting energy is the energy carried of light beam. The level of this energy shows the changes with wavelength of light. In both processes, a catalyst is used, however, the types of catalysts are different. In this study, a homogeneous catalyst, Cu salt which is widely and effectively used in WO processes, was used. On the other side, in PO process, TiO_2, which is suggested as the most efficient catalyst, was used. Since, both, the quality/quantity of consumed energy and used catalysts are different for these processes, it is difficult to compare them. The results in this study should only give an opinion for comparison of these processes for the given process conditions.

Colour removal

Wavelength-absorbance scanning for raw and treated wastewater was given in Figure 1. Maximum absorbance was observed at 260 nm in absorbance scan conducted in the wavelength range of 200 to 800 nm. Studied wastewater was brown in colour because of the present of quinone. Thus, absorbance at 260 nm wavelength was due not only to the structures that gave absorbance in UV region, but also from the present colours. The colour observed at the absorbance value measured at 260 nm can not be accepted as the actual colour. According to the absorbance values at 260 nm wavelength, the efficiency of colour removal for WO and PO processes were 33 % and 77.6 %, respectively. The colour removal in WO process was achieved only by means of thermal oxidation at autoclave conditions in the presence of H_2O_2. In some proportion additional colour removal in PO process was obtained as a result of removing of the organic matter that was adsorbed on the surface of TiO_2 by centrifuging together the photocatalytic oxidation. In spite of the fact that the amount of oxidant used in WO process was greater than the used in PO process, PO process is more effective for colour removal. Here, the type of catalyst used and the quality/quantity of consumed energy influenced the results. In PO processes, $UV/TiO_2/H_2O_2$ is the most appropriate preferred combination. In this process colour removal was high, since the oxidation mechanism began with the decolourization. Quality of UV light plays an important role in decolourization process. Besides used TiO_2 in PO process is the most appropriate catalyst.

The effectiveness of WO and PO processes on the biodegradability

As mentioned before, using chemical oxidation methods in order to complete oxidation of organic compounds is not suggested in practice since it increases the cost of treatment. So, wastewater should be pre-treated by these methods before the removal of organic compounds by conventional

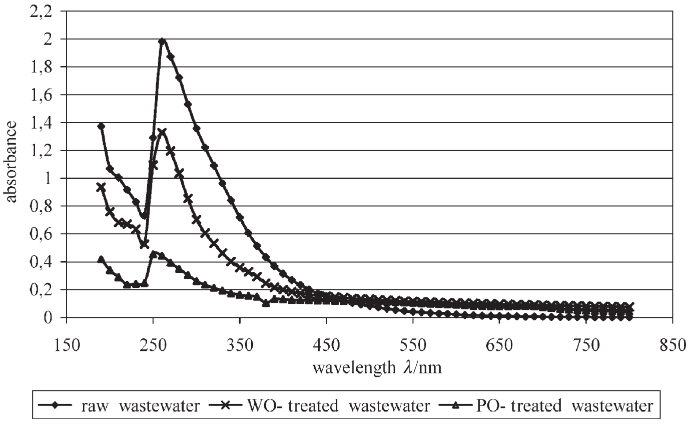

Fig. 1 – *Absorbance-wavelenght scanning of raw and treated wastewater*

biological treatment systems. It is also suggested, that complete oxidation of pre-treated wastewater should be done by conventional biological treatment systems.

In this study, the effectiveness on the improvement of biodegradability of WO and PO processes was presented by observing the biodegradability at BOD test conditions of raw and treated wastewater which was exposed to partial oxidation via WO and PO processes. BOD values observed against time for series given in Table 1 was presented in Figure 2.

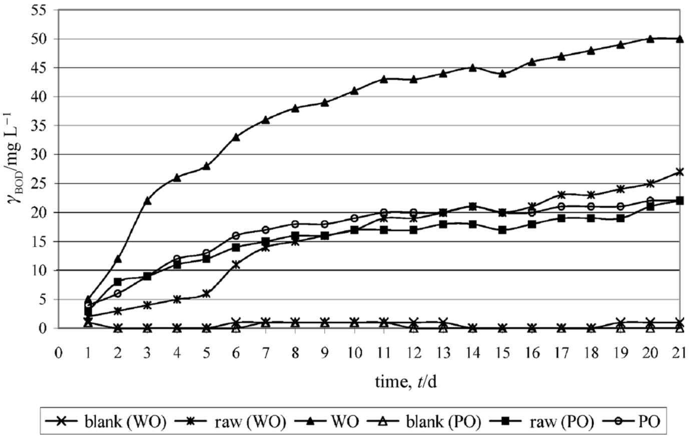

Fig. 2 – *Variation* BOD_t *versus time*

In order to determine the effects on the improvement of biodegradability of WO and PO processes, the mathematical analysis of BOD-time curves was performed. BOD-time curves were mathematically explained in terms of Equation 1.[16]

$$\mathrm{BOD}_t = \mathrm{L}_0(1 - \mathrm{e}^{-kt}) \qquad (1)$$

where;

BOD_t – the amount of oxygen consumed by organic compound in the first t days (mg L^{-1}).

L_0 – the ultimate BOD (mg L^{-1}) is the total amount of oxygen required by microorganisms to oxidize the carbonaceous portion of the organic compound to simple carbon dioxide and water.

k – BOD reaction rate coefficient, d^{-1}

In the literature, under the BOD test conditions, the organic compound which was oxidized in the first five days is believed to be 60 – 70 % of ultimate organic compound.[17] In our study we found that value as 65 %. According to this, at all series, ultimate BOD values (L_0) calculated from BOD_5 was presented in Table 3.

Table 3 – *Ultimate BOD values for WO and PO series and calculated k values*

Series	BOD_5 mg L^{-1}	Calculated L_0 mg L^{-1}	Observed L_0 mg L^{-1}	BOD_{10} mg L^{-1}	k d^{-1}
WO (raw)	6	9.2	27	17	0.099
WO	28	43	50	41	0.171
PO (raw)	12	18,5	22	17	0.148
PO	13	20	22	19	0.199

According to Figure 2, the organic compound degradation in blank WO and blank PO series can not been determined, because the BOD values for this series were below the measurement range. In Figure 2, the BOD_{21} values accepted as observed L_0 for WO (raw), WO, PO (raw) and PO series are 27 mg L^{-1}, 50 mg L^{-1}, 22 mg L^{-1} and 22 mg L^{-1}, respectively. The mathematical difference of calculated L_0 and observed L_0 for, both, WO (raw) and WO series is important. This difference can be explained like this: since Cu^{++}, used as the catalyst in wastewater, inhibits degradation of organic compound in the first days, L_0 value calculated from observed low BOD_5 value also came out to be low. However, in the course of time, because of the activity of microorganisms adapted to Cu^{++}, degradation rate has increased. The mathematical difference for PO series is not too big. Since calculated L_0 values for, both, PO (raw) and PO series reflected the observed L_0. Therefore, observed L_0 must be used as L_0 value in the reaction rate constant calculations. Calculated reaction rate coefficient (k) by using Eq. (1) considering the observed L_0 and BOD_{10} values was presented in Table 2. The model equation was formed by placing the values of k and L_0 in eq. (1). BOD_5 values of the series of WO (raw), WO, PO (raw) and PO were calculated from the model equation as 10.5 mg L^{-1}, 28.7 mg L^{-1}, 11.5

mg L^{-1} and 13.9 mg L^{-1}, respectively. The deviations of BOD_5 values obtained by model equation to the experimental ones were 75 %, 2.5 %, and 6.9 %, all in positive directions, and 4.2 % in negative direction for the series of WO (raw), WO, PO and PO (raw), respectively. The obtained 75 % deviation in WO series can be explained by the fact that microorganisms were affected more from the inhibition effect of Cu^{++} catalyst in the medium in which readily biodegradeable organic matter did not exist.

72.7 % and 34.5 % increase in k value were observed in WO and PO processes, respectively. For applied process conditions, the WO process was more effective than the PO process on the improvement of biodegradability. In similar study performed by *Can* and *Genç*,[18] by using 300 W pressure mercury lamp as the light source, a 20.4 % increased in reaction rate constant of fermentation industry wastewater was obtained by reaction time of 180 min in PO process. In this study, although the low increase in biodegradability (34.5 %) and high colour removal (77.6 %) were achieved with the PO process, the high increase in biodegradability (72.7%) and low colour removal (33.0%) were obtained with the WO process. Since the species of organic matter in wastewater was not known, the colour removal and the increase in biodegradability by PO and WO processes can be explained by possible mechanism. In PO process after the organic molecules were generally exposed to dehalogenation and decolourization, by extending the period of reaction, the main structure of molecule was made proper for mineralization by breaking it.[19,20] In this study where the advanced oxidation methods were considered as the pre-treatment steps, the appropriateness of organic matter for mineralization was measured by the biodegradation test. The low colour removal and the high increase in biodegradability obtained by WO process showed that the oxidation mechanism initiated by the formation of by-products that were appropriate to mineralization.[3,21]

BOD_5/COD ratio is very important index for any waste that can be biodegraded. Industrial wastewater that has approximately a BOD_5/COD mass ratio of 0.5 or higher is considered as biodegradable waste.[17] In order to evaluate the appropriateness of raw and treated wastewater in this respect, BOD_5/COD ratio was calculated. COD values for raw wastewater and wastewater that is exposed to WO and PO were determined as 90.2 mg L^{-1}, 79 mg L^{-1} and 51.7 mg L^{-1}, respectively. BOD_5/COD ratio calculated by considering COD and BOD_5 values, has increased from 0.13 to 0.25 by PO process and from 0.067 to 0.35 by WO process. As mentioned before, the difference in raw BOD_5/COD ratio can be explained by the inhibition effect of Cu^{++} in WO series. BOD_5/COD ratio has approximately increased 5.2 times by WO process and 1.9 times by PO process. In the study performed by *Can* and *Genç*,[18] it was identified that BOD_5/COD ratio for fermentation industry wastewater has increased from 0.11 to 0.18 at reaction time of 120 min in PO process.

When WO and PO processes are thought to be pre-treatment step where partial oxidation is achieved before biological treatment, they can be evaluated as an economic alternative for treatment. Pretreatment conditions should be optimized in order to get high biodegradability and low toxicity. At biological treatment unit, toxicity of biodegradable by-products which were formed at the pre-oxidation treatment step should be investigated. PO and WO processes have high cost because of consuming energy, oxidant, and catalyst. But, with some modifications in process conditions it is possible to reduce operating cost. Recovering of TiO_2 used in PO process by immobilizing it to the fixed surface after treatment and providing its reactivation, using Fe^{++} salts instead of Cu^{++} in WO process, and using air as an oxidant instead of H_2O_2 in both processes are some examples for modifications in process conditions.

Conclusion

In this study, the effectiveness of WO and PO processes on colour removal and improvement of biodegradability of wastewater, were examined. At applied conditions, by WO process 33 % and by PO process 77.6 % of colour removal was achieved. Following conclusions can be made based on this study that WO and PO processes were considered as a pre-treatment step to improve biodegradability prior to a conventional biological treatment.

Reaction rate coefficient (k) which explains the degradation rate of organic compound in wastewater, has increased 72.7 % and 34.5 % by WO and PO processes, respectively.

BOD_5/COD ratio which is an indicator of biodegradability, has increased 5.2 times by WO process, and 1.9 times with PO process.

Observed results showed that the colour removal rate and the increase in biodegradability were independent variable from each other in evaluating the efficiency of WO and PO processes.

List of symbols

BOD – biochemical oxygen demand, mg L^{-1}

BOD_t – the amount of oxygen consumed by organic compound in the first t days, mg L^{-1}

COD – chemical oxygen demand, mg L^{-1}

k – reaction rate coefficient, d^{-1}

L_0 – ultimate BOD, mg L^{-1}

n – rotation speed, min^{-1}

t – time, h

w – mass fraction, %

λ – wavelength, nm

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