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Corrosion behavior of 316L stainless steel in treated and untreated artificial effluent solutions (AESs)

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Some organic compounds in wastewaters not only pollute the environment but also cause corrosion to the wastewater transportation systems. In this study the corrosion behavior of treated textile wastewater was investigated by using AISI 316L stainless steel. Treatment was done by sonochemical (US), photochemical (UV) and sonophotochemical (US+UV) processing. These processes were used to degrade the dyestuffs which cause the pollution of textile wastewater. Artificial effluent solutions were prepared for use in the treatment processes. The concentrations of the solutions decreased with time for three treatment processes. The most reduced concentration was obtained after sonophotocatalytic treatment and the least was for sonochemical treatment. The OCP curves were found to move away from the noble direction for all the tested samples. The reduction tendency of the potential values for all samples was observed close to each other. The most active OCP values were for US+UV. In polarization results, the US sample showed a lower corrosion potential and higher corrosion current density. The corrosion results of samples tested in treated solutions were better than in untreated solutions. For the sonophotochemical process, stainless steel showed a better corrosion resistance than the others.

Keywords: Sonophotocatalytic process; photochemistry; sonochemistry; dyestuff degradation; pitting corrosion

INTRODUCTION

The textile dyeing and dye production facilities are the most problematic industries as regards releasing the dyes in an effluent form and polluting the environment. If these compounds are released without restraint, they may cause lots of health problems because the chemical and photolytic stability of the textile dyes are highly resistant in a natural environment. It is known that some azo dyes are formed from toxic aromatic amines which are carcinogenic for living organisms [1-4]. Therefore, the discharged effluents from the textile industries are important threats to the environment. About 15% of the total amount of dye produced in the World is lost during the dyeing processing and released to the environment together with textile effluents [1, 5]. The flow of these colorful effluents causes unaesthetic pollution of environment. Also the dyestuffs in the effluent phase can cause dangerous reactions including oxidation, hydrolysis or other chemical reactions [1, 5, 6].

Discharging effluents from textile factories not only pollute the environment but also destroy the pipes that are used to discharge the effluents, due to the impact of corrosion. It is known that corrosion as a phenomenon destroys the materials with time. Because of their high electrochemical reaction tendency, metals are the most common type of corrosion material. The destroyed materials become unused due to inappropriate design. In consequence, the systems of factories which carry the fluids and especially the effluent pipes are exposed to corrosion damage [7, 8].

For this reason the treatment of the effluents is important for the environment and the health of man. At the same time it is financially important to know the working life of the treatment system. The studies of the treatment of fabric effluents have been accelerated in recent years [1, 9]. Among these treatment methods are Advanced Oxidation Processes (AOPs): Fenton and Photo-Fenton catalytic reactions [10, 11], H_2O_2/UV processes [12, 13], Photocatalysis in a TiO_2 medium [1, 14], sonolysis and sonophotochemical treatment [15, 16] have been considered. Recently it was observed that especially the sonolytic and photocatalytic studies are more useful for the treatment of effluents. The treatment of effluents will affect the corrosion in the pipes. In this study, AISI316L stainless steel was used for making a simulation with effluent pipes. The intended use of this material is widespread with many industrial applications, especially chemical processing, the automotive industry and surgical implants. These exhibit a very high corrosion resistance in many aggressive environments [8, 17-18]. Therefore, in this study, the corrosive effect of the effluent including the textile dyes was treated by ultrasound energy (US) and UV irradiationindividually, and also by the application of both processes simultaneously on the pipes was investigated.

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EXPERIMENTAL PROCEDURE

The experiments were performed on AISI316L stainless steel, its chemical composition is given in Table 1. The prismatic specimens with dimensions of 25 x 25 x 2 mm^3 were cut from AISI316L stainless steel sheet. The samples were ground by 220–1200 mesh emery paper and then polished with alumina powder with a 1 μm grain size.

All the experiments were performed in artificial effluent solutions (AES) that were prepared with distilled water by using Methylene Blue and Congo Red dyestuffs with a molar concentration ratio of 1:1 uniformly. These were provided by Sigma Aldrich and used as received. The structures of the dyestuffs are shown in Table 2.

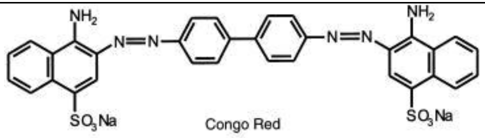
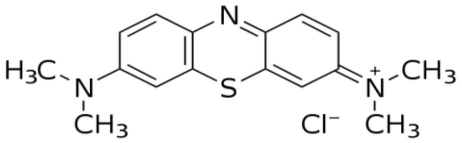
These solutions were processed by using ultrasound and UV irradiation before the experiments. For these processes, the parameters were as; 30 ppm of the concentration of the solutions , 30°C of temperature , 132 W/m^2 of light intensity, 50 % of the amplitude of ultrasound energy, 90 min. as the process time And 800 mg/l of TiO_2 photocatalyst. In the processes 500 ml of AES were used. Air was blown into the reaction medium by an air pump at a constant flow, to maintain the solution saturated with oxygen during the reaction. The pH was a natural value of the solution. The change in concentration was determined by a UV–vis Thermo Electron Evolution 500 spectrophotometer. First of all the absorbance values of the Methylene Blue and Congo Red were determined as 665 nm and 498 nm, respectively. The concentrations of the dyes were determined by the calibration curve that was a graph of the absorbance versus certain concentration values of the dyes. Also, the calibration graph was obtained with a spectrophotometer. Then the total concentrations of the dyes in the solution were calculated.

The electrochemical polarization experiments were performed using a GAMRY Series G750™ Potentiostat/Galvanostat/ZRA device. One side of the specimen with an area of approximately 0.38 cm^2 was exposed to the solution. The polarization measurements were carried out in unprocessed and processed AESs with US, UV and US+UV. For the first experiment untreated AES was used. For the second experiment only US was used on the AES, for the third experiment only UV irradiation was used and for the last experiment US and the UV irradiation (US+UV) were applied simultaneously. A stabilization period of 7200 s was employed before starting the measurement. The electrode potential was raised from -0.5V to 1 V compared to OCP with a scanning rate of 1mV/s and a current that flowed through the diffusion layer-substrate system. A three-electrode cell was used for the polarization measurements employing a Ag/AgCl electrode as the reference electrode, a graphite bar as the counter electrode and a working electrode, respectively. The surface morphologies after electrochemical examination were investigated using a scanning electron microscope Zeiss EVO LS 10.

Table 1.*Chemical composition of AISI 316L stainless steel (%)*

C	Si	Cr	Mn	Mo	P	S	Ni
0.016	0.490	16.640	1.820	2	0.030	0.026	10.100

Table 2.*The structures of dyestuffs*

Dyestuff Name	Molecular Formula	Structural Formula
Congo Red	$C_{32}H_{22}N_6Na_2O_6S_2$	
Methylene Blue	$C_{16}H_{18}N_3SCl$	

RESULTS AND DISCUSSION

The experiments were repeated three times for each treatment to indicate the reproducibility of the study. First of all the average values of the experimental data as the conversion rate were calculated for each treatment as US, UV and US+ UV. Then the H_0 and H_1 were hypothesized as; H_0: $M_1= M_2= M_3$ and H_1: $M_1 \neq M_2 \neq M_3$ where M are the average values of the experimental series. To determine the true hypothesis a statistic test of the variance analysis, which is f-distribution (F), is used. To achieve this goal the calculated F value and the F table values were compared at a 99% level of confidence. In this test, the F values were calculated by ANOVA (Analysis of Variance) tables formed by a MATLAB program for individual treatment. The $F_{\alpha}(v_1, v_2)$ value is determined from the F table. Here v_1 and v_2 are degrees of freedom and v_1=k-1, v_2=k.(n-1); k and the n values are 3 and 12 respectively. Where k is the number of repeated experiments for each treatment and n is the number of data for each experiment. For this study the $F_{0,01}(2,33)$ value is 5,31 from the F table [19, 20] which is greater than the calculated F values in the ANOVA tables as shown in Table 3(a) (b) (c). This means that the difference between the averages of the experimental data is accidental and they are from the same population. In other words the H_0 hypothesis is true and this situation proves the reproducibility of the experimental data by using their average values.

The conversion rate versus time graphs of US, UV and US+ UV treatments are given in Figure 1. This figure demonstrates the most effective treatment process for removing the dyes, which are pollutants.

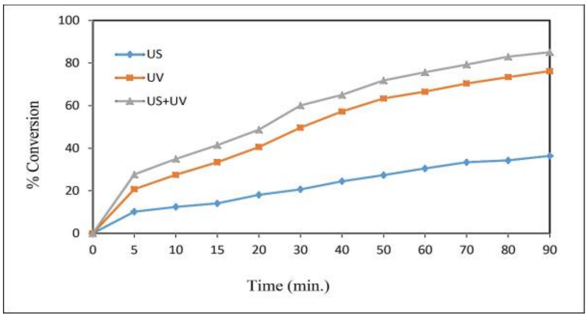


Fig. 1. Conversion rate of US, UV and US+ UV treatments versus time.

This will interrelate with the corrosion behavior of the treatment processes included less corrosive pollutant (dye amount) by identifying the most effective process. As seen in Figure 1, the concentrations of solutions decreased with time after three treatments.

The most reduced value was observed during sonophotocatalytic treatment. On the contrary, the least reduced value was obtained during sonochemical treatment. Also having a glance at the graphic, the conversion ratios of dyestuffs increased with the treatment in time. However, the largest increase was attained by UV+US and the smallest one was by US application. From the results, it can be said that the UV+US is more effective for removing the dyestuffs from the aqueous medium. This is attributed to their synergistic effect. It is known that the main factor for degrading the dyestuffs is forming the OH^* radicals in the medium because of their property to destroy as powerful oxidizing agents and attack organic compounds forming intermediates. As more radicals are formed the degradation ratio will increase [13, 20-25]. In US treatment, the ultrasound energy can cause the collapse of the cavitations producehigh transient temperatures and pressures in the aqueous solutions. These lead to the formation of free hydroxyl radicals via the homolysis of water [26, 27]. However, by UV treatment, upon absorption of a photon by TiO_2, an electron is promoted to the conduction band, generating what is commonly referred to as an electron-hole pair [6, 23-25]. The conduction band electron is available for reduction and the valence band hole is available for oxidation. The hole can subsequently react by electron transfer with a substrate to form a radical species or hydroxide (water) to form hydroxyl radicals. In condensed oxygenated aqueous media the surface of TiO_2 is completely hydroxylated and upon photoexcitation it generates hydroxyl radicals in an adsorbed state [7, 9, 28].

For having more OH* radicals these two treatments must be applied simultaneously because of the synergistic effect. During the reaction between these radicals and dyestuffs the intermediates occur. Then these intermediates react with hydroxyl radicals (OH*) to produce final products, such as low molecular weight carboxylic acids, while the hydroxyl radicals can be consumed by inactive species.

Figure 2 showed the open circuit potential (OCP) measurements of the samples tested in the untreated AESs and the treated solutions were obtained after the degradation processes following ultrasound (US), ultraviolet (UV) and ultrasound+ultraviolet (US+UV) applications. The obtained open circuit potential (OCP) curves were found to move away from the noble direction for all the tested samples. According to the OCP data, it has been observed that the curves of the samples approach a steady state after about 2000 s.As seen in Figure 2, the potential values shift in the negative direction for all samples.That clearly indicates that the surfaces of all the samples were very active to corrosion and there was no protective film formation on the sample surface to prevent the electrochemical dissolution. While the noblest OCP values were observed for the samples tested in the treated AES with US+UV, the most active OCP values were obtained from the samples tested in untreated AES.

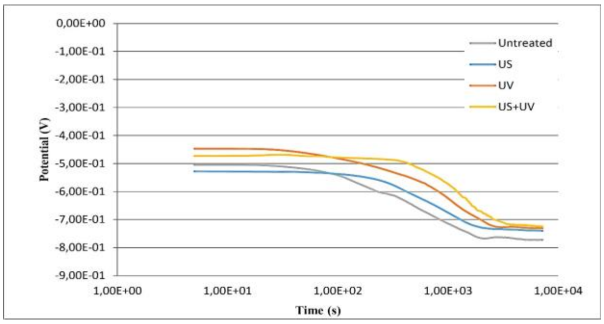


Fig. 2. Change of the OCP potential of samples tested in the AESs that are untreated and treated with US, UV and US+UV energies.

Polarization curves of the samples tested in the AESs that are untreated and treated with US, UV and US+UV processes are given in Figure 3. It was determined that the corrosion results for the samples tested in the solutions after the treatments were better than for the samples tested in untreated solution. A passive and short region was seen at the beginning of the anodic zone of UV treatment. The current values were almost stable while the potential values increased. A sudden and sharp current increase occurred at the end of this region. This can be attributed to pitting corrosion behavior [29].

The US sample also exhibited similar polarization curves with the UV sample. But, there was no passive pitting corrosion indication for this sample.

On the other hand, the similarity between the polarization curves of the UV and the US+UV samples can be clearly observed in Figure 3. If the corrosion current density and the corrosion potential values are taken into account, the best results have been obtained from the US+UV treatment.

Although the corrosion current density of the US+UV sample was slightly lower than the other samples, previous studies on degradation of dyestuffs indicated that the UV irradiation was more effective than the ultrasound energy [16, 30, 31]. Similar results were obtained from the polarization results. It was found that the US sample showed a lower corrosion potential and a higher corrosion current density. This means that corrosion previously begins for the US sample and then it corrodes more than the UV sample.

The corrosion results for the samples tested in the solutions after treatment were better than the samples tested in untreated solution and depend on the non-destructive products raised from the degradation processes. As known, carboxylic acids occur during the photochemical degradation of dyestuffs and the final products are CO_2 and H_2O at the end of these reactions. As seen in Figure 1, it was thought that carboxylic acids existed in the solution, because of the decrease in dyestuffs' concentration with time.

Table 3. a. ANOVA table of US treatment

'Source'	SS'	'df'	'MS'	F'	Prob>F'
'Columns'	59,70	2	29,85	2,83	0,07340
'Error'	348,12	33	10,55	[]	[]
'Total'	407,82	35	[]	[]	[]

Table 3. b. ANOVA table of UV treatment.

'Source'	'SS'	'df'	'MS'	F'	Prob>F'
'Columns'	86,57682	2	43,28841	0,933111	0,403459
'Error'	1530,92	33	46,39152	[]	[]
'Total'	1617,497	35	[]	[]	[]

Table 3. c. ANOVA table of US+UV treatment

'Source'	'SS'	'df'	'MS'	'F'	'Prob>F'
'Columns'	154,5632	2	77,28159	1,293993	0,287723
'Error'	1970,871	33	59,72336	[]	[]
'Total'	2125,434	35	[]	[]	[]

The carboxylic acids are dissolvable by H_2O and H^+ ions released into the solution. Moreover, before the final products, positive holes (h+) and hydroxyl radicals (OH*) occurr throughout the degradation process and some of them still exist in the solution [21, 32, 33]. It is supposed that the existence of positive holes and H^+ ions may cause a reduction in electron loss from the tested metal samples.

The corroded surfaces of all samples were examined with a SEM and the images are presented in Figure 4.

Intergranular corrosion damages are observed from the surface of the untreated samples in Figure 4a. It can be easily said that the untreated sample surface has undergone more corrosion damage when its surface image is compared to the others. For the treated samples, pitting type corrosion can be seen on their surface images (Figure 4 b, c, d). It was seen that corrosion damage decreased after the degradation processes. The SEM image of the US sample surface after a corrosion test is given in Figure 4b. A spread of many large and deep pits was observed on the sample surface. On the other hand, the surface images of the UV and US+UV samples showed that the pit numbers decreased and thus the corrosion damage was reduced. Moreover, relatively smaller and shallower pits were observed on the UV and US+UV sample surfaces compared to the pits on the untreated and US sample surfaces (Figure 4c and d).

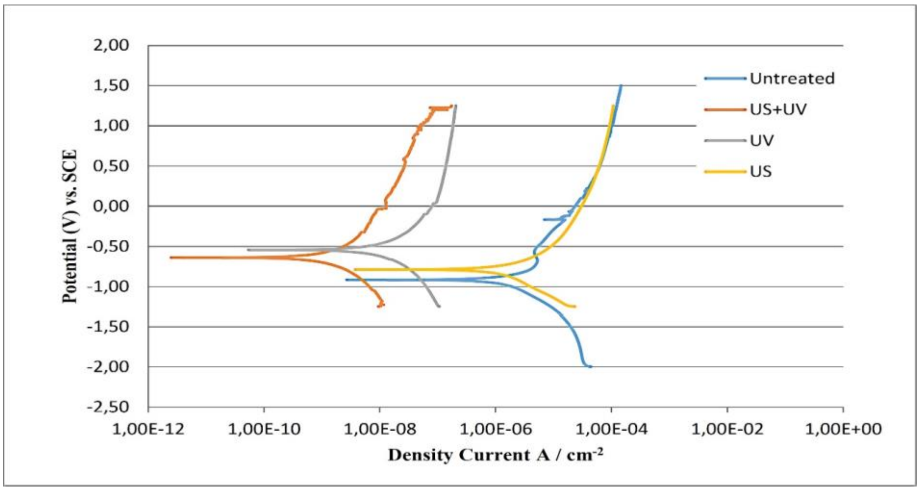


Fig. 3. Polarization curves of untreated and treated samples

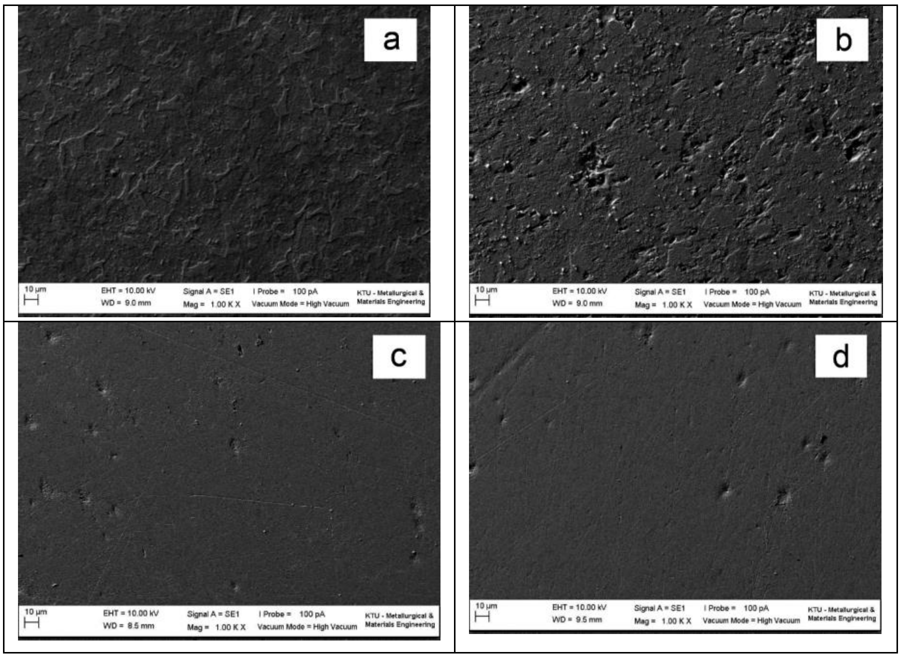


Fig. 4. SEM images of corroded surfaces for **a)** untreated, **b)** US treatment, **c)** UV treatment, **d)** US+UV treatment.

CONCLUSIONS

A solution including dyestuffs was treated with sonochemical, photochemical and sonophotochemical methods. The effects of degradation treatments on the corrosion behavior of 316L stainless steel were investigated in these treated solutions. In the light of these investigations, the following conclusions can be drawn from this study:

- It was seen from the conversion results that the most effective treatment for the degradation of dyestuffs was the US+UV treatment. The conversion rates at 90 minutes were about as 36%, 76% and 85% for US, UV and US+UV treatments, respectively.
- It was determined that the corrosion results of the samples tested in the treated solutions were better than the samples tested in untreated solution.
- Corrosion tests of sonophotochemical treated solution showed better corrosion resistance than the other treatments used in this study.
- While intergranular corrosion damage was seen on the surface of the samples tested in untreated solution, the pitting type of corrosion damage was observed on the samples tested in treated solutions.
- The sample surface tested in the US+UV treated solution showed a smaller amount of pitting and dimensions compared to the treated samples.

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КОРОЗИОННО ПОВЕДЕНИЕ НА НЕРЪЖДАЕМА СТОМАНА 316L ПРИ ТРЕТИРАНЕ С МОДЕЛНИ ОТПАДЪЧНИ ВОДИ

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(Резюме)

Някои органични съединения в отпадъчните води не само замърсяват околната среда, но и причиняват корозия на водните транспортни средства. В тази работа е изследвана корозионната активност на третирани отпадъчни води от текстилната индустрия върху неръждаема стомана AISI 316L. Третирането бе извършено чрез ултразвук (US), фотохимично въздействие (UV) и комбинация от двете (US+UV). Тези процеси бяха използвани за разграждането на багрила, замърсяващи отпадъчните води. Бяха приготвени моделни води. Концентрациите на багрилата се понижаваха с времето при трите изследвани процеса. Най-ниски концентрации бяха постигнати при комбинацията от ултразвуково и фотохимично въздействие, а най-слаб ефект имаше ултразвуковото въздействие. Кривите за потенциала при отворена верига (OCP) бяха далеч от теоретичното за всички тествани проби. Намаляващата тенденция за стойностите на потенциала бе наблюдавана при всички проби. Най-високи бяха стойностите на OCP при комбинирано действие. От резултатите при поляризация ултразвуковото въздействие доведе до най-нсък корозионен потенциал и най-висока плътност на тока. Пробите, тествани с третирани разтвори показаха по-добри резултати отколкото без третиране. Неръждаемата стомана показа по-високо съпротивление спрямо корозия след комбинмирано третиране, отколкото при останалите случаи.