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Combination of TiO_2-photocatalytic process and biological oxidation for the treatment of textile wastewater

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Abstract−We did a comparative kinetic study of biological oxidation of textile wastewater in an activated sludge, an activated sludge immobilized on biofilm, and a combination of TiO_2 photocatalytic process and moving bed reactor biofilm system. Combining photocatalysis with a biological treatment could be a good strategy to remove non-biodegradable compounds. Mathematical models such as Grau second-order and modified Stover-Kincannon kinetic models were applied to determine the kinetic coefficients of COD removal process in biological treatment. The kinetic coefficients were determined by linear regression based on the experimental data. The results showed that the photocatalysis pretreatment of refractory compounds has a positive effect on the obtained kinetic parameters. As a result, COD content and color of wastewater were decreased; however, the saturation value constant and maximum utilization rate of the modified Stover-Kincannon kinetic models (by 63%) were increased relative to untreated wastewater by TiO_2 as a pretreatment.

Keywords: Photocatalysis, TiO_2, Biological Treatment, Textile Wastewater, Kinetic Study

INTRODUCTION

The textile-processing industry regularly produces large quantities of highly colored effluents with toxic and biorecalcitrant compounds [1]. Dyes, and especially the reactive ones, are regarded as the largest class of synthetic compounds [2]. Basically, textile wastewater results from waste streams of different activities like desizing, scouring, bleaching, mercerizing, dyeing and printing [3]. The wastewater released from a dying process in the textile industry is highly colored with low values of high biochemical oxygen demand (BOD) and high chemical oxygen demand (COD) [4]. Currently, various treatment processes like electrocoagulation process are being applied to eliminate color and toxic organic compounds from textile effluents [5,6]. The biological treatment process is generally more cost effective than physical and chemical processes. The activated sludge process, which oxidizes the pollutants by microorganisms, is well-known as a result of high effluent quality. As an acceptable fact, biological treatment is not capable of removing toxic and recalcitrant compounds produced by chemical industries, which threatens the microbial community [7-9]. Hence, advanced oxidation processes (AOPs) are considered useful for decolorizing and reducing recalcitrant loads from textile wastewaters. The AOPs generate hydroxyl radicals ($OH^{\bullet}$), which are highly reactive and non-selective oxidants toward organic compounds [10-13]. Until now, various methods of AOP comprising ozonation [14], UV/H_2O_2, Fenton oxidation, photo-Fenton processes [9,15,16] and photocatalytic degradation [17,18] have been applied for the treatment of textile wastewater. In AOP, excessive potential for breaking down of organic contaminants in the liquid and gas phases by heterogeneous photocatalysis process with semiconductor oxides has been proven in the literature [19]. The fundamental mechanism of photocatalysis is based on generating electron-hole pairs after irradiation with adequate photons in terms of energy [20,21]. Also, a hydroxyl radical is produced from the decomposition of water. Titanium dioxide is widely used as photocatalyst because of its high photocatalytic activity. In addition, TiO_2 is easy and cheap to produce due to its strong chemical firmness, lack of toxicity, commercial availability, and the optical and electronic properties [21]. Alinsafi et al. [2] reported the decolorization of textile industry wastewater by using TiO_2 particles immobilized on a glass slide and a nonwoven glass fiber fabric either. The degradation of azoic and metal phthalocyanines dyes under UV radiation and solar irradiation has been investigated in the mentioned study. The results showed an increasing in decolonization efficiency from 21% to 74% under solar irradiation, and the COD removal rate was in the range of 0.2-0.9 g $COD/h/m^2$. In another study, solar photolysis and photocatalytic processes for the treatment of textile industrial wastewater were applied [22].

Ghorishi at el. [4] investigated the treatment of non-biodegradable textile wastewater by using catalytic degradation and biological process. The results indicated that the combination of chemical and biological oxidation could reduce color and increase the removal efficiency of BOD, COD and suspended solids (TSS). The treatment of tannery wastewater by subsequent ozonation - aerobic biological sequential batch reactor was investigated by Srinivasan et al. [23]. The degradation of chlorophenols by subsequent photochemical-biological oxidation was investigated by Essam et al. [22]. They reported that a complete biological elimination of the remaining pollutants was achieved in the activated sludge after pretreating all samples with photo-chemical degradation. In addition,

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it was found that the combination of UV/TiO_2/H_2O_2 and biological treatment provides high detoxification so that the dechlorination and COD removal efficiencies were 99% and 88%, respectively. The procedure involves a first step with a photocatalytic experiment in which the pollutants are partially oxidized and converted into more biodegradable compounds; afterwards, a second biological step is performed in which the contaminants are completely degraded or mineralized. Chemical pretreatment is necessary to change the structure of the contaminants by converting them into nontoxic and readily biodegradable intermediates. By this method, less time and cost is consumed.

Yahiat et al. [11] reported the degradation of cyproconazole by coupling photocatalysis and a biological treatment with *Pseudomonas fluorescens*. The degradation of crystal violet dye from wastewater by applying coupled biological and photocatalysis peroxidation process was carried out by Chen et al. [24]. The results showed that the optimal condition with 94% of photocatalytic reaction efficiency was obtained when the values of reaction time, pH and retention time were 1.5 h, 7 and 2.0 min, respectively. Coupled photocatalytic-biological systems for treating various wastewaters have been studied by Marsolek et al. [25]. They examined the relationship between pretreated wastewater by advanced oxidation process and enhanced performance of biological treatment. Commonly, COD removal is increased in bioreactors with decreasing aromatic compounds in the effluent of photoreactors; however, the combination of advanced oxidation and biological processes must be optimized. Chebli et al. applied the combination of photocatalysis and biological treatment for removing azo dye [26].

Nowadays in biological domain, to remove nutrients and/or toxic components from wastewater, integrated processes with the benefits of suspended growth and biofilm process have been attractive. A biofilm can be depicted when an attached growth occurs on a stationary solid surface (static biofilms) or suspended carriers (particle supported biofilms) [27]. One of the most attractive hydraulic systems with suspended carriers is moving bed biofilm reactor (MBBR) which has been developed over time. MBBR has been promoted mainly for the reason that more biomass concentration can be sustained and subsequently higher removal efficiency may be achieved in this system.

We applied a combined process comprising heterogeneous photocatalysis process with TiO_2 and aerobic MBBRs were applied for treating textile wastewater. Another aim of this study was to determine the process kinetic coefficients of removing organic compounds using activated sludge, MBBR and a coupled photocatalytic-biodegradation system. The second-order (Gray) and Stover-Kincannon models were used for kinetic study of organic substances removal.

MATERIALS AND METHODS

1. Materials

The wastewater used for laboratory-scale was obtained from a textile plant (Kerep Naz Kermanshah). Table 1 shows some of the physical and chemical characteristics of the textile wastewater. TiO_2 Degussa P-25 (anatase 75%, rutile 25%, BET specific surface area of 48 m^2/g, and mean particle size of 25 nm) was used as a photocatalyst in this bioreactor. LECA is a special type of clay granule which is baked in a rotary kiln at a very high temperature (with grain size 4-10 mm). In this study, LECA was provided from Azarbayjani Company, Kermanshah, Iran.

Table 1. Characteristics of the textile wastewater used in the present study

Parmeters	Value
Chemical oxygen demand (mgO_2 L^{-1})	1,650
Biochemical oxygen demand (mgO_2 L^{-1})	390
BOD/COD	0.23
pH	11
Color (A_{335})	0.81

2. Experimental Methods

The photocatalytic experiments were performed in a photoreactor consisting of a cylindrical Pyrex photoreactor (diameter 16 cm; height 10 cm; total capacity 2,000 mL); it was used for photodegradation of textile wastewater. The photoreactor was equipped with an aeration system. The system was illuminated by a 125 and 250 W (UV-C) mercury lamp (Philips, the Netherlands) with a peak light intensity of 254 nm, standing 12 cm overhead the center of the Pyrex glass reactor. The distance between the solution and UV source was adjusted according to the experimental conditions. The temperature of the suspension in the reactor was kept constant at 30 °C.

Aerobic biological oxidation experiments were completed in a one-liter bioreactor. Activated sludge was collected from an oil refinery wastewater treatment plant. It was washed at least two times with water, filtered on a Buchner system and inoculated in the bioreactor. The bioreactor was operated to achieve steady state. For all the experiments, temperature was held in the range of 22-26 °C and also the COD: N: P ratio was constant at 100 : 5 : 1 [28]. In this study 40% of reactor volume was filled by LECA beads as the biofilm support to achieve higher surface area, lower density, and lower price. The main reason for light expanded clay aggregation is the flow of air into and out of them. Note that between 73% -and 77% of grain was filled by air. Grains should create high surface (525 m^2/m^3) to grow microorganisms on them.

The support elements were suspended in the bioreactor by a mixer and an aeration pump. Generally, the formation of biofilm can be categorized into five stages: conditioning layer, bacterial attachment, EPS production, biofilm maturation and finally detachment. Therefore, the bioreactor was performed for 15 days to acclimatize activated sludge before starting the main experiments. To increase the value of the removal efficiency in the bioreactor, a combination of photocatalytic and biological processes was examined.

The photocatalytic experiments were started with an initial COD concentration of 0.25 g L^{-1} and temperature and pH were adjusted to the desired value. Several samples were taken periodically to analyze the COD concentration. At the end of each photocatalytic run, the effluent was discharged into the bioreactor and the biological experiments were performed as described previously.

COD and BOD concentrations were measured by using the procedures of standard methods [29]. pH values were measured by Metrohm 827 pH/LF portable pH/conductivity-meter, Schott Instruments GmbH, Mainz, Germany. Color removal was quantified by measuring reduction of optical density (OD) at 335 nm by a UNICO

2001SUV spectrophotometer. The absorbance readings of the each sample obtained against water as the blank and the degree of color removal were then computed based on the differences recorded.

3. Kinetic Models Evaluation for COD Removal

Mathematical models are used in fundamental researches of biological processes to examine hypotheses, determine the significance of relationships between variables, design of experiments, and analyze experimental results. These models are applied to monitor and predict the performance of treatment plants and pilot scale systems.

At the present time, simplified models with fewer variables are easier to apply which are required for designing industrial bioreactors in treatment plants.

3-1. Grau Second-order Substrate Removal Model

The second-order kinetic model is demonstrated in Eq. (1) [30].

$$-\frac{ds}{dt}=K_sX\left(\frac{S}{S_0}\right)^2 \tag{1}$$

If Eq. (1) is integrated and then linearized, Eq. (2) will be obtained:

$$\frac{S_0\theta_H}{S_0-S}=\theta_H-\frac{S_0}{K_sX} \tag{2}$$

While the second term of the right section of Eq. (2) is accepted as a constant, Eq. (3) will be obtained,

$$\frac{S_0\theta_H}{S_0-S}=b\theta_H+a \tag{3}$$

S_0-S/S_0 declares the efficiency of substrate removal and is symbolized as E. Hence, the final equation can be written as follows:

$$\frac{\theta_H}{E}=a+b\theta_H \tag{4}$$

3-2. Modified Stover-Kincannon Model

In this model the substrate utilization rate is declared as a function of organic loading rate used for biofilm reactors like rotating biological. The effective volume of the bioreactor was considered in this version of the Stover-Kincannon model, as the assessment of active surface area in attached growth systems is difficult, which this assumption was suggested by Borghei et al. at first for Moving Bed Bioreactors [31]. This model is as follows:

$$\frac{ds}{dt}=\frac{U_{max}\left(\frac{QS_0}{V}\right)}{K_B+\left(\frac{QS_0}{V}\right)} \tag{5}$$

where dS/dt is defined in Eq. (6):

$$\frac{ds}{dt}=\frac{Q}{V}(S_0-S) \tag{6}$$

Eq. (7) was obtained from linearization of Eq. (6):

$$\frac{ds}{dt}=\frac{Q}{V}(S_0-S)=\frac{U_{max}\left(\frac{QS_0}{A}\right)}{K_B+\left(\frac{QS_0}{A}\right)} \tag{7}$$

Eq. (8) was obtained from linearization of Eq. (7):

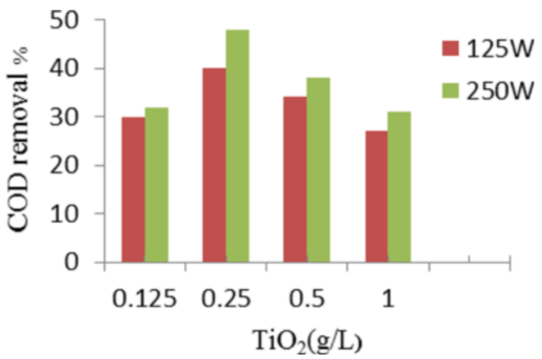

Fig. 1. Photocatalytic efficiency of textile wastewater degradation (initial COD concentration: 1,650 mg/L, light source: UV-C lamp, irradiation time: 2 h).

$$\frac{V}{Q(S_0-S)}=\frac{K_B}{U_{max}}\frac{V}{QS_0}+\frac{1}{U_{max}} \tag{8}$$

RESULTS AND DISCUSSION

1. Photocatalytic Treatment

The photocatalytic experiments were accomplished for crude textile wastewater. The reactor was filled up 500 cc of textile wastewater, so the two light sources 125 W and 250 W were inserted separately, which results are shown in Fig. 1. Increasing TiO_2 concentration improved COD degradation. During two hours of treatment, photocatalytic COD removal efficiency from textile wastewater was 29% and 48% at TiO_2 concentrations of 0.125 and 0.25 gL^{-1}, respectively; however, further increasing in TiO_2 concentration to 0.5 g/L^{-1} had no effect on the rate of degradation. This was attributed to an enhancement in surface area for the generation of hydroxyl radicals with increasing TiO_2 concentrations, while, in the concentrations above 0.25 gL^{-1} the rate of degradation was independent from the catalyst concentration. This effect is called the screening effect. These results are in agreement with a previous report [22] that photodegradation of textile wastewater decreased with increasing the concentrations of photocatalyst. The operating condition of photoreactor is the most effective parameter for this restrict, so that higher TiO_2 concentrations for rapid photodegradation are needed. As a result, increasing reaction rate with increasing TiO_2 concentration can be expected when turbidity of a mixed solution does not indicate an increasing trend with increasing TiO_2 concentration. Generally, increasing TiO_2 concentration causes an increase in the turbidity of solution, which may significantly scatter light. From the results, COD and color removal efficiencies in photocatalysis process were obtained up to 48% and 30%, respectively, as the TiO_2 concentration was 0.5 g of L^{-1}.

2. Biological Treatment in Sludge Bioreactor

The sludge bioreactor was performed continuously at four hydraulic retention times (HRTs) of 8, 12, 16, and 20 h. At HRTs of 8, 12, 16 and 20 h, the steady state values of COD removal efficiency were 38%, 40%, 48%, and 53%, respectively. The treatment efficiency of this process is shown in Fig. 2. The COD removal efficiencies increased as HRT was increased as a result of higher oxidation potential. Low HRT values cause low removal rates, whereas high

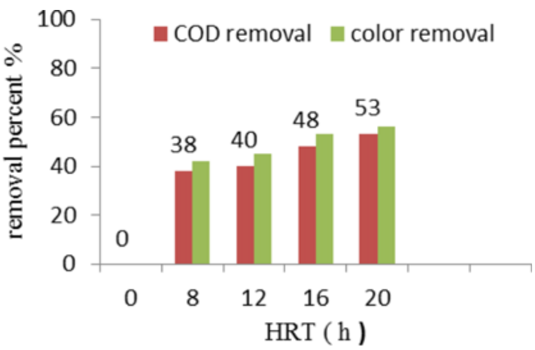

Fig. 2. Effect of hydraulic retention time (HRT) of biological reactor.

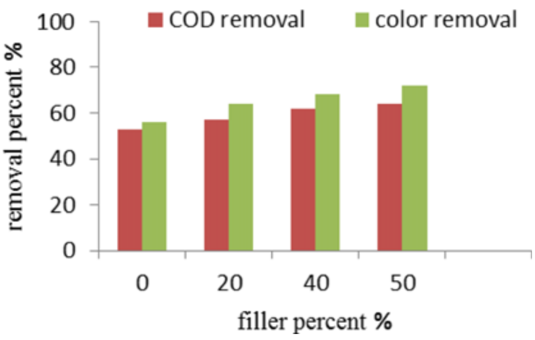

Fig. 3. Effect of filler percent on COD and color removal.

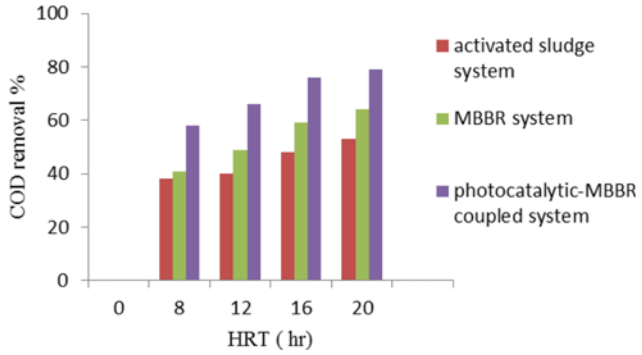

Fig. 4. Effective of photocatalytic oxidation on biodegradability of wastewater.

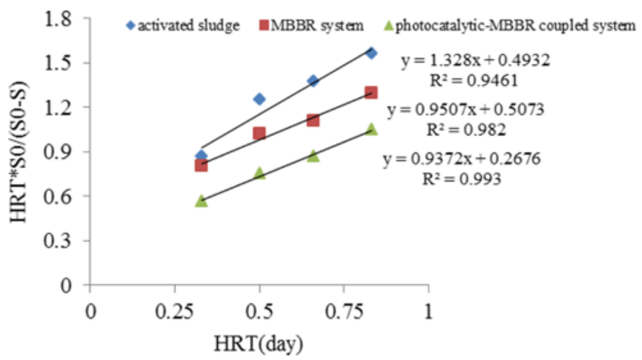

Fig. 5. Determination of kinetic constants for Grau second-order COD removal model.

HRT values are not economical. The low COD removal efficiency indicated that the sewage might contain substantial amount of non-biodegradable organic matters.

3. Biological Treatment in Moving Bed Biofilm Reactor

The MBBR was filled with LECA carrier used to treat textile effluent. To determine the effect of filler size on treatment efficiency, 20%, 40%, and 50% of the reactor volume was filled by LECA particles and the tests were performed at 20 hours of HRT. A diagram of the changes in the removal rates of COD and color at different values o f filling ratio of the carrier is shown in Fig. 3. Increasing the filling ratio the degradation efficiencies of dye and COD increased as well, contrasting a decrease in the volume of influent wastewater. The maximum of COD and color removal efficiencies were 64% and 72%, respectively, at the filling ratio of 50%. These results are consistent with a previous report [32].

4. Biological-photocatalytic Coupled System

To progress removal efficiencies from the textile wastewater, the combination of photocatalytic and biological processes was examined. The textile wastewater was pretreated by heterogeneous TiO_2 with an initial COD of 1,650 mg/L^{-1}, afterwards biological treatment in the MBBR was performed. Generally, the photocatalytic peroxidation could break down the molecular structures of non-biodegradable organic compounds into smaller molecules which are more biodegradable for aerobic biodegradation. Rodriguez et al. investigated the photo-Fenton treatment of textile wastewater and its influence in the biodegradability of the photo-treated solution. The results showed that the UV-VIS spectra approve the removal of the biorecalcitrant components responsible for the color in the effluent [33]. At HRT of 20 h the average effluent COD was decreased further to 364.5 mg L^{-1}, and the average removal efficiencies of COD and color were 79% and 87%, respectively.

5. COD Removal Kinetics

5-1. Second-order Substrate Removal Model (Grau Model)

To determine the coefficients of Grau second-order model for COD removal efficiency, Eq. (4) was graphed in Fig. 5. The values of a and b (dimensionless Grau second-order constants) were calculated using the slope and intercept of Fig. 5, respectively. The multi-component Grau second-order substrate removal rate constant (k_s) was calculated from the equation $a=S_0/(K_s.X)$. The constants determined through applying Grau second-order model are summarized in Table 2.

Table 2. Comparison of kinetic constants in the Grau second-order model

Processes	S (mg COD L^{-1})	HRT (day)	a	b	K_s	R^2
Activated sludge system	775.5-1023	0.33-0.83	0.493	1.328	0.956	0.946
MBBR system	594-973.5	0.33-0.83	0.507	0.950	0.929	0.982
Photocatalytic- MBBR coupled system	346.5-693	0.33-0.83	0.267	0.937	1.76	0.993

Table 3. Summarizes the constants determined from the applicable Stover-Kincannon models

Processes	S (mg COD L^{-1})	HRT (day)	U_{max}	K_B	R^2
Activated sludge system	775.5-1023	0.33-0.83	3.35	4.47	0.950
MBBR system	594-973.5	0.33-0.83	3.74	3.91	0.971
Photocatalytic- MBBR coupled system	346.5-693	0.33-0.83	6.1	5.67	0.994

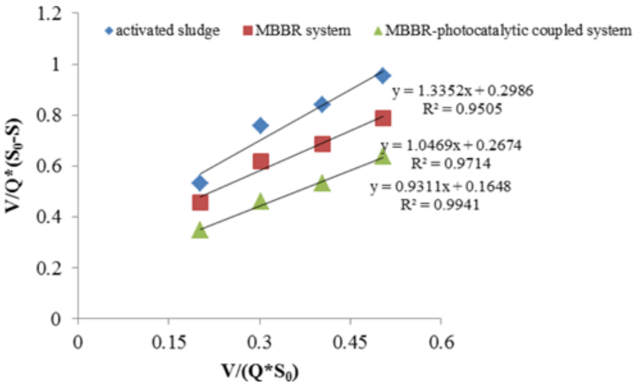

Fig. 6. Determination of kinetic constants for modified Stover-Kincannon model.

5-2. Modified Stover-Kincannon Model

Fig. 6 is a plot of the kinetic coefficients of the modified Stover-Kincannon model obtained from the plot of [V/Q (S_0-S)], inverse of the removal rate, versus V/QS_0. The obtained plots were linear. The intercept and the slope were determined by linear regression. Saturation value constant (K_B) and maximum utilization rate (U_{max}) were computed from Fig. 6, which are disclosed in Table 3.

CONCLUSIONS

Textile wastewater is a major source of pollution. This study presents that a combined process can be used for treating textile wastewater and reducing the pollution load. A laboratory-scale of photocatalysis process for the pretreatment of textile wastewater has been developed to determine the removal efficiency of color and COD after 2 h. The average yields of COD and color removal were 48% and 30%, respectively. The results show that the effluent of photocatalytic and biological processes separately cannot meet the effluent standards for direct discharging into the surface water sources. The maximum of COD and color removal efficiencies were obtained as 79 and 87%, respectively, at 20 h of HRT. Kinetic parameters were determined through linear regression using the experimental data. The experimental results were in good concurrence with the predicted data by the models, such as Grau second-order and Stover-Kincannon models. The results indicated that the kinetic models were capable of describing the bio-kinetic behavior of the reactor and the increasing trend of substrate removal rate constant (K_s) in the Grau second-order. Another kinetic model used for the COD reduction process in activated sludge bioreactor and MBBR system is the Modified Stover-Kincannon model, which led to the following values: U_{max}=3.35 and 3.74 $gL^{-1}day^{-1}$; K_B=4.47 and 3.91 $gL^{-1}day^{-1}$, respectively. A similar kinetic study was performed for the biological stage of the combined process, which 6.1 $gL^{-1}day^{-1}$ and 5.67 $gL^{-1}day^{-1}$ were achieved for U_{max} and K_B, respectively. The results indicated a slight improvement in the kinetic parameters for the moving bed biofilm reactor system when a photocatalysis pretreatment was applied. The photocatalytic pretreatment of the textile wastewater enhances the subsequent biodegradation through changing the structures of the components. Therefore, the photocatalytic-MBBR process is a promising technology for textile wastewater treatment.

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