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Treatment of 3-indole butyric acid with solar photo-catalytic reactor

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ABSTRACT

Solar photo-catalytic process is an emerging and promising technology both as an alternative treatment to conventional wastewater treatment methods and enhancement of biodegradability of highly toxic and recalcitrant pollutants. In this study, results for the treatment of 3-indole butyric acid solutions using pilot scale solar photo-catalytic treatment process are presented. The effecting parameters, such as adsorption of 3-indole butyric acid on TiO_2, pH, the initial concentration of 3-indole butyric acid and catalyst concentration, on the treatment of 3-indole butyric acid using solar photo-catalytic system were investigated. Solar photo-catalytic processes demonstrated high COD (>80%), TOC (>80%) and 3-indole butyric acid (>90%) removal efficiencies for the samples in this study. The increase of the 3-indole butyric acid concentration from 10 to 150 mg/L decreases the removal rate constant from 0.0757 to 0.0088 1/min in 240 min of oxidation using 100–1500 mg/L TiO_2 at 3–9 pH.

Keywords: 3-Indole butyric acid; Pilot scale treatment; Solar photo-catalytic treatment; TiO_2; Advanced oxidation; Plant growth regulator

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1. Introduction

Pesticides and their derivatives are generally toxic refractory chemicals, which are hazardous to the environment. 3-Indole butyric aid (IBA) is one of the important pesticide derivatives which is widely used and enhances the growth and development of food crops and ornamental plants when applied to soil, cuttings or leaves [1]. Indole and its derivatives have unpleasant smell but can cause more important damage to living organisms. These pesticides are highly toxic and are even mutagenic and carcinogenic [2].

The control of pesticides in water is an important measure in environmental protection. Among the many processes proposed and/or being developed to break down pesticides, biodegradation has received the greatest attention [1]. However, biological treatment may be limited in application for degradation of the complex and toxic organics as pesticide [3]. Therefore, advanced oxidation processes (AOPs) (which generate powerful hydroxyl radicals oxidation power = 2.8 eV vs. normal hydrogen electrode) have gained importance for degradation of the most organics in industrial effluents [4,5]. The hydroxyl radicals can be easily produced using UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone. An alternative way to obtain free radicals is the photo-catalytic mechanism occurring at the surface of semiconductors (like titanium dioxide (TiO_2)) and this indeed substantially enhances the rate of generation of free radicals and hence the rates of degradation [6]. A major advantage of the photocatalytic oxidation based processes are the possibility to effectively use sunlight

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or near UV light for irradiation, which should result in considerable economic savings especially for large-scale operations [7].

The solar heterogeneous photocatalytic detoxification process consists in utilizing the near-UV part of the solar spectrum (wavelength shorter than 380 nm), to photoexcite a semiconductor catalyst in the presence of oxygen. In these circumstances oxidizing species, either bound hydroxyl radical (OH^-) or free holes, which attack oxidizable contaminants, are generated producing a progressive breaking of molecules yielding to CO_2, H_2O and dilute inorganic acids. The most commonly used catalyst is the semiconductor TiO_2 (cheap, non-toxic and abundant product) [8].

A lot of studies dealing with the solar photo-catalytic oxidation of pesticides in water and wastewater have been published [9–13]. However, treatment of plant growth regulators such as IBA using pilot scale solar photo-catalytic (SPR) oxidation has not been widely studied and discussed in the literature. Thus this study aims to predict the suitability of the SBR for the treatment of wastewater containing IBA. The process efficiency affected by the factors such as adsorption of IBA on TiO_2, pH, the initial concentration of IBA and catalyst concentration were investigated.

2. Materials and methods

2.1. Reagents and chemicals

IBA (CAS no: 133-32-4) (molecular weight = 203.24 g/mol) was obtained pure form from the Merck Chemical Company in Darmstadt, Germany. Its structure and UV spectrum is given in supplementary Fig. 1 [4].

All experiments were performed using synthetically prepared wastewater containing 101.62 mg/L (0.5 mM) IBA. Solutions were prepared using deionized water (R = 18 MΩ cm, DOC < 0.1 mg C/L, Millipore). Several other chemicals, including, NaOH, H_2SO_4, water with 0.1% trifluoroacetic acid (TFA) and acetonitrile (ACN) with 0.1% TFA, were of HPLC grade and were also obtained from Merck. TiO_2 was used as a photocatalyst. It was used as received. Titanium dioxide P25 (anatase 80%, rutile 20%, surface area 50 m^2/g and particle size 27 nm) is from Degussa GmBH, Germany.

2.2. Pilot-scale solar photo-catalytic reactor (SPR)

The SPR experiments were carried out with a solar reactor which has a parabolic trough reflector. The SPR was containing transparent borosilicate glass tubes of 650 mL capacity with 47 mm diameter, 50 cm length, mounted on a parabolic trough reflector of aperture length 60 cm and aperture width 12.5 cm (in Fig. 2). Setting the reactor angle (0–45°) was done manually. Storage tank was made of amber coloured pyrex glass and wastewater was recirculated through the Teflon tube with the help of a peristaltic pump (Heidolph Pump Drive 5006). All the connection parts contacting with the wastewater were made of Teflon material to avoid the problem of corrosion and chemical reaction.

The stock suspensions were magnetically stirred in the dark during the operation. System flow was set to 0.8 L/min and retention time was kept constant (300 min) during all experiments. The initial volume of wastewater was 2.5 L for photocatalytic experiments and 100 mL for dark adsorption experiments. TiO_2 suspension was added after taking an initial sample. Thereafter, the

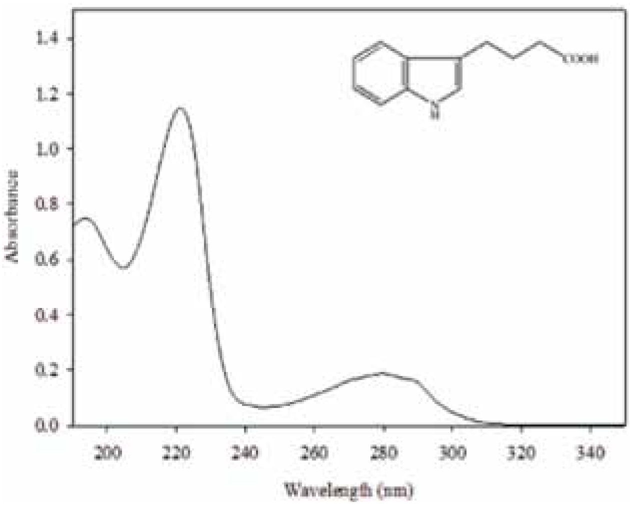

Fig. 1. Chemical structure and UV spectrum of IBA (λ_{max} = 221 nm) [4].

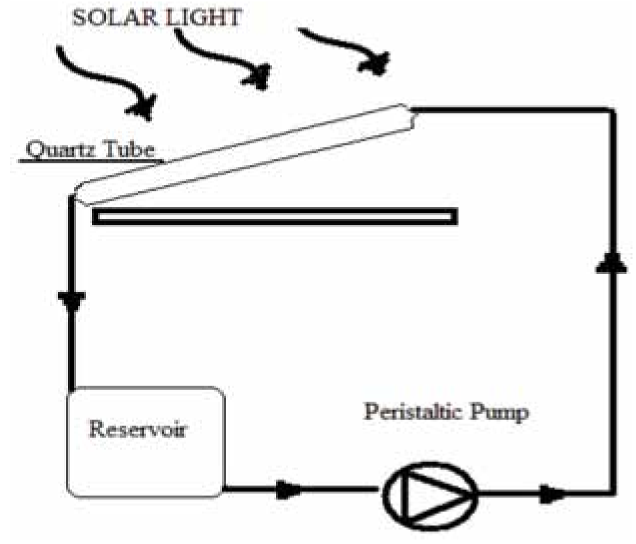

Fig. 2. Schematic display of the SPR.

samples were collected at regular intervals of time. The time period of experiments was fixed from 9.00 a.m. to 04.00 p.m.

Irradiation was carried out in the open air condition. Solar light intensity was measured for each sample and the average light intensity over the duration of each experiment was calculated. Firatoglu and Yesilata [14] investigated the effect of solar light in Turkey conditions for all year (for 37 latitude). According to this study, optimum angle for solar systems reportes as 0^o (for June and July) and 14^o (for August) [14]. From these reasons, the sensor was always set in the position of maximum intensity and the angle of tube reactors was set according to maximum intensity values at $0–14^o$ angles for studied period. All photo-catalytic experiments were carried out under similar conditions on sunny days of June–August 2010. pH, temperature and solar intensity were monitored regularly throughout the experiment. Solar intensity was measured using Delta OHM BO9847 Digital solarimeter during all the tests for each hour and the average intensity was calculated as 1500 ± 230 W/m^2.

2.3. Adsorption studies

The adsorption studies were carried out in the dark to study the adsorption of IBA on the TiO_2 surface under similar experimental conditions as that of photoreduction. For adsorption experiments, batch experiments were performed with 50 mL samples taken in glass flasks. These flasks were kept under ambient conditions but were covered with a thick brown sheet of paper to avoid the penetration of light. Fifty millilitres of the IBA solution (100 mg/L IBA) was kept in contact with the different concentrations of TiO_2 (100–1500 mg/L) 300 min using a mechanical shaker. The time period of experiment was similar to that of the light experiments. After adsorption the solution was centrifuged at 4000 rpm to separate the catalyst. The concentration of the IBA solution was determined. The amount of IBA adsorbed on the catalyst was calculated by mass balance.

In heterogeneous photo-catalytic degradation process the adsorption of IBA onto the catalytic surface is the primary step of the reaction. The adsorption experiments were carried out in order to evaluate the equilibrium constants of adsorption. The pH directly affects the adsorption mechanism [6,15–17]. Therefore, the effect of pH for adsorption of IBA on TiO_2 molecules was studied first. pH of solutions were adjusted to 3–9 with sulphuric acid or sodium hydroxide under constant TiO_2 (100 mg/L) and IBA (100 mg/L) concentrations.

The most widely used models to describe the equilibrium behaviour of metal adsorption are the well-known Freundlich and Langmuir sorption isotherms. The Langmuir equation is expressed in Eq. (1), as follows:

$$q_{eq} / Q_0 = KC / (1 + KC) \tag{1}$$

where q_{eq} is the substance amount of adsorbate adsorbed per gram of the adsorbent (mg/g); Q_0, the maximum amount of the IBA per unit weight of TiO_2 to form a complete monolayer on the surface bound at final (equilibrium) concentration of solute in the solution (mg/g); C, final (equilibrium) concentration (mg/L), and K is the adsorption constant in L/mol.

The lower the value of K means the higher affinity of TiO_2 particles. The Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. The Q_0 and K can be determined from the linear plot of C/q_{eq} versus C.

2.4. Analytical procedure

Total organic carbon (TOC) was determined using a Shimadzu-5050A TOC analyzer. The COD was analyzed following the APHA standard method with potassium dichromate [18]. The IBA concentrations were analyzed using an Agilent 1200 Series HPLC with a diode array detector (DAD) (Agilent Technologies, CA, USA). Reverse-phase liquid chromatography (3 mL/min flow, water with 0.1 TFA and ACN with 0.1 TFA at a 78:22% [v/v] ratio) with a C8-3.5 µm-75 mm (l) × 4.6 mm (i.d.) ZORBAX SB column was used for separation. To detect IBA, the detector wavelength was set at 221 ± 20 nm. IBA standard solutions were prepared in water in the 0.5–100 mg/L concentration range. Limit of detection of HPLC for IBA solutions was determined as 0.1 mg/L.

3. Results

3.1. Blank tests

For the determination of the effect of photo-catalyst on IBA removal, blank tests were carried out. In the absence of photo-catalyst, the IBA concentration was found stable on irradiation with the solar light 3–9 pH. In the absence of solar light there is no any IBA removal have been detected. In the presence of TiO_2 and in the absence of solar light, about a 1.5–5% decrease of IBA was observed due to adsorption capacity (3–9 pH and 100 mg/L TiO_2 concentration).

3.2. Adsorption isotherms versus pH

Maximum adsorption was determined at pH = 6. The adsorption of IBA on TiO_2 surface at different pH values shows that an increase of pH from acidic to alkaline resulted in a significant reduction of adsorption. This situation was defined as the changing of surface charge property of TiO_2 molecules with pH values of the solution [16]. In acidic solution, TiO_2 surface is positively charged. In the basic solution the surface is negatively charged. The point of zero charge (zPc) for TiO_2-P25 pH = 6.8 [16]. Hence pH of the solution affected the adsorption of IBA molecules on TiO_2 molecules.

The data obtained from the adsorption experiments were fitted to the linear form of the Langmuir equation and adsorption capacity (Q_0) of the TiO_2 molecules used in this study was found to be 2.31 mg IBA per gram of TiO_2 molecules.Constant K is calculated as 0.048. The regression coefficient (R^2) for TiO_2 molecules was found as 0.971 at the conditions of pH = 6 and 100 mg/L TiO_2. According to these results, removal of IBA molecules with adsorption is neglected in the next steps.

3.3. Effect of pH

Medium pH has a complex effect on the rates of photo-catalytic oxidation and the observed effect is generally dependent on the type of the pollutant as well as the zPc of the semiconductor used in the oxidation process i.e. more specifically on the electrostatic interaction between the catalyst surface and the pollutant [6]. The adsorption of the pollutant and hence the rates of degradation will be maximum near the zPc of the catalyst [15]. The effects of pH from 3 to 9 on the photo-catalytic degradation of IBA are shown in Fig. 3.

As it can be clearly seen from Fig. 3, solar photo-catalytic degradation efficiencies of IBA decreases at higher and lower pH values. Fast degradation of IBA were realized at neutral pH values (maximum at pH 6) in accordance with the literature reported above [15–17]. The behaviour of the photocatalytic degradation rate of most organic compounds generally fits pseudo-first order kinetics as the following:

$$-(dC / dt) = k_d C \tag{2}$$

where k_d (1/h) is the apparent rate constant and is affected by IBA concentration. Integration of that equation (with the same restriction of $C = C_0$ at $t = 0$) will lead to the expected relation:

$$\ln(C_0 / C) = k_d \cdot t \tag{3}$$

k_d values of IBA removal using photo-catalytic oxidation were calculated from the plot of $\ln(C_0/C)$ versus t with different initial concentration of IBA. Maximum pseudo-first-order kinetic coefficients were determined at these pH values for all investigated parameters such as IBA, COD and TOC (Table 1). Hence, neutral pH values are accepted as optimum for IBA. On the other hand, discussed in the above, IBA solutions were not significantly adsorbed on the photo-catalyst surface at neutral pH values. Therefore, oxidation is main process (at the semiconductor surface) for the degradation of IBA during the TiO_2 solar photo-catalytic treatment [16,19]. At the end of the 300 min treatment period, overall IBA, COD and TOC removal ranged between 79% and 96%, 34% and 39%, 28% and 31% at varying pH values, respectively.

3.4. Effect of TiO_2 concentration

After determining the best pH resulting in lowest IBA in the effluent, the effect of TiO_2 concentration was investigated by TiO_2 concentrations between 100 and 1500 mg/L. Initial concentration of IBA was selected as 100 mg/L for the determination of the removal effect

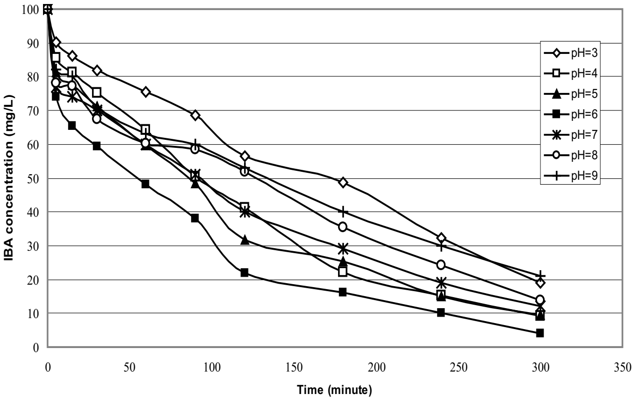

Fig. 3. Effect of pH on the removal of IBA in the SPR (100 mg/L IBA, 100 mg/L TiO_2).

Table 1
Pseudo-first-order kinetic coefficients and R2 values for pH optimization studie

pH	$K_{d\,\mathrm{IBA}}$ (min^{-1})	R^2	$K_{d\,\mathrm{COD}}$ (min^{-1})	R^2	$K_{d\,\mathrm{TOC}}$ (min^{-1})	R^2
3	0.0046	0.97	0.0028	0.97	0.0021	0.98
4	0.0077	0.99	0.0047	0.96	0.0039	0.98
5	0.0074	0.99	0.0048	0.97	0.0044	0.96
6	0.0096	0.98	0.0084	0.98	0.0073	0.99
7	0.0065	0.97	0.0068	0.97	0.0061	0.97
8	0.0057	0.98	0.0041	0.98	0.0037	0.98
9	0.0046	0.97	0.0021	0.98	0.0018	0.97

of TiO_2 concentration. And initial COD and TOC concentrations were detected as approximately 208 and 78 mg/L, respectively. Fig. 4 shows the effect of varying TiO_2 dosages on the performance of SPR.

The degradation rate for the mineralization and decomposition increases with the increase in catalyst concentration [14], but catalyst concentration should only be used until an optimum value. Usage of excess catalyst reduces the amount of photo-energy being transferred in the medium due to opacity offered by the catalyst particles [20]. It should also be noted that the optimum value of catalyst strongly depends on the geometry and working conditions of the photo-reactor. Due to the existing of TiO_2 particles creates the turbidity in solution phase and the penetration of light in the reactor is impeded by higher concentrations of catalyst [17].

As it can be seen from Fig. 4, all concentrations of TiO_2 resulted in residual concentration of IBA less 2 mg/L. Higher concentrations of TiO_2 did not increase the IBA removal efficiency significantly (>1000 mg/L TiO_2) (in Fig. 5).

Therefore, as given in Fig. 5, higher dosages of catalyst do not positively effect removal efficiencies of IBA, COD and TOC. But, increasing dosages of TiO_2 decreases the retention time of photo-catalytic reactions. At the end of the 60 min reaction time 98.8% and 99.2% IBA removal efficiencies were determined for 1000 and 1500 mg/L TiO_2 dosages, respectively. Therefore, catalyst dosage definitely affected the retention time. For final decision making on the determination of optimum catalyst concentration for IBA removal, final COD, TOC and IBA removal efficiencies were evaluated (in Fig. 6)

According to the figure, IBA removal efficiency (>90% for all calatlyst concentrations) are not significantly affected with catalyst dosages at the end of the 240 min reaction period. But, COD and TOC removal efficiencies are increasing with the increasing TiO_2 dosages. On the other hand, increasing catalyst dosages strongly may affect operating costs. Therefore, COD and TOC removal efficiencies of all applied TiO_2 concentrations played crucial role to define appropriate catalyst concentration. According to these results, 250–1500 mg/L TiO_2 dosages showed almost the same IBA, COD and TOC removal efficiencies. Because there is no any discharge standard or regulation about IBA yet it seems possible to conclude that SBR is an efficient process to decompose IBA.

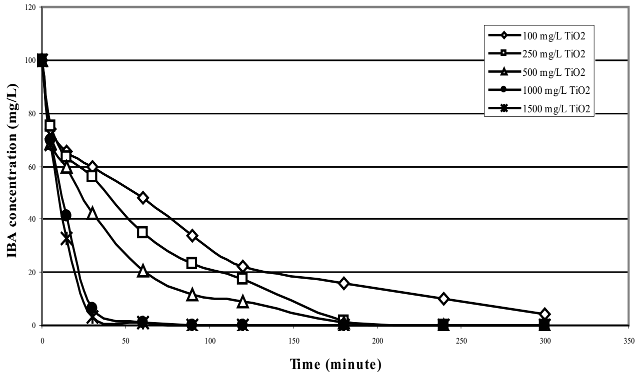

Fig. 4. Effect of TiO_2 dosage on the removal of IBA in the SPR (100 mg/L IBA, pH = 6).

3.5. Effect of IBA concentration

The effect of various initial IBA concentrations on the photo-catalytic degradation has been investigated from 25 to 300 mg/L on TiO_2 catalyst with 100 mg/L con-

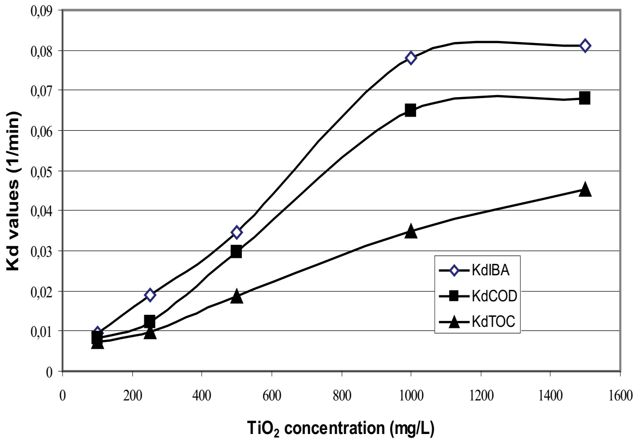

Fig. 5. Influence of TiO_2 dosage on pseudo-first-order kinetic coefficients in the SPR (100 mg/L IBA, pH = 6).

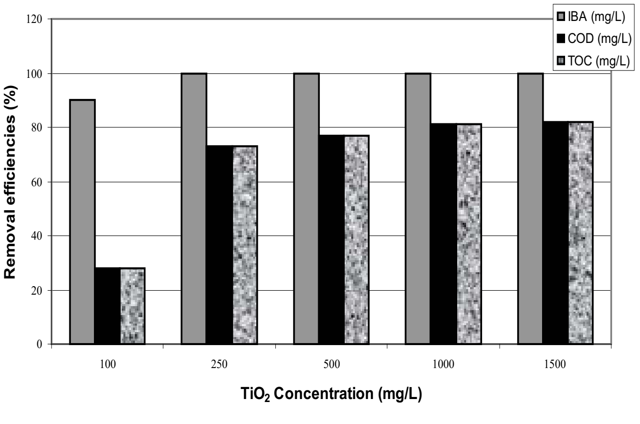

Fig. 6. Comparison of removal efficiencies of IBA, COD and TOC with different dosages of TiO_2 in the SPR (pH = 6, irradiation time = 300 min).

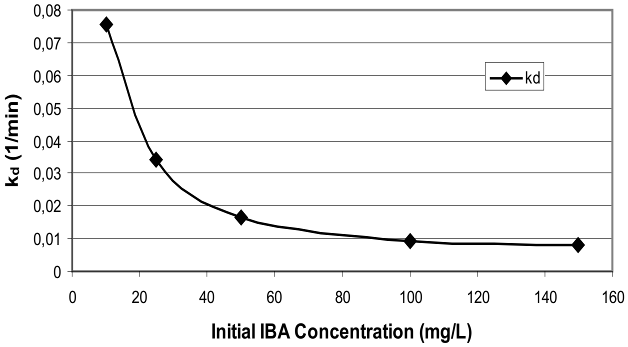

Fig. 7. The influence of initial concentration of IBA in the SPR (pH = 6 and 100 mg/L TiO_2).

centration. The results are shown in Fig. 7. It is found that the increase of the IBA concentration from 10 to 150 mg/L decreases the removal rate constant from 0.0757 to 0.0088 min^{-1} in 240 min. Similar results are reported for the photo-catalytic oxidation of other pesticides. The influence of initial concentration of IBA on the photocatalytic degradation rate found to be pseudo-first order kinetics (in Fig. 7). Actually, this situation has been expressed as "the lower concentration, the higher reaction rate" in literature [21]. But Herrmann [21] explained this situation as increasing concentrations of pollutants creates straight lines with the full coverage of pollutants and a consequent apparent zero order.

In a similar study carrying out by Qamar and Muneer [1], removal of IBA and 3-indole acedic acid (IAA) using solar photo-catalytic treatment have been investigated. The authors have found optimum conditions for IBA as pH = 8.8, catalyst concentration 2000 mg/L (TiO_2 Degussa P25) and 60.974 mg/L (0.30 mM) IBA concentration. In our study, optimum pH has been investigated as 6. Optimum catalyst concentration and IBA concentrations were found as 1000 mg/L and 10 mg/L (for 100 mg/L TiO_2 concentration), respectively. According to these results, removal efficiencies and optimum conditions was found to be different than that of Qamar and Muneer [1] study on IBA under laboratory conditions with photochemical reaction vessel. These optimization differences can be explained by reactor design and experimental conditions.

4. Conclusion

This study was aimed to determine the optimum operational parameter for SPR encouraging efficiency levels were obtained for observed parameters. The optimum operating conditions determined in the experimental tests are pH 6, TiO_2 1000 mg/L, and IBA 10 mg/L for SPR. Removal efficiencies for IBA, COD, and TOC were determined 100%, 82%, 76%, respectively.

In this study, the photo-catalytic degradation of IBA was obeyed pseudo-first-order kinetic. From the practical application point of view, it seems possible to decompose IBA using solar photo-catalytic process in a very short time. Detection and determination of endocrine disrupting effects of indole and its derivatives will be in the agenda of scientists in near future. Considering the abundance of solar irradiation time as in Turkey (7.2 h/day), the use of the SPR process with solar irradiation in water and wastewater treatment would be an advantage for both energy and cost when compared to conventional treatment systems.

Acknowledgements

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