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Removal of toxic organic compounds from synthetic wastewater by a solar photocatalysis system

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ABSTRACT

The present study was aimed at investigating the feasibility of a solar photocatalytic system to degrade toxic materials generated from different activities (e.g., xylene from petroleum refineries, tetracycline from pharmaceuticals factories, and chloropyrifos from constructions and pesticides) using the coupled homogenous-heterogeneous solar photocatalytic process. The system consists of ten Pyrex tubes (25 mm inside diameter and 125 cm long) connected in series and mounted on a parabolic trough collector (PTC) with other associated facilities. Different operating variables were studied to predict the performance of the solar reactor like, pH of solution, loading of heterogeneous catalyst, loading of homogeneous catalyst, H_2O_2 concentration, and liquid flow rate. The maximum degradations obtained, using coupled heterogeneous-homogeneous solar photocatalytic process, were 100% within 30 min. for tetracycline at (Fe^{2+}= 50 mg/l, TiO_2 = 100 mg/l, H_2O_2 = 200 mg/l, pH = 3 and liquid flow rate = 1000 l/min), 100% for xylene within 30 min at (100mg TiO2/l, 50mg Fe2+/l, 100 mg H_2O_2/l, pH = 3 and liquid flow rate = 1000 l/min), and for chlopyrifos, a maximum degradation of 100% was obtained within 1.5 h at (150 mg Fe^{2+}/l, 250 mg H_2O_2/l , and 400 mg TiO_2/l, pH = 3 and liquid flow rate = 1000 l/min). Results of this study confirmed the capability of the designed solar system to degrade different types of toxic organics.

Keywords: Photo-Fenton; Solar photocatalysis; Titanium dioxide; Ferrous sulphate; Synthetic wastewater; Hazardous organics

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1. Introduction

Antibiotics (e.g. tetracycline) have been considered as highly stable and non-biodegradable compounds. They have toxic effects on many organisms even at low concentrations. Aquatic life all over the world has suffered from the presence of trace amounts of these toxic materials due to the extensive usage of tetracycline. Chloropyrifos is used as pesticides for control of termite in civil construction, and crops of field. Recently it has been revealed that children exposed to chlorpyrifos at age below one year have an increased risk of delays in mental and at age 3 have an increased occurrence of pervasive developmental disorders [1]. Published data indicated that groundwater supplies are often contaminated by petroleum-derived hydrocarbons (such as BTX) which leak from middle distillate underground storage tanks. Many countries have exposed to this environmental problem. Many researches [2–5] have focused their attention on the treatment of these environmentally hazardous materials. Literature are rich in studies of toxic organics removal from wastewater by conventional methods, such as by using adsorption [6], biodegradation [7], and membrane separation [8]. These are simple and non-destructive, i.e., it is only transferring the ions from the solution phase into another phase which leads to further environmental problems. Recently photocatalysis has evolved as an alternative feasible technique for treating wastewater containing

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hazardous organic compounds. This advanced technique can be utilized as a pretreatment tool for the enhancement of wastewater treatment and/or could be used for direct degradation of low concentrated pollutants. The part of the AOPs which uses the power of solar photons to produce oxidant radicals is called "Solar Photocatalytic Oxidation Processes" (SPCOs) [9,10]. It is well known that countries of the Arabian Gulf are receiving solar incident energy for almost 300 day per year. The measured average incident UV-energy is 45–55 Wm^{-2} for class UV-A, and for class UV-B, the average VU-solar energy is 0.19–0.33 Wm^{-2} [11]. This makes it promising to use the UV-solar energy for many environmental and industrial applications such as wastewater treatment and synthesis of polymeric materials. Table 1 lists the average daily incident solar radiation (kW m^{-2}) on 37° inclined surface at Baghdad city in 2016.

Abid et al. [12] studied experimentally the feasibility of a solar reactor system for the removal of different types of toxic organic pollutants (e.g., synthetic methyl violet dye and phenol) from water with titanium dioxide as the photocatalyst. Various operating parameters were studied to investigate the behavior of the designed reactor like initial substrate concentration, loading of catalyst, pH of solution, and H_2O_2 concentration. A preliminary design of a solar photocatalysis system as an alternative treatment method for wastewater effluents from an Iraqi textile mill was also introduced. The influence of hydrogen peroxide on the phenol degradation by means of photo-Fenton technology was studied by [13]. Huang [14] reported that the degradation efficiency decreased extremely in the presence of access amount of H_2O_2. He indicated that this tendency may be attributed to the H_2O_2 scavenging toward producing $^{\bullet}OH$ radicals. Monteagudo et al. [15] concluded that the molar relationship between the mineralized TOC of phenolic compounds and the consumed H_2O_2, when employing the solar photo-Fenton treatment, was constantly between 1 and 3. Published works on the coupled homogenous-heterogeneous solar photocatalytic process concerning the degradation of toxic organic compounds are scarce.

The main objective of the present work is to explore the use of the coupled homogenous heterogeneous photocatalytic process for the degradation of organics which are widely used in different human activities such as tetracycline (from medical activity), xylene (from petroleum and petrochemical activities) and chloropyrifos (from construction and agricultural activities), in wastewater utilizing a solar irradiated reactor.

Table 1
Average daily incident solar radiation (kW m^{-2}) on 37° inclined surface at Baghdad city in 2016

No.	Average daily global incident solar radiation, $kW·m^2$	Average daily UV incident solar radiation, $kW·m^{-2}$	Month
1	5.7	0.456	May
2	6.8	0.544	June
3	5.7	0.456	July
4	4.5	0.360	August
5	5.9	0.472	September

2. Materials and methods

2.1. Materials

Tetracycline ($C_{22}H_{24}N_2O_8$) ≥98.0% and Chloropyrifos ($C_9H_{11}C_{l3}NO_3PS$) of analytical grade were purchased from Sigma Aldrich. Xylene (C_8H_{10}) was purchased from Al-Dora refinery, Baghdad. Hydrogen peroxide solution (35% (w/w)) was obtained from Merck. To control pH of solution, H_2SO_4 (98%), and NaOH (Flakes) from Fluke Co. were used. The nanocatalyst (TiO_2, 80% anatasa) of size (5–30 nm) was obtained from Xinyue Chemical Co., China. Ferrous Sulfate ($FeSO_4·7H_2O$) was purchased from Panreac Chemicals Company, Spain. The water used to make up solutions was RO water.

2.2. Methods

2.1.1. Experimental setup

All experiments were performed in a photocatalytic reactor with a total volume of 50 L. The photocatalytic reactor was operated as a batch mode process. The system consists of sunlight collectors, synthetic wastewater preparation tank, circulation pump and a control panel. The solar collector is mounted on a fixed steel platform tilted 37° (local latitude) of the University of Technology, Baghdad with respect to the horizontal plane and facing south. The solar reactors were made up of ten Pyrex glass cylindrical tubes 125 cm in length and 30 mm outside diameter. The tubes were connected to each other in series by polyethylene cylindrical fittings. A circulating pump was used to feed synthetic wastewater from the tank to the solar collectors via a calibrated flow meter and control valve. Stainless steel UV-reflective panels were oriented as a parabolic trough shape and placed on the steel structure which was focused on the Pyrex glass tubes. Equipment specifications of the present study are listed in Table 1. This geometry enables light entering from almost any direction to be reflected into the focal line of the tubes, and the light entering the tubes can also be employed for the photocatalytic reaction. The wastewater preparation tank was made of PVC. The synthetic water and reagents were added to the tank from an opening in the lid. Two thermocouples were placed at the inlet and outlet of the Pyrex tubes module to measure the reactor inlet and outlet temperature. The whole system was controlled using a control panel.

2.1.2. Analytical methods

Pollutant concentration is a function of the dominate wavelength which is measured by spectrophotometric method no. 2120 Standard Method, using a Shimadzu UV-Visible spectrophotometer (UB-1201 PC). The sunlight intensity was measured using Davis 6152C Vantage Pro2 Weather Station radiometer. To estimate the concentration of dissolved oxygen, an on-line DO-Model (H12400) was used. pH of the suspension was measured using an on-line pH meter Model (Hanna pH 211). Calibration curves of tetracycline, Xylene and Chlorpyrifos concentrations vs. light absorbance are illustrated in Figs. 2a–c, respectively. The performance of the solar reactor will be discussed in terms

Fig. 1. Photographic view of the experimental setup.

of organic pollutant conversion, x%, as a measure of the organic destruction ability as defined by Eq. (1)

$$x\% = \left[\frac{C_o - C(t)}{C_o}\right]\times 100 \tag{1}$$

where C_o and $C(t)$ are the initial and instantaneous measured concentrations of organic pollutant, respectively.

3. Results and discussion

3.1. Influence of pH

pH is considered an important operating parameter. Prakash et al. [16] reported that pH has a pronounced effect on the removal of copper and cadmium ions from synthetic industrial wastewater using chitosan and nylon 6. Fig. 3 illustrates the variation in concentration of tetracycline, xylene, and chloropyrifos, respectively against pH of solution after 30 min of solar irradiation keeping other operating variables unchanged at (H_2O_2 150 mg/L, TiO_2 100 mg/L, Fe^{+2} 50 mg/L). Results were obtained experimentally by varying initial pH of polluted solution from 2 to 9 for the different pollutants concentration. It is clear from Fig. 3 that the rate of degradation goes on increasing with the increase in pH and becomes maximum at pH = 3 and then starts decreasing with further increase in pH. This trend may be attributed to the surface charge of TiO_2. In acidic pH (<5.8), a higher adsorption of anionic organics on the photocatalyst surface occurs. This is due to the positively charged surface of TiO_2 thereby attracting the anionic ions, hence increasing the organics degradation in the acidic solution. However, It is well-known that the zero point charge (pH_{pzc}) of TiO_2 surface is occurred at pH around 5.8 to 6.9, outside this range the surface of the catalyst is either positively or negatively charged as shown in Eqs. (2) and (3)

$$\mathrm{TiOH + OH^- \leftrightarrow TioH^{2+}} \quad \mathrm{pH < pH_{pzc}} \tag{2}$$

$$\mathrm{TiOH + OH^- \leftrightarrow TiO^- + H_2O} \quad \mathrm{pH > pH_{pzc}} \tag{3}$$

Therefore, at pH below 5.8 an attraction occurs between the surface of TiO_2 and the molecules of pollutants accompanied with a high rate of adsorption onto the surface of TiO_2 which increases the degradation rate of organics. However,

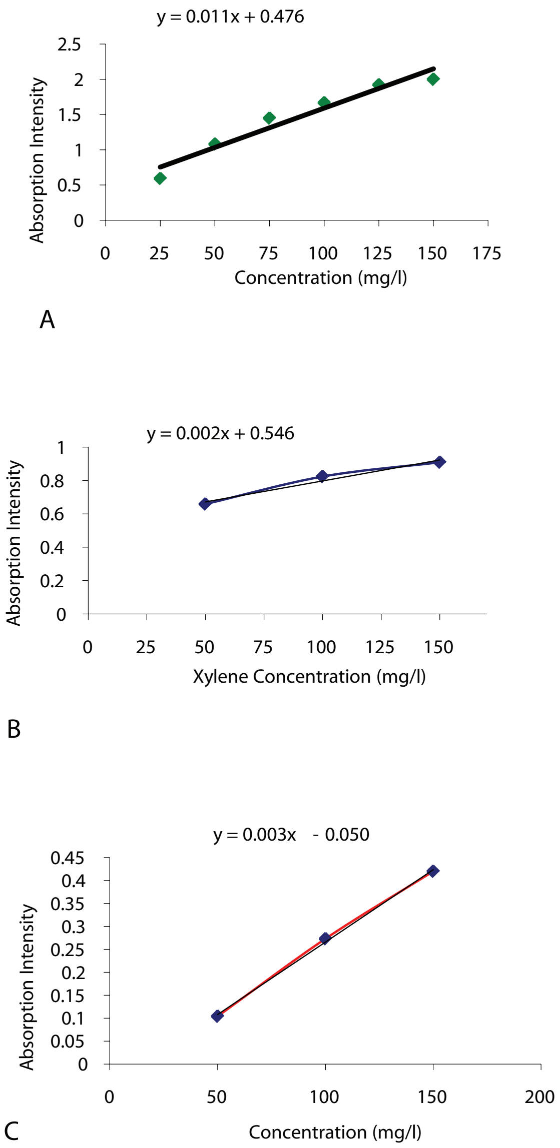

Fig. 2. Calibration curves of concentration for [tetracycline (A), xylene (B), and (C) chlorpyrifos] in water against absorption intensity.

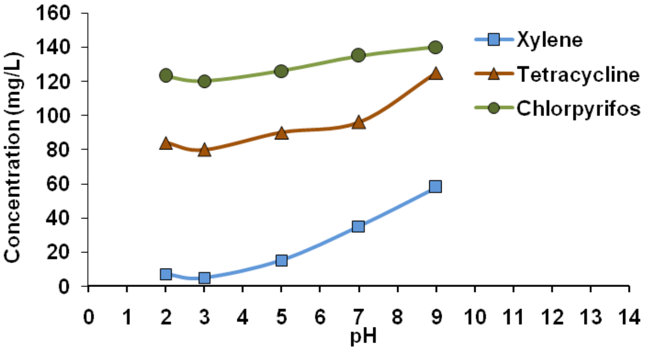

Fig. 3. Relationship between pH and concentration after 30 min at (H_2O_2 150 mg/l, TiO_2 100 mg/l, Fe^{+2} 50 mg/l).

as pH increased from 7 to 9, the percentage degradations of xylene, tetracycline and chloropyrifos decreased as the concentration of OH^- ions in the solution increased steadily and a different trend is observed in the alkaline solution where a negative charge is acquired by the TiO_2 surface which repels molecules of the organics from the catalyst surface resulted in decreasing the degradation rate. The effect of pH on Fe^{2+} maybe explained mainly by two reasons, as the pH was greater than 3, the process efficiency decreased because the coagulation of Fe^{3+} complexes reduced the catalytic effect of Fe^{2+} to decompose H_2O_2 for generation of $^\bullet OH$ radicals . At a more acidic pH, below 3, protonation of H_2O_2 to form H_3O^{2+}, which slowly reacts with Fe^{2+} ions, may also be responsible for the decrease in the formation of hydroxyl radicals. This trend of effect pH on iron ions has been also observed by Abid et al. [17]. The experimental results revealed that the degradation efficiency was increased in the following order: chloropyrifos < tetracycline < xylene. This could be explained from the UV spectra of solutions point of view. It is well known that according to Plank's equation ($\lambda = \frac{h\,c}{E_G}$, where E_G is the TiO_2 band-gap energy, h is the Blanck's constant and c is the speed of light), the UV radiation able to produce this gap must be of a wavelength (λ) equal or lower than that calculated by Blanks equation. This means that higher radiation energy (i.e., photon energy) is needed for the solution of lower wavelength. The molecular structure of the studied compounds which have UV spectra wavelengths as following [18]: xylene (= 325 nm); tetracycline (= 275 nm); chloropyrifos (= 230 nm), compatible with the above mentioned experimental observation. Our results agree well with the findings reported in [12–15].

3.2. Effect of H_2O_2 loading

Figs. 4a–b show the effect of H_2O_2 addition on the concentration of tetracycline, and chloropyrifos, respectively keeping other operating variables unchanged at (pH = 3, Fe^{2+} = 50 mg/l, H_2O_2 = 100 mg/l). It can be observed from these figures, that the efficiency of degradation increased from 48% to 100% as the H_2O_2 loading increased from 100 mg/L to 200 mg/l at 30 min of illumination time. At the same time of illumination, the degradation efficiency of chloropyrifos increased from 20% to 57% as the H_2O_2 loading increased from 100 mg/l to 400 mg/l. According to Fig. 4b, the blue curve indicates, without H_2O_2 loading, the effect of solar light and TiO_2 on conversion of chlorpyrifos was 38% while the conversion was 47 and 58% at H_2O_2 addition of 100 and 200 ppm respectively at 180 min of illumination. It is well-known that H_2O_2 serves the degradation process in two paths, first to prevent the recombination of electron-hole generated by the effect of solar irradiation on TiO_2 surface, second to generate the hydroxyl radicals by reactions with solar light and with Fe^{2+} ions. So the continuous addition of H_2O_2 affects positively on the reduction of the organics concentration in the synthetic wastewater. This is almost due to the formation of more $^\bullet OH$ radicals under solar irradiation according to Eqs. (4) and (5)

$$H_2O_2 + hv \rightarrow 2\ OH \tag{4}$$

$$H_2O_2 + e^-_{eb} \rightarrow {}^\bullet OH + OH^- \tag{5}$$

where hv represents the energy of photon in Joule, and e_{cb} is the electron at the conduction band. Eq. (4) explains the mechanism of H_2O_2 to increasing the probability for formation of $^\bullet OH$ radicals on the surface of the catalyst and hindering the electron-hole recombination [16]. Chlopyrifos needed higher concentrations of H_2O_2 to enhance the degradation of 88.0% which was obtained after 3 h of illumination with an addition of 400 mg H_2O_2/l.

3.3. Effect of TiO_2 loading

Concentration of the photocatalyst in the liquid suspension was varied from 75 to 300 mg/l to explore its influence on the degradation efficiency of the organics under solar illumination keeping other operating variables unchanged at pH = 3, Fe^{2+} = 125 mg/l, H_2O_2 = 200 mg/l. Figs. 5a, b plot the variation in degradation of tetracycline and chloropyrifos, respectively. It can be observed from these figures, that the degradation efficiency of tetracycline increased from 13% to 100% as the TiO_2 loading increased from 0 mg/L to 300 mg/l at 30 min of illumination time. For chloropyrifos, the degradation efficiency increased from 9% to 30% at the same time of illumination. This increasing were attributed to the increase in active sites of the photocatalyst with increasing in catalyst load-

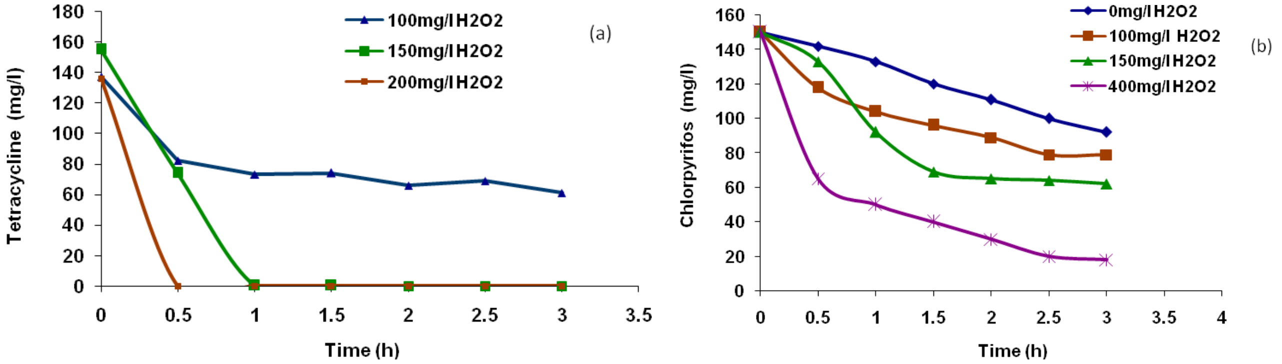

Fig. 4. Variation of tetracycline (a) and chlorpyrifos (b) conc. in wastewater against illumination time at different concentration of H_2O_2 (pH = 3, Fe^{2+} = 50 mg/l, TiO_2 = 100 mg/l).

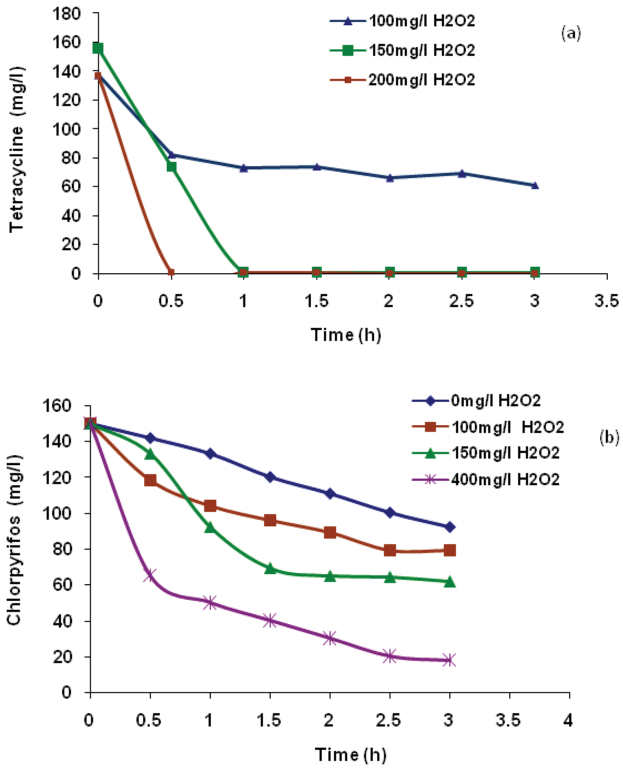

Fig. 5. Variation of tetracycline (a) and chlorpyrifos (b) conc. in wastewater against illumination time at different concentration ofTiO_2 (pH = 3, Fe^{2+} = 125 mg/L, H_2O_2 = 200 mg/L).

ing, although the increasing in degradation trend of chloropyrifos was lower, since the molecular bonding of the latter needs more solar irradiation energy with more oxidative agent (H_2O_2) to degrade. As can be seen, at a specified catalyst loading the degradation efficiency appeared to increase rapidly at the first part of experimental period while the rate of increase seems to be slower at the second part. This may be attributed to the rate of reaction which is higher at the beginning of the photo-degradation process due to the high concentration of reactants. However, as the organics concentration decreased the reaction rate proceeds slowly, accordingly. Our results were in agreements with the findings of [17,18].

The intensity of UV solar energy is time dependent. It is measured by an UV radiometer mounted at the same angle as the solar collector. As radiation data are collected continuously, it is very easy to calculate the global average incident radiation on the collector surface (UV_{avg}, W/m^2). The amount of energy collected by the reactor (per unit volume) from the start of the experiment until each sample is collected may be found by Eq. (6):

$$Q_{UV/n} = Q_{UV,n-1} + \Delta t_n * UV_{av} * A/V \quad (6)$$

where Δt = time interval between each sample (= 30 min), A = area of reactor (= total surface area of glass tubes) = 1.175 m^2, V (total volume of the system) = 39 L, n = number of samples, UV_{avg}= 47.2 Wm^{-2} during the month of September in 2017.

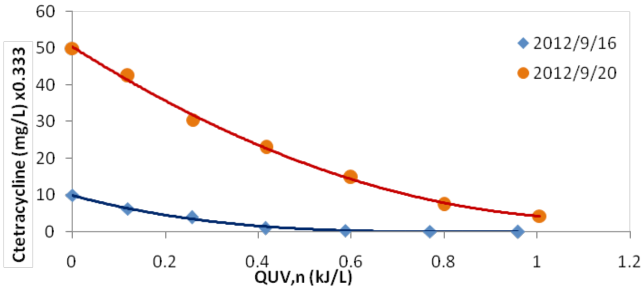

Fig. 6. Variation of tetracycline concentration in wastewater against illumination time at different concentration of tetracycline (pH = 3, Fe^{2+}= 125 mg/L, TiO_2 = 50 mg/L, H_2O_2= 150 mg/L).

The results are shown in Fig. 6, which plots the variation in tetracycline concentration against accumulative UV energy per unit volume of dispersion after 180 min of illumination at operating conditions (pH = 3, Fe^{2+} = 125 mg/L, H_2O_2 = 200 mg/L) with varying concentrations of tetracycline. The plot depicts that solar energy has a positive impact on the degradation rate of dye, since the oxidation of organics is directly proportional to the concentration of positively charged holes formed by absorption of UV radiation. As can be seen from Fig. 6, the dependence of reaction rate on light intensity (I) undergoes transition from linearity to a non-linear dependence ($I^{0.5}$) as intensity increases. It appears that at high light intensity, the recombination of the electron-hole pair is enhanced, while at low fluxes organic oxidation can compete with recombination. Further, the rate becomes independent of light intensity at higher fluxes and the expected rate limiting factor becomes the mass transfer. These conclusions are also supported by [19,20].

3.4. Effect of ferrous sulfate loading

Figs. 7a–c illustrate the effect of (Fe^{2+}) addition on the degradation of tetracycline, chlorpyrifos and xylene, respectively keeping other operating variables unchanged at (pH = 3, 100 mg TiO_2/L, 200 mg H_2O_2/L). As can be seen in these figures, the organics degradation increased as the dose of (Fe^{2+}) increased. In Fig. 6a, the degradation of tetracycline approaches 100% within 1 h at 50 mg Fe^{2+}/l. However, the degradation of tetracycline approaches 93.0% within 30 min as the loading of (Fe^{2+}) increased to 125 mg/l. Considering chlorpyrifos (see Fig. 6b, the degradation was 46.6% within 1 h at loading of 75 mg Fe^{2+}/l, and it approached 67.0% as the dose of (Fe^{2+}) increased to 300 mg Fe^{2+}/l within 1 h. As can be shown in Fig. 7c, the degradation of xylene was 100% within 1 h at 75 mg Fe^{2+}/l, when the loading of 100 mg Fe^{2+}/l the removal of xylene approaches 95.0% within 30 min. This noticeable trend of ferrous sulfate is due to the rapid reaction of (Fe^{2+}) with H_2O_2 to produce large quantities of •OH radicals according to Eq. (6). This reaction has a high specific reaction rate (K) which is about 53–76 L mol^{-1} s^{-1} as estimated by [21]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \quad (7)$$

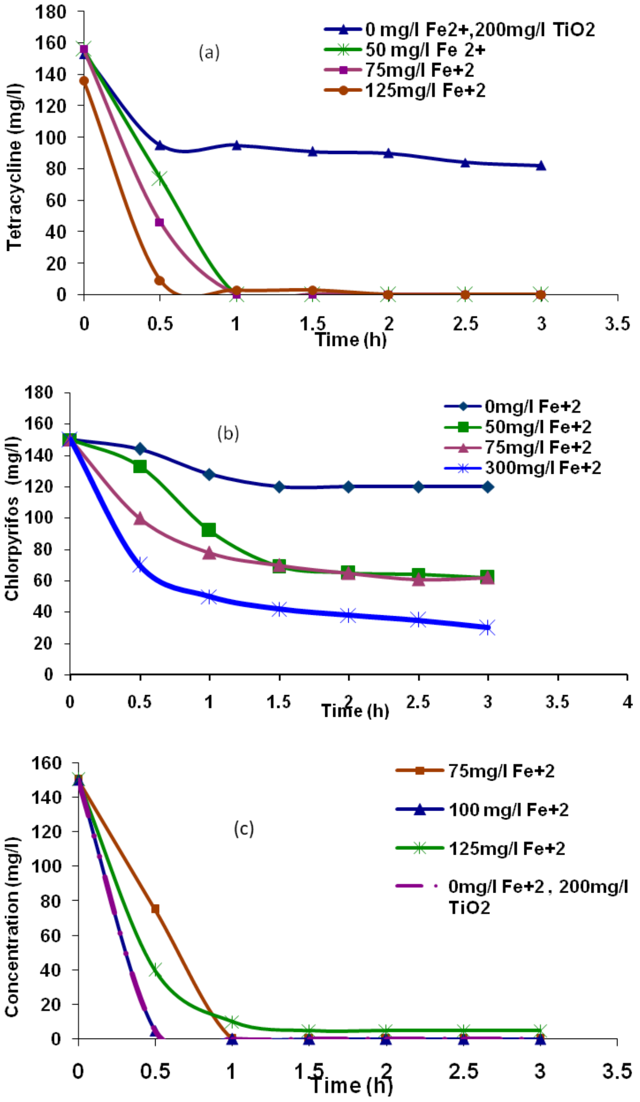

Fig. 7. Variation of tetracycline (a), chlorpyrifos (b) and xylene (c) concentrations in wastewater against illumination time at different concentration of Fe^{2+} (pH = 3, TiO_2 = 100 mg/l, H_2O_2 = 200 mg/l).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{2+} + OH_2 + H^+ \tag{8}$$

However, after that, the reaction shown in Eq. (7) continues with much slower rate with specific reaction rate constant (K) = 1 to 2 × 10^{-2} L mol^{-1} s^{-1}. The reaction rate of Fe^{2+} in Eq. (6) is about 43 times the reaction rate of Fe^{3+} in Eq. (7), estimated as the ratio of [$K(Fe^{2+})/K(Fe^{3+})$]. Therefore, the performance of the solar photo-Fenton process could be enhanced by the continuous addition of Fe^{2+} ions during the illuminated reaction.

Finally, multiple regression analysis was performed to determine the most significant parameter among the studied parameters (H_2O_2, TiO_2 and Fe) affecting the removal efficiency. The analysis showed all the three parameters, have significant effect on the removal efficiency, while TiO_2 showed the highest significant effect.

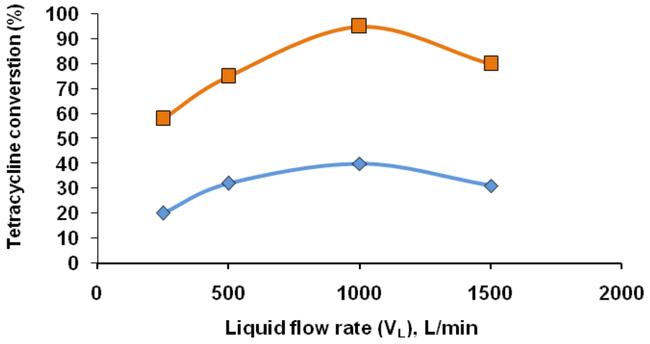

Fig. 8. Variation of tetracycline conversion in wastewater against liquid flow rate at different concentration ofTiO_2 (■: $CTiO_2$ = 100 mg/L; ♦: $CTiO_2$ = 0 mg/L), (pH = 3, F^{e2+} = 125 mg/L, H_2O_2 = 200 mg/L).

3.5. Effect of liquid flow rate

The effect of liquid flow rate on the degradation of organics was tested by changing the flow rates from 250 L/min to 1500 L/min with different TiO_2 loadings keeping other operating variables unchanged at (pH = 3, Fe^{2+} = 125 mg/L, H_2O_2 = 200 mg/L). Fig. 7 plots the tetracycline concentration against illuminated time. It could be noticed that the degradation efficiency appears to increase gradually as the flow rate increased from 250 L/min to 1000 L/min where the degradation of tetracycline approaches maxima. However, further increase in flow rate causes the removal of tetracycline to drop steadily. This could be explained from the view point of flow characteristics which is laminar at low flow rate with poor mixing of solid catalyst all over the irradiated solution. This mixing behavior is improved when the flow rate approaches 1000 L/min. But as the flow rate increased more, a decrease in organics degradation occurred. This may be attributed to the decrease of residence time of organic compounds inside the solar reactor due to the higher liquid superficial velocities.

4. Conclusion

The feasibility of a coupled homogenous-heterogeneous solar photocatalytic system to degrade toxic materials generated from different activities (e.g., xylene from petroleum refinery, tetracycline from pharmaceuticals factory, and chloropyrifos as pesticides) was studied. Results showed that pH = 3 and liquid flow rate = 1000 L/min were the optimum values for the degradation of each studied toxic material. The maximum degradations obtained, using the solarphotocatalytic process, were 100% within 30 min. for tetracycline at F^{e2+}= 50 mg/L, TiO_2 = 100 mg/l, H_2O_2 = 200 mg/l, 100% for xylene within 30 min at 100 mg TiO_2/l, 50 mg Fe^{2+}/L, 100 mg H_2O_2/L, and for chlopyrifos, a maximum degradation of 100% was obtained within 1.5 h at 150 mg Fe^{2+}/l, 250 mg H_2O_2/l , and 400 mg TiO_2/l. The present results confirmed the capability of the designed solar system to degrade different types of toxic organics with acceptable efficiency.

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