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SOLAR PHOTOCATALYTIC TREATMENT OF SIMAZINE FROM SYNTHETIC WASTEWATER

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Abstract: In this research, a solar pilot plant designed for solar photocatalytic applications have been used to investigate the feasibility of simazine degradation in an aqueous solution. Simazine degradation was investigated in both homogeneous and heterogeneous photocatalysis systems by photo-Fenton and titanium dioxide, respectively. Simazine remediation was studied at different reagent doses to identify the optimum condition, H_2O_2 (400-2400 mg/L), Fe^{2+} (5-30 mg/L) and TiO_2 (100-500 mg/L). The optimum remediation conditions for solar homogenous system was observed at H_2O_2 and Fe^{2+} concentrations of 1200 and 20 mg/L, respectively. The best remediation conditions for solar heterogeneous system was identified at TiO_2 and H_2O_2 concentrations of 300 and 2000 mg/L, respectively. The best COD removal efficiency at both homogenous and heterogeneous systems were 43.8% and 43%, respectively. Simazine removal were about 96.7% and 92% for homogenous and heterogeneous systems, respectively.

Keywords: *Advanced oxidation processes, Fenton, Photo -Fenton.*

التحفيز الضوئي الشمسي لمعالجة المياه المصنعة الملوثة بالسمازين

الخلاصة: في هذه الدراسة تم استخدام منظومة تعمل بنظامي الاكسدة المتقدمة المتجانس والغير متجانس باستخدام الطاقة الشمسية في دراسة تحلل المبيد العشبي (Simazine) في المحاليل المائية. وقد تم ذلك تحت تأثير تراكيز مختلفة من المواد التالية: H_2O_2 (400-2400 mg/L) , TiO_2 (100-500 mg/L) .Fe^{2+} (5-30 mg/L) بلغت نسبة إزالة ال COD في نظام الاكسدة المتجانس والغير متجانس 43.8% و43% على التوالي. في هذه الدراسة كانت الظروف المثلى لإزالة المبيد هي عند تركيز 1200 ملغ/لتر من H_2O_2 و 20 ملغم/لتر من Fe^{2+} باستخدام الاكسدة المتقدمة المتجانسة في حين ان الظروف المثالية للإزالة باستخدام نظام الاكسدة المتقدمة الغير متجانس كانت عند تركيز 300 ملغم/لتر TiO_2 و 2000 ملغم/لتر من H_2O_2. أفضل نسبة إزالة لل COD في نظامي الاكسدة المتقدمة المتجانس والغير متجانس كانت 43.8% و43% على التوالي. نسبة إزالة المبيد العشبي Simazine بلغت 96.7% و92% في نظامي الاكسدة المتقدمة المتجانس والغير متجانس على التوالي.

1. Introduction

One of the crucial environmental problems is the pollution of aquatic environment by chemicals used in agriculture [1]. A variety of wastewater effluents reported a trace concentration of numerous contaminants such as pesticides, pharmaceuticals and personal care products [2]. The use of herbicides and insecticides has grown to worrying levels, since the Second World War [3]. Evidence on water pollution with pesticides started to appear at about 1945. Most of these evidences were detected due

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to physiological response of aquatic creatures. Recently, applying the chromatographic separation techniques has led to the confident identification of pesticides in aquatic environments [4]. Consequently, the US environmental protection agency (EPA) banned five pesticides due to their frequent appearance in the aquatic environment that are simazine, metolachlor, alachlor, cyanazine and atrazine [3]. Pesticides are known by their toxic characteristics. Simazine is one of the most widely used pesticide that is used to control annual grasses and weeds in crop fields [1]. Simazine belongs to triazine family of chemicals.

Table (1) exhibits some of the physio chemical properties of simazine. The US EPA believes that the Maximum Contamination Level (MCL) of 4 ppb of simazine would not cause any potential harm to human [3]. In Europe, some countries such as Norway has completely banned the use of pesticides [3]. The European Commission believes that the MCL of pesticides in drinking water is 0.1 µg/L [3]. In addition, the concentration of single and total pesticides have been limited to 0.1 µg/L and 0.5 µg/L, respectively, according to the World Health Organization (WHO) [5].

Conventional treatment methods including chemical, physical and biological approaches have been applied for pesticide remediation [6]. Theses includes acid-base hydrolysis, chlorination, solvent extraction, fixation, membrane separation, filtration, electrodialysis, ion exchange, reverse osmosis and enzymatic treatment [6].

However, these conventional techniques requires expensive equipment and high-energy requirements and showed moderate efficiency in pesticide elimination. The production of toxic sludge in a large volume usually requires treatment or disposal has also limited the use of these methods [6]. Pesticides remediation using conventional wastewater treatment plants is invalid due to their toxic characteristics and bio-recalcitrant [1, 7]. Thus, further developed remediation methods is required. Recently, Advanced Oxidation Processes (AOPs) were given a great attention for the removal of toxic pollutants due to their significant capability for the transformation of these contaminants into harmless compounds in an affordable cost. This is due to the generation of highly reactive hydroxyl radical ($OH^{\bullet}$) [8].

Table 1. Physio chemical properties of simazine.

Molecular name	6-Chloro-N2,N4-diethyl-1,3,5-triazine-2,4-diamine (simazine)
Molecular formula	$C_7H_{12}ClN_5$
Molecular weight (g/mol)	201.657
Vapor pressure mm Hg at 20 (°C)	6.1×10^{-9}
CAS number	[122-34-9]
Melting point (°C)	225-227
Water solubility at 20°C (mg/L)	5
Density at 20°C (g/cm^3)	1.3
Henry's law constant (atm m^3 /mol)	9.48×10^{-10}

The AOP systems are classified according to the methods of radical's generation that are direct generation by physical routes, addition of oxidants and the use of solid catalysts [9]. Mixtures of Fe(II) and H_2O_2 are widely used for the generation of highly reactive species are known as Fenton reagent. A rapid reaction between the organic matter and the free radical take place either by hydrogen abstraction from the aliphatic organic molecule or by addition to a double bond resulting in an organic radicals [10]. Oxygen is expected to react with these radicals initiating a sequence of oxidation reactions forming mineralization products of H_2O and CO_2 [11].

The main disadvantage of AOPs is high operation cost, which can reduce its application scale due to the electrical demand for ozone generator and UV lamps. However, large application scale is viable due to advent of improved reactor design, higher efficiency UV lamps, visible light catalyst and the help of computational energy modeling. Large application scale of both solar and UV based photocatalysis is of great possibility. Malato et al. [12] investigated the photocatalytic minerilization of formetanate, imidacloprid, diuron and methomyl in an aqueous solution in a pilot plant. Complete elimination of the parent pesticides have been achieved for all pesticides. Limited number of research have been reported on photolysis, photocatalytic degradation and oxidation of simazine [3, 13, 14]. Most of these researches were conducted to investigate the impact of a single AOP system on pesticide elimination.

Consequently, further researches are still required to improve AOPs performance and to develop new immobilized photocatalysis for simazine degradation [9]. Rivas et al [3] investigated the influence of temperature, pH and iron concentration at a fixed H_2O_2 concentration on simazine elimination by mean of Fenton reagent (Fe(II) and H_2O_2). In contrast, this study will investigate the influence of H_2O_2 dose as a variable. The geographical location of Iraq makes the application of AOPs cost effective method implementing solar energy in the system. This research will investigate the feasibility of simazine degradation in homogenous and heterogeneous systems by photo-Fenton and titanium dioxide, respectively, implementing solar radiation.

2. Materials and Methods

2.1. *Materials*

Simazine with a purity of 99.4% grade was obtained from Riedel-de-Haen. $FeSO_4.7H_2O$ with purity of 99.9% was purchased from Panreac. Titanium dioxide with purity of 99% was obtained from Himedia. H_2O_2 with purity of 35% was acquired from Hopkin and Williams. Sulfuric acid with purity of 97% was obtained from Riedel-deHaën. Sodium hydroxide with purity of 99% was purchased from Merck Malaysia Sdn. Bhd. Samples were prepared by dissolving the essential quantity of chemical in distilled water. Solutions of 5 normal of both H_2SO_4 and NaOH were used for pH adjustment.

2.2. *Equipment*

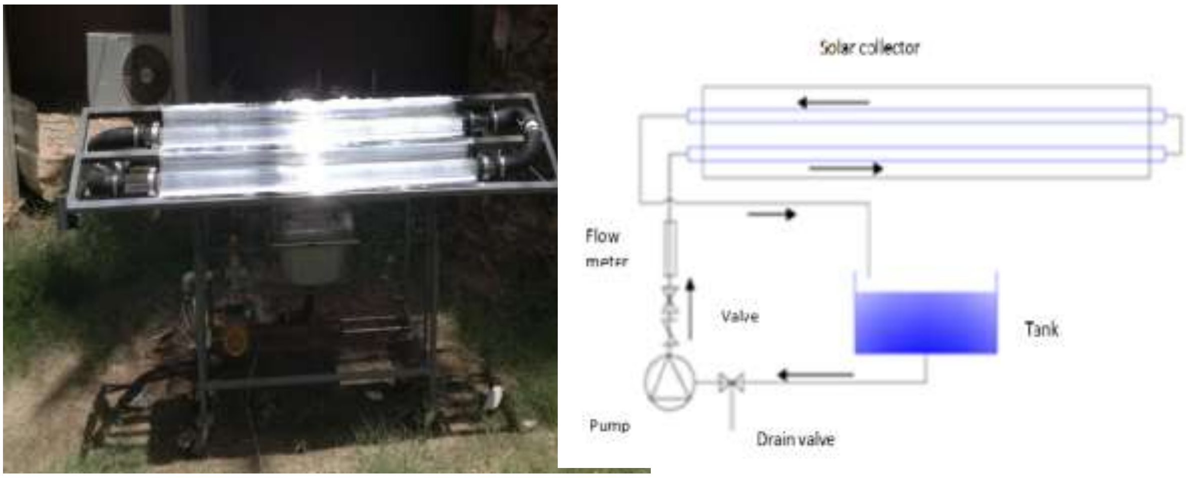
The pilot plant, which was constructed by the previous work was used in this study [15]. Fig. 1a shows a photograph of the solar pilot plant. It was installed at Baghdad University / Environmental Engineering Department.

The pilot plant includes a hydraulic circuit designed to operate in batch mode. A schematic demonstration of the pilot plant is shown in Figure (1b). The hydraulic circuit consists of solar collector, tank, centrifugal re-circulation pump, connecting tubing and valves (see Fig. 1b).

The total volume of the water used in the experiment was 16 L, while the water volume in the solar collector was 5 L. Two Compound Parabolic Collectors (CPCs) were constructed in series. The CPCs were located on stationary supports, inclined by about 33°. This was to obtain optimal performance. The CPCs represents the solar collector. The CPCs reflectors includes plates was made of stainless steel and coated with foil. The photoreactor includes two borosilicate glass tubes.

The length, inner diameter, outer diameter of the borosilicate glass tubes are 1.32m, 46.4mm and 50mm, respectively. The connection tubes are made of PVC and each with a diameter of 62.5mm. The main tank (16 L in volume) is beneficial to provide aeration and samples for analysis. In addition, it is continuously supplies the reactor with the reaction effluent by centrifugal pumps (Reshani pumps, China). Throughout the experiment, the discharge was adjusted to 1.4 m^3/hr by means of flow meter (model LZS, Turkey). The pH level was observed using pH meter (WTW, Germany).

A UV radiometer (Sper Scientific Electronics Co. LTD, Taiwan, and model UVA/B-850009) was used to measure the UV radiation. The radiometer consists of three parts. The first part is the diffuser that is beneficial to define the correct angular response. The second part is the filter that ensures measuring the deliberated radiation only. While, the third part is to yield a linear voltage and it known as photodiode.



(a) (b)

Figure 1. a : Photograph of the solar pilot plant, b : Schematic demonstration of the pilot plant [15].

2.3. *Methods*

The experimental procedure for the homogeneous and heterogeneous systems were as described below.

2.3.1. *Homogenous system*

The procedure involves cleaning and filling the solar reactor with distilled water. This was to prevent the existence of any possible compounds in the reactor. The pilot plant were covered with a small plate to inhibit photochemical reactions and to examine Fenton reactions in shady conditions. An aqueous solution of simazine was prepared by dissolving in distilled water and introduced to the reactor. To achieve complete dissolution and perfect homogenization of the contaminants the solution was allowed to recirculate repeatedly for about 30 minutes. At this point, the initial sample was taken and pH level was adjusted to 3 in order to prevent iron precipitation.

The required amount of ferrous sulphate was prepared by dilution in distilled water and introduced to the reactor. In order to initiate the oxidation reaction, hydrogen peroxide was added after 15 minutes. The Fenton reaction was started after about 15 minutes by adding H_2O_2. After 15 minutes of recirculation, the photo-Fenton reaction was started by removing the cover from the pilot plant. Six samples were taken with 20 minutes interval and the local UV irradiation was dignified by the UV radiometer with each sample. This procedure was conducted fixing the concentration of ferrous sulfate at 20 mg/L, while varying H_2O_2 concertation 400, 800, 1200 and 1600 mg/L. The procedure was repeated electing the optimum dose of H_2O_2, while changing the concentration of Fe^{2+} in the range 5, 10, 20 and 30 mg/L.

2.3.2. *Heterogeneous system*

The experimental procedure was similar to that of homogenous system except the following differences. The pH level was adjusted to 4.6 [16]. The required amount of TiO_2 was introduced to the reactor and recirculated in the reactor for about 45 minutes. This was to ensure decent adsorption of the pollutants on TiO_2 surface. To initiate the oxidation reaction, the desired concentration of hydrogen peroxide was added to the reactor and recirculated for about 15 minutes. Seven samples were taken within 40 minutes interval and the local UV irradiation was obtained by the UV radiometer with each sample. This procedure was conducted fixing the concentration of H_2O_2 at 1200 mg/L, while varying TiO_2 concertation 100, 200, 300, 400 and 500 mg/l. The procedure was repeated electing the optimum dose of TiO_2, while changing the concentration of H_2O_2 in the range 800, 1200, 1600, 2000 and 2400 mg/L. Duplicate samples were taken and average value was reported.

2.4. *Analysis*

Simazine was analyzed using a High Performance Liquid Chromatography (HPLC) (PerkinElmer series 200, USA), equipped with a UV-detector and a C18 column obtained from Supelco Discovery. The mobile phase composition was acetonitrile/water with a ratio of 60/40 [1].

The UV-detection was operated at 214 nm [1]. Fig. 2 shows the standard curve obtained from the HPLC for simazine. Simazine peak was identified at time 5.5 minutes. The chemical oxygen demand (COD) was analyzed using a COD photometer system (RD-125, Lovibond Company, Germany).

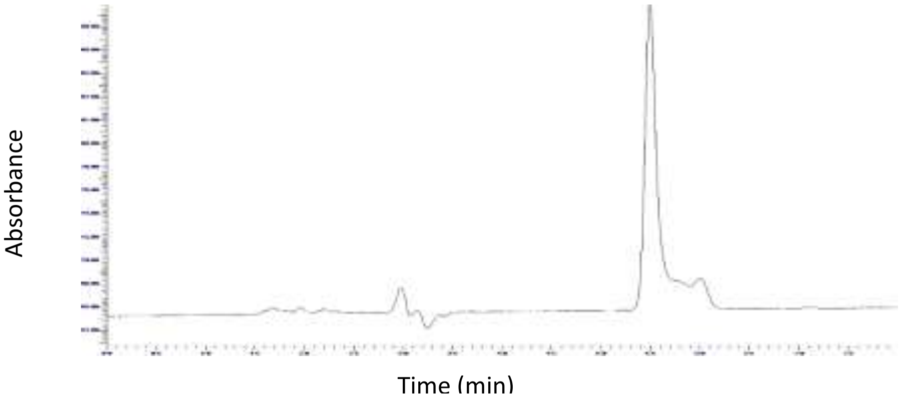


Figure 2. The standard curve obtained from the HPLC for simazine.

2.5. *Standardized treatment time*

Due to the variation of the average intensity of solar radiation with time, atmospheric conditions and geographical location. The treatment time was standardized based upon an average solar intensity in a clear day, which is about $30W/m^2$ [13]. The following equations were used for the calculation of t_{30w}.

$$t_{30w,i} = t_{30w,i-1} + \Delta t_n \frac{UV\,V_R}{30V_T} \tag{1}$$

$$\Delta t_n = t_i - t_{i-1} \tag{2}$$

Where:

Δt_n refers to time interval between sampling, UV refers to average solar intensity in clear sunny day (W/m^2), V_R and V_T are the reactor and total (the volume of liquid in the entire system) liquid volumes, respectively.

3. Results and discussion

3.1. *Homogeneous system*

3.1.1. *Effect of H_2O_2*

The influence of initial H_2O_2 concentration on the degradation of simazine was observed at 400, 800, 1200 and 1600 mg/L, while the concentration of Fe^{2+} and pH level were fixed at 20 mg/L and 3, respectively. The pH level was adjusted at acidic level to avoid the precipitation of iron [3]. Fig. 3 shows the correlation between the removal efficiency of simazine (COD mineralization efficiency) and the normalized illumination time (t_{30w}). Fig. 3 reveals that the COD mineralization efficiency increased massively from about 17.9% to 48%, while the concentration of H_2O_2 increased from 400 to 1600 mg/L. This reveals a great enhancement in the mineralization efficiency of simazine. This was due to the continuous generation of $HO^•$ radicals available to attack pollutants structure. Therefore, the degradation increased due to the reaction between Fe^{+2} and H_2O_2 in the presence of solar radiation. It should be noticed that the removal efficiency has increased slightly from 44.6% to 48%, while the concentration of H_2O_2 increased from 1200 to 1600 mg/L (see Fig. 3). This means that a slight improvement in the removal efficiency requires a great addition of H_2O_2 and no further enhancement is expected. According to Chon et al. [9] excess addition of H_2O_2 will diminish the overall reaction rate due to the creation of less penetrative $HO^•$ radicals. This may be related to the behavior of H_2O_2 as an $OH^•$ radical scavenger. Thus, the best removal efficiency was obtained at 1200 mg/L of H_2O_2. Similar observations were reported by Catalkaya and Kargi [1].

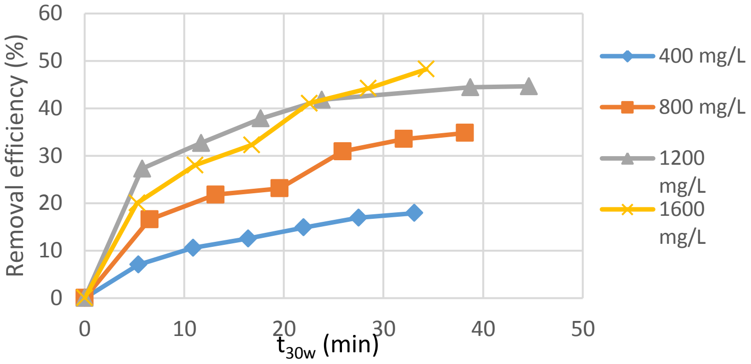


Figure 3. Effect of initial H_2O_2 concentrations ranged from 400 to 1600 mg/L on the COD mineralization of simazine by solar photo-Fenton system at Fe^{2+}=20 mg/L, pH level=3 and simazine=20 mg/L.

3.1.2. Effect of Fe^{2+}

The influence of initial Fe^{2+} concentration on the degradation of simazine was observed at 5, 10, 20 and 30 mg/L, while the concentration of H_2O_2 and the pH level were fixed at 1200 mg/L and 3, respectively. Fig. 4 shows the relation between the mineralization efficiency of simazine and t_{30w}.

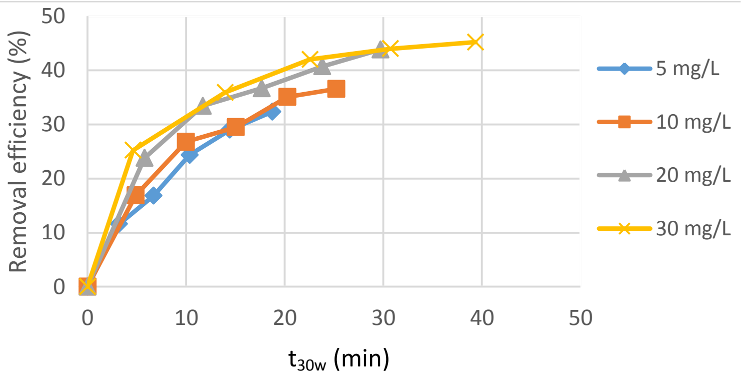


Figure 4. Effect of initial Fe^{2+} concentrations ranged from 5 to 30 mg/L on the COD mineralization efficiency of simazine by solar photo-Fenton system at H_2O_2=1200 mg/L, pH=3 and simazine=20 mg/L.

Fig. 4 illustrates that increasing Fe^{2+} concentration can improve the mineralization efficiency of simazine. The removal efficiency has increased moderately from about 43.8% to 45% at Fe^{2+} concentration of 20 and 30 mg/L, respectively. Rivas et al. [3] reported similar observation. Consequently, Fe^{2+} concentration of 20 mg/L was selected as the best concentration for the remediation of simazine. In addition, high Fe^{2+} concentration produces dark zones and turbidity in the photo-reactor. This can adversely affect the efficiency of the reactor due to the scattering of light [18].

The obtained results are in agreement with the previous literature highlighting the improvement in pesticide elimination, while increasing Fe^{2+} concentration [1, 19, 20].

Fig. 5 displays a comparison between simazine removal efficiency of the mineralization of the pesticide under best conditions of photo-Fenton system. Fig. 5 reveals that simazine has almost disappeared attaining a removal efficiency of about 96.7%. However, no significant COD mineralization was acquired, which was about 43.8% (see Fig. 5). This can be related to the destruction of the parent simazine creating carboxylic and aliphatic byproducts [21]. These compounds are hardly attacked by the free hydroxyl radical due to the existence of triazine ring [21].

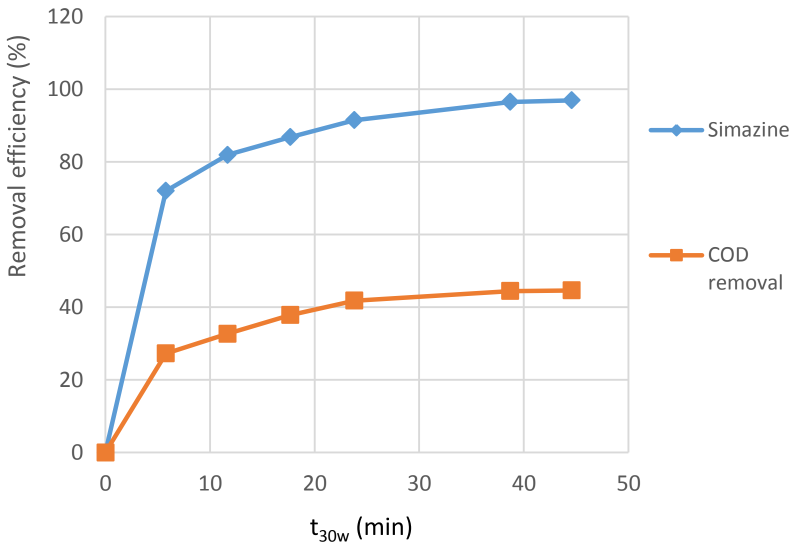


Figure 5. Comparison between simazine concentration and COD mineralization using homogeneous solar photo-Fenton system at H_2O_2=1200 mg/L, simazine=20 mg/L, Fe^{2+}=20 mg/L and pH=3.

3.2. Heterogeneous system

3.2.1. Effect of TiO_2

Heterogeneous photocatalysis experiments were conducted to investigate the viability of using TiO_2 in the degradation of simazine. The effect of TiO_2 on the degradation of simazine was examined at 100, 200, 300, 400 and 500 mg/L. Simazine concentration, H_2O_2 and pH level were 20 mg/L, 1200 mg/L and 4.6, respectively. Fig. 6 illustrates the correlation between t_{30w} and the COD mineralization efficiency of simazine.

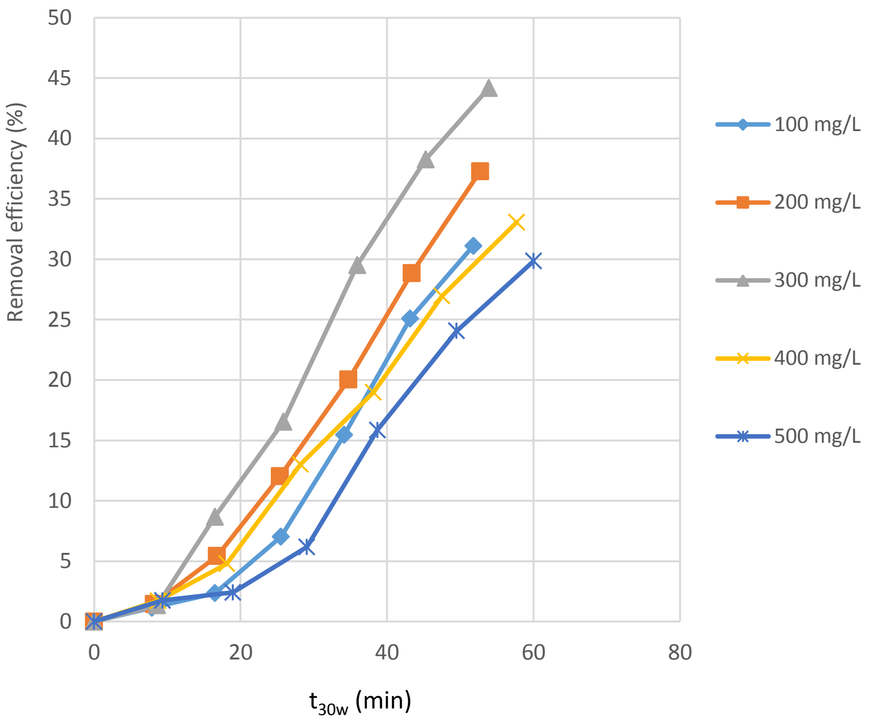


Figure 6. Effect of initial TiO_2 concentrations ranged from100 to 500 mg/L on the COD mineralization efficiency of simazine by heterogeneous solar photocatalyst system at H_2O_2=1200 mg/L, simazine=20 mg/L and pH=4.6.

Fig. 6 reveals that the COD mineralization efficiency of simazine has increased from 33% to 44.2% as the initial concentration of simazine increased from 100 to 300 mg/L, respectively. This means that, increasing the concentration of TiO_2 resulted in a large number of active site available for the photocatalytic reaction.

However, the removal efficiency has decreased greatly from 44.2% to 29.8% as the dose of TiO_2 increased from 300 to 500 mg/L, respectively (see Fig. 6). According to Saber et al. [16], increasing the TiO_2 concentration can reduce the photocatalytic degradation rate due to the reduction in the number of active sites that is essential for light absorption. Furthermore, a reduction in light penetration and grate light scattering is expected at high TiO_2 concentration due to the attenuation of UV light [22]. Thus, the influence of dosage increment has diminished. Consequently, the optimum concentration of TiO_2 was 300 mg/L.

3.2.2. Effect of H_2O_2 concentration.

In solar heterogeneous photocatalysis system, the impact of the initial concentration of H_2O_2 on the degradation of simazine was investigated at (800, 1200, 1600, 2000 and 2400 mg/L). This was to identify the optimum concentration of H_2O_2 essential for the degradation of simazine. The concentration of simazine, TiO_2 and pH level were fixed at 20 mg/L, 300 mg/L and 4.6, respectively. Fig. 7 demonstrates the correlation between t_{30w} and the COD mineralization efficiency of simazine.

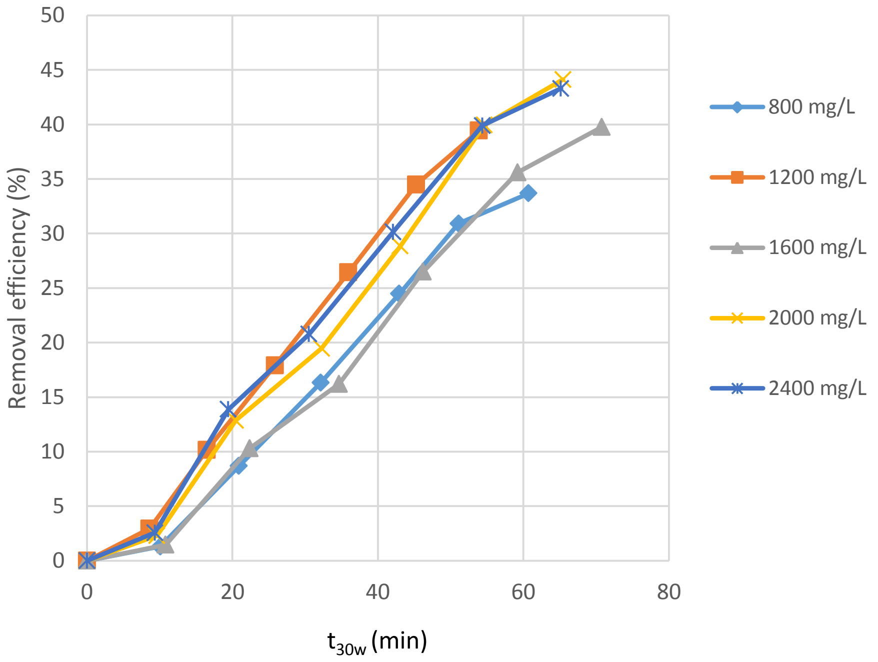


Figure 7. Effect of initial H_2O_2 concentrations ranged from 800 to 2400 mg/L on the COD mineralization of simazine by heterogeneous solar photocatalyst system at TiO_2=300 mg/L, simazine=20 mg/L and pH=4.6.

Fig. 7 shows that the COD mineralization of simazine varies depending on the dose of H_2O_2. The removal efficiency of simazine has increased from 32.6% to 43%, while increasing H_2O_2 concentration from 800 to 2400 mg/L, respectively. This indicate that increasing the dose of H_2O_2 can improve the removal efficiency of simazine, which point out to higher concentration of hydroxyl radical. It should be noticed that simazine removal efficiency has increased moderately from 43% to 43.2%, while increasing H_2O_2 concentration from 2000 to 2400 mg/L, respectively.

Therefore, H_2O_2 concentration of 2000 mg/L was selected as the optimum remediation condition. The photocatalytic degradation of various pesticides and herbicides can be further developed by adding H_2O_2 as an electron accepter [16]. This electron accepter is significant for the inhibition of electron/hole (e^-/h^+) pair recombination and the creation of free hydroxyl radicals [16]. However, overdose of H_2O_2 can adversely affect the degradation process of the contaminants due to the reaction of the free radicals with hydrogen peroxide, which behave as an inhibiting agent.

Fig. 8 displays a comparison between simazine removal efficiency and the COD mineralization of simazine under best conditions of solar Fenton system. Fig. 8 reveals that simazine has almost disappeared attaining a removal efficiency of about 92%. However, no significant COD mineralization was acquired, which was about 39.4%. This indicates the destruction of parent simazine to other compounds during a series of reactions.

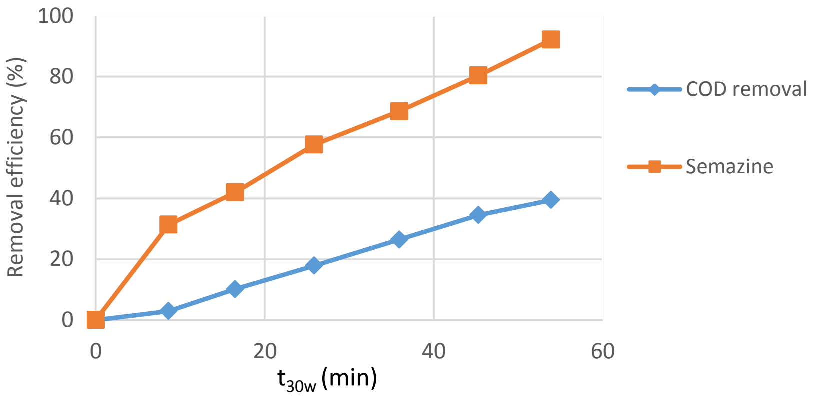


Figure 8. Comparison between simazine concentration and COD mineralization using solar heterogeneous system at H_2O_2=2000 mg/L, simazine=20 mg/L, TiO_2=300 mg/L and pH=4.6.

4. Conclusions

To sum up, the feasibility of simazine degradation at a solar pilot scale plant was carried out employing both homogeneous and heterogeneous photocatalysis systems. Simazine remediation is possible using either homogeneous or heterogeneous photocatalysis system. The optimum remediation conditions for solar homogenous system was achieved at H_2O_2 and Fe^{2+} concentrations of 1200 and 20 mg/L, respectively. On the other hand, the best remediation conditions for solar heterogeneous system was achieved at TiO_2 and H_2O_2 concentrations of 300 mg/L and 2000 mg/L, respectively. The best COD removal efficiency at both homogenous and heterogeneous systems were 43.8% and 43%, respectively. Homogenous system is more preferable than heterogeneous system due to the requirement of TiO_2 filtration. Complete mineralization of simazine is not expected due to the existence of triazine ring.

It was noticed that, over dose of TiO_2, H_2O_2 and Fe^{2+} would adversely affect the degradation process. It should be noticed that the toxicity test during the photo-treatment has not been performed.

However, it is of high importance due to hazardous effect of photo degradation by-products; therefore, considering this test in future research would be valuable. Future research should also identify the intermediate reaction products to comprehend a full mechanism of reaction.

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