

## Kabul Edilmiş Araştırma Makalesi (Düzenlenmemiş Sürüm)

## Accepted Research Article (Uncorrected Version)

### Makale Başlığı / Title

Atrazine treatment with heterogeneous Photo-Fenton like oxidation using statically approach

İstatistiksel yaklaşım kullanarak heterojen Foto-Fenton benzeri oksidasyon ile Atrazin artımı

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Abstract

Atrazine (ATZ) which is a triazine herbicide can be used for the weeds on agricultural land and it is classified as an endocrine disrupting pesticide. ATZ is persistent in water and soil due to its slow degradation by means of sunlight and microorganism. Heterogeneous Fenton process is an effective technique for atrazine because of the oxidation and adsorption of hydroxyl radical. The hydroxyl radical formation has been accelerated by addition of hydrogen peroxide and magnetite. Heterogeneous Fenton like oxidation were executed to remove atrazine in water. Effects of independent variables namely the concentration of hydrogen peroxide and magnetite on atrazine removal efficiency investigated by using the surface response analysis. Atrazine degradation was completely achieved with an hour. H<sub>2</sub>O<sub>2</sub>/Magnetite/ATZ ratio resulting by optimum atrazine removal efficiency (97.5%) was determined as 10/5/0.7, respectively.

Keywords: Atrazine, Heterogeneous Fenton like oxidation, Box Behnken

Öz

Atrazin (ATZ) bir triazin herbisitdir ve tarımsal arazilerde yabancılardan temizlik için kullanılır. ATZ, su ve toprakta yavaş parçalanması nedeniyle endokrin bozucu bir pestisit olarak sınıflandırılır. ATZ, güneş ışığı ve mikroorganizmalar tarafından yavaş parçalanır. Heterojen Fenton süreci, atrazin için etkili bir teknik çünkü hidroksil radikali ile oksitlenmesi ve adsorpsiyonu mümkündür. Hidroksil radikali oluşumu, hidrojen peroksit ve manyetit ile hızlandırılmıştır. Heterojen Fenton benzeri oksidasyonlar, atrazin giderimini sağlamak için gerçekleştirilmiştir. Bağımsız değişkenlerin, yani hidrojen peroksit ve manyetit konsantrasyonlarının atrazin giderim verimliliğine etkisi yüzey yanıt analizi kullanılarak araştırılmıştır. Atrazin parçalanması bir saat içinde tam olarak gerçekleştirilmiştir. H<sub>2</sub>O<sub>2</sub>/Manyetit/ATZ oranı optimum atrazin giderim verimliliği (97.5%) için 10/5/0.7 olarak belirlenmiştir.

Anahtar kelimeler: Atrazin, Heterojen fotofenton benzeri oksidasyon, Box-Behnken

1 Introduction

Atrazine (ATZ) which is a triazine herbicide can be applied to the control broadleaf and grassy weeds on agricultural land and it is classified as an endocrine disrupting pesticide. Due to its endocrine disrupting properties, atrazine affects the human body and hormones.

Atrazine is highly soluble in water. It does not adsorb strongly to sediments. It can be seen generally in aquatic life. The atrazine concentration can be changed in aquatic life depending on treatment plant operating conditions. Atrazine half-life in the surface water resources changes from 41 to 237 days and in half groundwater resources ranges from 15 months to 20 years [3]. The maximum atrazine concentration in drinking water is 0.1 mg/L [4]. According to researches, ATZ was listed in priority substances by the European Union the Directive 2013/39/EU. In spite of being banned, it has been used in some countries such as North America and Australia. Atrazine formula and properties are also presented in Table 1.

The treatment of atrazine has gain more importance in recent years due to toxicity and low biodegradability. Photolysis of atrazine in water under sunlight occurs in a half life 335 days. Photolysis of atrazine did not realize with wavelengths greater

than 300 nm. ATZ is persistent in water and soil due to its half life and slow degradation by means of sunlight and microorganism. Atrazine cannot be treated by biological methods due to its resistant to microorganism for degradation. In addition, it has been known to inhibit the microorganism activity in biological treatment unit. For that reason, new technologies should be used for the treatment of atrazine in order to improve of its degradation or to remove it before discharging into the environment. Conventional treatment processes can be used for ATZ removal. However, atrazine cannot be treated with these methods and ATZ degradation may be improved by oxidation processes such as AOPS.

Table 1: Atrazine properties

CAS Number	1912-24-9
Molecular weight	215.7 g/mole
Molecular Formula	C <sub>8</sub> H <sub>14</sub> N <sub>5</sub> Cl
Water Solubility	33 mg/L at pH 7
Vapor Pressure	2.89*10 <sup>-6</sup> mm Hg @ 25°C
Solubility in organic solvent	18000 mg/L in methanol
Log K <sub>ow</sub>	2.68 @ 25°C

Refractory and toxic organic compounds can be degraded or mineralized by advanced oxidation processes (AOPs) known as effective and useful process, because these processes can produce hydroxyl radical which is a nonselective and most powerful oxidant (2.8 V). Hydroxyl radicals can react faster

than the other oxidation processes. Fenton process has been known as one of the most effective methods in all methods to degrade and mineralize the organic compounds in wastewater. Generally, classical Fenton process and homogeneous Photo-Fenton process can be used to treat refractory, toxic and not biodegradable compounds. Atrazine can be easily degraded by using Fenton based processes. In one study, atrazine was treated by Fenton process and atrazine concentration was changed to 0.1 mg/L from 100 mg/L [6]. Unfortunately, there are some disadvantages in classic Fenton process: first of all, ferridons should be separated after the treatment and this situation makes the Fenton process uneconomic and not preferable. Other disadvantage of Fenton process is that this process only works acidic conditions such as pH 3.5. This situation restricts the reaction conditions and does not desirable. In order to deal with some obstacles according to homogeneous Fenton process, the Fenton or heterogeneous Fenton process, in which soluble ferric ferrous ions are changed by containing solids like magnetite, hematite, goethite and soon have been recently investigated.

The heterogeneous Fenton process is an effective method to degrade atrazine [6] because of the oxidation of pollutants by Fenton method was more useful and effective than heterogeneous photocatalysis to degrade and mineralize the pesticide [7],[8],[9]. It is demonstrated that  $H_2O_2$  and magnetite. The significant advantage of heterogeneous Fenton process over the classic Fenton oxidation is that heterogeneous Fenton process occurs at all pH values. Magnetite and pyrite are the most effective iron oxides as compared to the others because of the Fe (II) and Fe (III) in their structure, which makes the

Magnetite ( $Fe_3O_4$ ) which is an efficient solid catalyst has generally selected as an iron catalyst in heterogeneous Fenton like or heterogeneous Photo-Fenton process. Magnetite ( $Fe_3O_4$ ) has cubic inverse spinel structure. Its chemical formula can be written as  $Fe^{2+}Fe^{3+}_2O_4$  [11]. Chemical structure of magnetite is given in Figure 1.

In the Fenton process, magnetite shows several properties: (1) magnetite contains  $Fe^{2+}$  which initiate the Fenton mechanism and this reaction is necessary to continue the Fenton reaction; (2) magnetite also contains  $Fe^{3+}$  and  $Fe^{2+}$  can be reversibly react with pollutants to oxidize; and (3)  $Fe_3O_4$  has peroxidase activity which can active  $H_2O_2$ . Magnetite ( $Fe_3O_4$ ) is an excellent catalyst for advanced oxidation processes due to catalytic activity and redox properties. Magnetic separation can be used to separate magnetite in wastewater after the reaction.

**1.1 Design of experiments**  
 Generally, one factor in multivariable systems altered at a time to observe effects of variables. However, this approach cannot give useful or predictable responses. For that reason, nowadays, experimental statically design should be advised to optimize the reaction conditions. Response surface methodology called as RSM is generally chosen. This design contains 3 level factorial design, central composite design [12] [13], Box-Behnken design [14]. Between all response surface designs, Box-Behnken design requires fewer experimental runs. In addition, this design demonstrates to removal efficiency at variable concentrations which were not conducted experimentally [15] [16]. In this study, advanced oxidation process (heterogeneous Photo-Fenton like process) applied to evaluate atrazine oxidation and degradation according to atrazine removal efficiency. The effects of initial atrazine, magnetite and  $H_2O_2$  concentrations on atrazine removal efficiency were studied by means of Box-Behnken method. The most favorable conditions of independent variables for the atrazine treatment were determined by statistically as a main objective of this study. Although, Fenton process can be preferred using Box-Behnken method to treat some wastewaters, Heterogeneous Photo-Fenton like method especially using magnetite is not executed to treat a special micropollutant which is banned from European committee in Europe and this micropollutant cannot be treated easily by biological methods. For that reason, this study presents new experimental idea and results.

## 2 Material and method

### 2.1 Analytical methods

Atrazine ( $C_6H_9N_5Cl$ ) was purchased from TCI. Atrazine analyses were done by Thermo Scientific TSQ Quantum MAX LC MS/MS. Reaction conditions of LC/MS/MS: Injection Volume: 25  $\mu$ l, MS Acquire Time: 15 min. X  $\mu$ l. Atrazine analyses using LC/MS/MS; Mobile Phase A: %95  $H_2O$  %5 MeOH, 4mM Ammonium Formate, %0.1 Formic Acid. Mobile Phase B: %95 MeOH %5 MeOH %0.1mM Ammonium Formate, %0.1 Formic Acid. Atrazine concentrations between 0.25 and 1000 ppb were used to determine calibration curve with a linearity of  $R^2 = 0.974$ . Hydrogen peroxide as an oxidant (35% w/w) was used and obtained from Merck. In the heterogeneous Photo-Fenton like oxidation, magnetite source of iron was used and purchased from Merck (99%).

### 2.2 Experimental procedure

Heterogeneous Photo-Fenton like oxidation was executed at room temperature (23°C) with different magnetite and  $H_2O_2$  concentration which were determined by statistical program. Concentration of atrazine was changed to 0.1 mg/L from 1 mg/L. pH of wastewater was adjusted with sulfuric acid solution addition at pH 3.5. Thermo scientific Orion pH meter 720a was used to measure pH of wastewater.

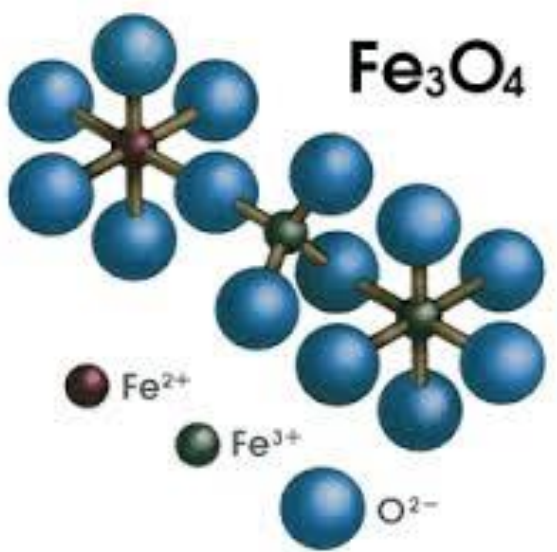


Figure 1: Magnetite Structure

Variable	Symbol	Low (-1)	Center (0)	High (+1)
Atrazine mg/L)	X <sub>1</sub>	0.1	0.55	1
H <sub>2</sub> O <sub>2</sub> (mg/L)	X <sub>2</sub>	0	5	10
Magnetite (mg/L)	X <sub>3</sub>	0	2.5	5

After pH adjustment of wastewater, magnetite (catalyst) was added and mixed well. Then, hydrogen peroxide (oxidant) was added to reactor. The UV lamp was opened up as soon as possible. At this time was accepted as the beginning of the experiment or time zero. At the determined times, samples were taken from the reactor to evaluate atrazine removal and pH variations. Raw and treated atrazine samples were centrifuged to prevent clogging in LC/MS/MS column and immediately analyzed to avoid some reactions.

### 2.3 Experimental setup

Heterogeneous Photo-Fenton like oxidation experiments were conducted in the photochemical reactor which was given in Figure 2. Photochemical reactor is made of glass and its volume is 2.2 l. In order to protect eyes and overcome leakage from UV lamp to outside the reactor was shrouded with an aluminum foil. A photochemical reactor includes some ports to feed oxidant and catalyst, sample removals, to measure temperature and to withdraw samples. The reactor was equipped with a magnetic stirrer to provide a proper mixing with a stirring bar.

UV lamp was axially centered and placed in a quartz tube. lamp properties are 16 W low pressure mercury vapor lamp and maximum emission at 254 nm. The UV radiation intensity was determined as 4.98\*10<sup>16</sup> Einstein/s via ferrioxalate actinometry method. The lamp was placed in a water cooling jacket to adjust temperature and execute runs at room temperatures, because of production heat from the light source.

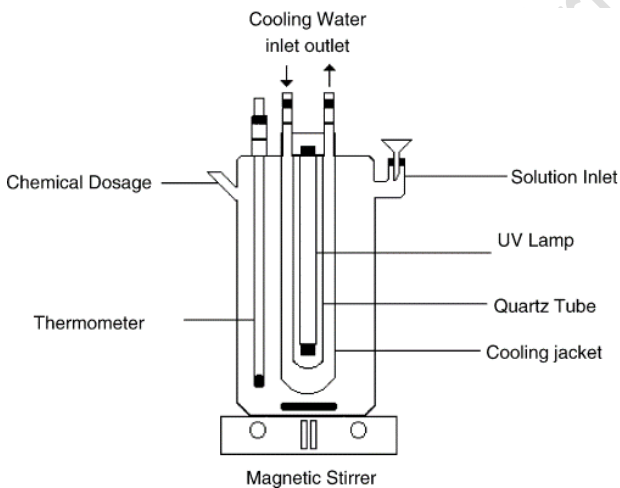


Figure 2: Schematic diagram of UV Reactor.

## 3 Results and discussion

Atrazine (X<sub>1</sub>), H<sub>2</sub>O<sub>2</sub> (X<sub>2</sub>) and magnetite (X<sub>3</sub>) as the independent variables were chosen in the design. In addition, percent atrazine removal (Y) as a dependent variable (or objective function) was chosen in the design. The low (-1), center (0) and high (+1) levels of each variable were determined by a static approach and shown in Table 2.

Table 3: Heterogeneous Photo-Fenton like oxidation runs designed by a static design.

Table 2: Levels of variables in a 3<sup>3</sup> factorial design

While initial atrazine concentration (X<sub>1</sub>) varied between 0.1 and 1 mg/L, hydrogen peroxide concentration (X<sub>2</sub>) varied between 0 and 10 mg/L. The magnetite concentration (X<sub>3</sub>) varied from 0 to 5 mg/L. Independent variables effects (atrazine, hydrogen peroxide and magnetite) on objective function (percent atrazine removal) were evaluated. Experimental conditions were selected by means of my previous oxidation studies.

The dependent variable (or objective function) was the percent atrazine removal (Y). Heterogeneous Photo-Fenton like oxidation experiments designed by a 3<sup>3</sup> factorial design are given in Table 3. Atrazine removal efficiencies as observed and estimated results via a static design are also given in Table 4.

### 3.1 The regression model

The application of RSM offers an empirical relationship between the objective function (Y) and the independent variables (X) can be approximated by a quadratic (second order) polynomial equation as follows (Eq 1):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

This static design was preferred due to fewer combinations of the independent variables to estimate the second order polynomial regression model. Coefficients in the regression model were determined by means of a total of 15 runs. Coefficients were calculated such as one block term, three linear terms, three quadratic terms and three interaction terms. The objective function for atrazine removal efficiency is the determined coefficient is presented by Eqs. (2)

$$Y_1 = 47.91 + 149.02X_1 + 1.43X_2 - 6.97X_3 + 2.46X_1X_2 + 3.97X_1X_3 + 0.20X_2X_3 - 135.97X_1^2 - 0.26X_2^2 + 0.70X_3^2 \quad (R\text{-Squared} = 0.992) \quad (2)$$

According to the coefficients in Equation (2), it can be seen that percent atrazine removal efficiency decreases with high amounts of magnetite concentrations (X<sub>3</sub>) especially at low initial atrazine concentration. The X<sub>1</sub> variable has a more significant effect on atrazine removal efficiency when compared to magnetite independent variable.

Table 5 presents the analysis of variance results which indicate the predictability of the model. Predictions for atrazine removal efficiencies are in good agreement with the observed experimental data. A coefficient of determination (R<sup>2</sup>) is larger than 0.99. In addition, the computed F value is much greater than that of the tabular F (14, 14) value of 3.70. This means the treatment is highly significant. P values of less than 0.05 indicated the effectiveness of independent variables on objective function. P values were evaluated for independent variables to determine the effectiveness of variables.

Run No	Atrazine (mg/L)	H <sub>2</sub> O <sub>2</sub> (mg/L)	Magnetite (mg/L)	Atrazine Rem(%)
1	0 (0.55)	-1 (0)	+1 (5)	81.40
2	+1 (1)	+1 (10)	0 (2.5)	75.30
3	0 (0.55)	0 (5)	0 (2.5)	91.20
4	-1 (0.1)	-1 (0)	0 (2.5)	49.90
5	+1 (1)	-1 (0)	0 (2.5)	55.20
6	+1 (1)	0 (5)	-1 (0)	73.90
7	0 (0.55)	0 (5)	0 (2.5)	90.45
8	-1 (0.1)	+1 (10)	0 (2.5)	47.90
9	0 (0.55)	0 (5)	0 (2.5)	91.40
10	0 (0.55)	+1 (10)	-1 (0)	91.50
11	+1 (1)	0 (5)	+1 (5)	84.30
12	-1 (0.1)	0 (5)	-1 (0)	60.20
13	0 (0.55)	-1 (0)	-1 (0)	91.40
14	-1 (0.1)	0 (5)	+1 (5)	53.00
15	0 (0.55)	+1 (10)	+1 (5)	91.50

Table 4: Atrazine removal efficiencies as observed and predicted results via statically design

Run No	Atrazine (mg/L)	H <sub>2</sub> O <sub>2</sub> (mg/L)	Magnetite (mg/L)	Predicted ATZ rem. (%)	Observed ATZ rem. (%)
1	0.55	0	5	81.40	82.06
2	1	10	2.5	75.30	75.85
3	0.55	5	2.5	91.20	91.02
4	0.1	0	2.5	49.90	49.35
5	1	0	2.5	55.20	57.73
6	1	5	0	73.90	74.01
7	0.55	5	2.5	90.45	91.02
8	0.1	10	2.5	47.90	45.38
9	0.55	5	2.5	91.40	91.02
10	0.55	10	0	91.50	90.84
11	1	5	5	84.30	81.11
12	0.1	5	0	60.20	63.39
13	0.55	0	0	91.40	88.76
14	0.1	5	5	53.00	52.89
15	0.55	10	5	91.50	94.14

Table 5: The analysis of variance test for Atrazine removal efficiency

Source	SS	D.F.	MS	F Value	p-Value
Model	4121.98	9	458	46.74	0.0003
A-Atrazine	754.66	1	754.66	77.02	0.0003
B-H <sub>2</sub> O <sub>2</sub>	100.11	1	100.11	10.22	0.0241
C-Magnetite	5.78	1	5.78	0.59	0.4772
AB	122.10	1	122.10	12.46	0.0167
AC	77.44	1	77.44	7.90	0.0375
BC	25.00	1	25.00	2.55	0.1711
A <sup>2</sup>	2796.54	1	2796.54	285.40	< 0.0001
B <sup>2</sup>	152.22	1	152.22	15.53	0.0109
C <sup>2</sup>	70.00	1	70.00	7.14	0.0442
Residual	48.99	5	9.80		
Lack of Fit	48.49	3	16.16	64.44	0.0153
Pure Error	0.50	2	0.25		
Cor Total	4170.97	14			

R-squared= 0.992, sum of squares (SS), Mean Square (MS)

### 3.2 Removal of atrazine

Variations of atrazine removal efficiencies with the independent variables (atrazine, magnetite and hydrogen peroxide concentrations) under different reaction conditions were estimated by coefficients determined statically design. Initial atrazine concentration effects on atrazine removal efficiencies at different concentrations during 60 min of reaction time are shown in Figure 4. At these reaction conditions, initial magnetite concentration was selected as 5 mg/L.



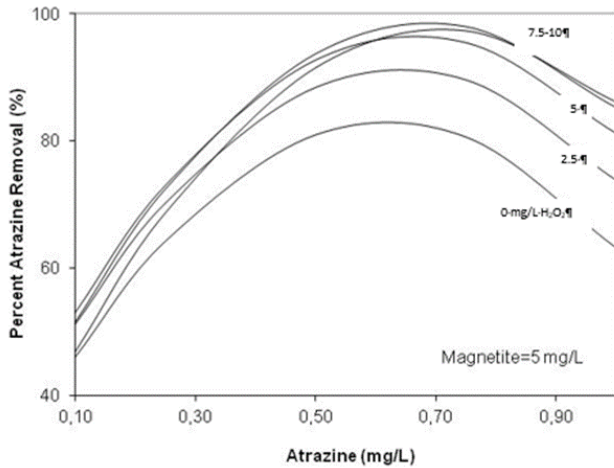
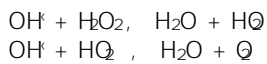


Figure3: Atrazine removal efficiencies achieved with different atrazine and H<sub>2</sub>O<sub>2</sub> concentrations (Magnetite:5 mg/L, Reaction

As shown in Figure 4, atrazine removal efficiencies were 54, 85 and 98% when atrazine concentrations of 0.1, 0.7 and 1 mg/L respectively at a magnetite concentration of 5 mg/L. As can be seen in Figure 4, hydrogen peroxide requirement to remove atrazine was approximately 7.5 mg/L at high magnetite concentration. Higher than this concentration, ATZ removal efficiency did not change or decreased. As a result, high oxidant concentration even rise to low atrazine removal efficiency due to excess oxidant and catalyst. In other words, high H<sub>2</sub>O<sub>2</sub>/Fe molar ratio produced insufficient removal efficiencies. Free-radical scavenger can be produced by high H<sub>2</sub>O<sub>2</sub> concentrations. In addition, probably H<sub>2</sub>O<sub>2</sub> behavior as an inhibitor for itself reduces hydroxyl radical



Same situation observed in other studies [17], [18], one study pesticide removal efficiencies decreased at high H concentrations because of the adverse effects of excess H. Atrazine degradation was completely achieved with H concentration of 7.5 mg/L and magnetite concentration of mg/L during 60 min reaction time. However, atrazine degradation was affected by initial atrazine concentration. Atrazine removal efficiencies were 98 and 85% when initial atrazine concentration of 0.7 mg/L and 1 mg/L, respectively, H<sub>2</sub>O<sub>2</sub> concentration of 7.5 mg/L and magnetite concentration of 5 mg/L. According to initial atrazine concentration, optimum oxidant/catalyst dose should be determined by statically design program in order to optimum molar ratio to achieve sufficient atrazine removal.

At high atrazine doses such as 0.7 mg/L, atrazine degradation was completely occurred with higher H<sub>2</sub>O<sub>2</sub> and magnetite doses. In other words, molar ratio of oxidant to catalyst is very important parameter. Above 0.7 mg/L atrazine concentration, molar ratio of hydrogen peroxide to magnetite was less. When inadequate amount of H<sub>2</sub>O<sub>2</sub> or magnetite are used, complete atrazine degradation did not observed during reaction time (one hour). At molar ratio of 2, approximately 45% atrazine removal efficiency was obtained at 0.1 mg/L initial atrazine concentration due to excess oxidant and catalyst dose. Insufficient removal efficiencies were achieved by high molar ratio. Most important issue for atrazine treatment is to evaluate

molar ratio of oxidant and catalyst. Optimum reaction conditions should be arranged by means of statically design approach according to initial atrazine concentration.

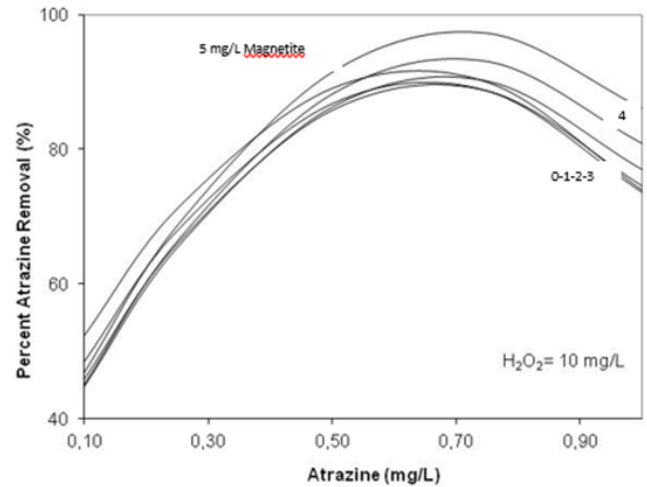


Figure4: Atrazine removal efficiencies achieved with different atrazine and Magnetite concentration (H<sub>2</sub>O<sub>2</sub>:10 mg/L, Reaction time:60 min, pH:3.5).

As can be shown in Figure 4, atrazine removal efficiencies were 47, 97.5 and 86% when initial atrazine concentrations of 0.1, 0.7 and 1 mg/L respectively at a magnetite concentration of 5 mg/L and at H<sub>2</sub>O<sub>2</sub> concentration of 10 mg/L. When magnetite concentration decreased to 1 mg/L, percent atrazine removals was 48.3, 89.6 and 73.5% when initial atrazine concentrations of 0.1, 0.5 and 1 mg/L, respectively. As can be shown in Figure 4, atrazine degradation was not completely achieved with low magnetite concentration. This phenomenon also observed at low H<sub>2</sub>O<sub>2</sub> concentration due to insufficient concentration of oxidant and catalyst to produce # radicals.

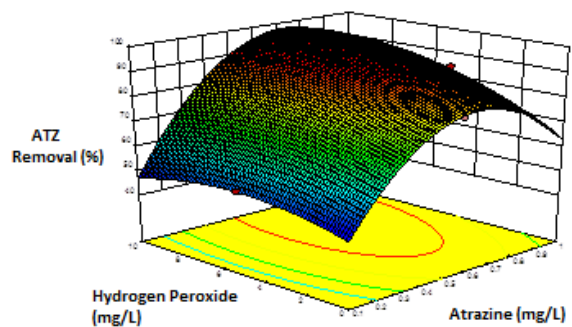


Figure5: Atrazine removal efficiencies achieved with different atrazine and H<sub>2</sub>O<sub>2</sub> concentrations (Magnetite:5 mg/L, Reaction time:60 min, pH:3.5).

Results of atrazine removal by means of different oxidant and catalyst dose are given in Figure 6 as 3D format. Atrazine removal efficiencies can be clearly presented and evaluated in this format. After evaluation of experiments, it can be said that the optimum H<sub>2</sub>O<sub>2</sub>/Magnetite/Atrazine concentration producing the highest atrazine removal efficiency (50%) was 5/5/0.1 at low atrazine dose of 0.1 mg/L, while this molar ratio was 10/5/1 producing 86% atrazine removal efficiency at high atrazine dose of 1 mg/L.

The the analysis of variance showed that all variables (atrazine, H<sub>2</sub>O<sub>2</sub> and magnetite) and the interactions X<sub>1</sub>X<sub>2</sub>, X<sub>1</sub>X<sub>3</sub>, X<sub>2</sub>X<sub>3</sub>, X<sub>1</sub><sup>2</sup>,

X<sub>2</sub><sup>2</sup>) were significant. All independent variables are important and affect the atrazine degradation by heterogeneous Photo-Fenton like oxidation as mentioned in Table 5.

When the H<sub>2</sub>O<sub>2</sub> concentration is increased to 5 mg/L from 0.2 mg/L, oxidation process is converted to UV/Magnetite process from UV/Magnetite process. Atrazine treatment yield increases to 95% from 80% by means of changing oxidation process. Process variation is important in the treatment of atrazine and UV/H<sub>2</sub>O<sub>2</sub>/Magnetite process which is a modification of two processes instead of using UV/H<sub>2</sub>O<sub>2</sub> process or UV/Magnetite process, is found to be more effective.

### 4 Conclusion

Heterogeneous Photo-Fenton like oxidation as an advanced oxidation process was applied to atrazine in order to degrade. In order to optimize reaction conditions in advanced oxidation process, statically design approach used. The most usefull response surface methodology, Box-Behnken statistical design which was used for this aim. Atrazine, H<sub>2</sub>O<sub>2</sub> and magnetite concentrations were chosen as independent variables while atrazine removal efficiency was selected as dependent variable (objective function).

Atrazine removal efficiency decreases with initial atrazine concentration (X<sub>1</sub>) while increasing with the H<sub>2</sub>O<sub>2</sub> concentration (X<sub>2</sub>) and magnetite concentration (X<sub>3</sub>). The H<sub>2</sub>O<sub>2</sub> variable has a more significant effect on atrazine removal efficiency when compared to magnetite. Dose of independent variables has significant effect on dependent variables or objective function. Atrazine removal efficiency (nearly 95%) was achieved by heterogeneous Photo-Fenton like oxidation process. In advanced oxidation process. The highest atrazine removal efficiency (97.5%) was obtained with a H<sub>2</sub>O<sub>2</sub>/Magnetite/Atrazine ratio of 10/5/0.7 mg/L. Optimum oxidant and catalyst doses changed with the initial atrazine concentrations. In addition, kind of process is also important in the treatment of atrazine and UV/Magnetite process which is a modification of two processes instead of using UV/H<sub>2</sub>O<sub>2</sub> process or UV/Magnetite process, is found to be more effective. In future studies, real wastewater samples should be used to observe effectiveness of this process and its operating costs may be calculated and compared each other.

### 5 References

[1] Martin Neto L, Traghetto G, Vaz P, Crestana S, Sposito G. Atrazine degradation by heterogeneous photo-Fenton process: effect of reaction conditions and atrazine concentration. *Water Res* 35:2525-2533, 2001.

[2] Chan K.H. Atrazine degradation by heterogeneous photo-Fenton process. *Hazard Mater* 18 (13), 227-237, 2005.

[3] Murphya M, Blecker M, Coady K, Tompsett B, Arlones D. Morphology and histology in ranid frogs collected in a contaminated area. *Aquat Toxicol* 76:233-245, 2006.

[4] Dehghani M, Nasserin, Amin SA. Atrazine degradation by heterogeneous photo-Fenton process. *Pak J Biol Sci* 13(2)66-72, 2010.

[5] Benzaquen J, Benzo M, Misa M, Alfano M. Atrazine degradation by heterogeneous photo-Fenton process. *Water Sci. Technol* 67:210-216, 2013.

Ribeiro A, Nunes O, Pereira M. Atrazine degradation by heterogeneous photo-Fenton process. *Environ. Int* 75, 33-51, 2015.

[7] Klammerth M, Miranda N, Malato S, Aguera A, Fernandez-Alba A, Maldonado M. Atrazine degradation by heterogeneous photo-Fenton process. *Catal. Today* 144:124-130, 2009.

[8] Maldonado M, Passarinho J, Oller L, Gernjak W, Fernandez P, Blanco J. Atrazine degradation by heterogeneous photo-Fenton process. *J. Photochem. Photobiol. A: Chem* 185:354-363, 2007.

[9] Perez M, Penuela G, Maldonado M, Malato O, Fernandez Ibanez P, Oller L, Gernjak W. Atrazine degradation by heterogeneous photo-Fenton process. *Appl. Catal. B* 4, 272-281, 2006.

[10] Hou L, W. Zhang Q, Jerome R, Duprez D, Zhang H, Royer S. Atrazine degradation by heterogeneous photo-Fenton process. *Appl. Catal. B* 144: 739, 2014.

[11] Cornell RM. Atrazine degradation by heterogeneous photo-Fenton process. *Occurrence and Uses. Wiley, Weinheim* 2003.

[12] Boza A, De La Cruz, Jordan G, Lauregui H, Haza U, Aleman A. Atrazine degradation by heterogeneous photo-Fenton process. *Drug Dev. Ind. Pharm* 26: 1303-1307, 2000.

[13] Box GE, Wilson K. Atrazine degradation by heterogeneous photo-Fenton process. *Royal Statistic Society* 13, 112, 1951.

[14] Singh S, Dodge J. Atrazine degradation by heterogeneous photo-Fenton process. *J. Pharm* 125:243-255, 1995.

[15] Sastry S, Z. Atrazine degradation by heterogeneous photo-Fenton process. *Plackett Burman design for screening of formulation* 7: 3105-112, 1998.

[16] Hamed E. Atrazine degradation by heterogeneous photo-Fenton process. *Control Release* 73, 329-338, 2001.

[17] Glaze W, Kang J. Atrazine degradation by heterogeneous photo-Fenton process. *Ind. Eng. Chem. Res* 34: 2314-2323, 1995.

[18] Betrán J, Qvejerós G. Atrazine degradation by heterogeneous photo-Fenton process. *Ind. Eng. Chem. Res* 35: 8838-8919, 1996.