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

İstatistiksel yaklaşım kullanarak heterojen foto-Fenton benzeri oksidasyon ile atrazin arıtımı

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Abstract

Atrazine (ATZ) which is a triazine herbicide can be used for the control weeds on agricultural land and it is classified as an endocrine disrupting pesticide. ATZ is persistent in water and soil due to its half-life and slow degradation by means of sunlight and microorganism. The heterogeneous Fenton process is an effective technique for degrading atrazine because of the oxidation and adsorption of pollutants by hydroxyl radical. The hydroxyl radical formation has been accelerated by addition of hydrogen peroxide and magnetite. heterogeneous Photo-Fenton like oxidation were executed to remove atrazine in this study. Effects of independent variables namely the concentrations of atrazine, hydrogen peroxide and magnetite on atrazine removal efficiency were investigated by using the surface response analysis. Atrazine degradation was completely achieved with an hour. Optimal H_2O_2/Magnetite/ATZ ratio resulting by optimum atrazine removal efficiency (97.5%) was determined as 10/5/0.7, respectively.

Keywords: Atrazine, Heterogeneous photo-fenton like oxidation, Box-Behnken

Öz

Atrazin (ATZ) triazin herbisit olup tarım arazileri üzerindeki kontrol bitkileri için kullanılmaktadır. Endokrin bozucu bir pestisit olarak sınıflandırılmaktadır. ATZ, yarı ömrnün uzun olması, güneş ışığı ve mikroorganizma ile parçalanması yavaş olması nedeni ile nedeniyle su ve toprakta kalıcıdır. Heterojen Fenton prosesi ile kirletici maddelerin hidroksil radikali ile oksitlenmesi ve adsorpsiyonu mümkün olup atrazinin parçalanması için etkili bir yöntemdir. Hidroksil radikal oluşumu hidrojen peroksit ve manyetit kullanımı ile artırılabilmektedir. Bu çalışmada atrazini giderebilmek için heterojen Foto-Fenton benzeri oksidasyon yöntemi uygulanmıştır. İstatiksel yöntemi olan yüzey yanıt yönteminde; atrazin, hidrojen peroksit ve manyetit konsantrasyonlarının bağımsız değişkenlerin atrazin giderme verimi üzerindeki etkileri araştırılmıştır. Atrazinin tamamen parçalanması bir saatlik reaksiyon süresinde gerçekleştirilmiştir. Optimum H_2O_2/Manyetit/ATZ oranı 10/5/0.7 olarak belirlenmiştir ve optimum oranda atrazin giderme verimi %97.5 olarak elde edilmiştir.

Anahtar kelimeler: Atrazin, Heterojen foto-fenton 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 [1],[2]. Due to endocrine disrupting properties, atrazine affects the human body and hormones.

Atrazine's biodegradability is low and it moderately solubles 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 and ATZ's concentration generally shows considerable fluctuation. Atrazine's half-life in the surface water resources changes from 41 to 237 days and its half-life in groundwater resources ranges from 15 months to 20 years [3]. The maximum atrazine concentration in drinking water is permitted by the USEPA and WHO is 3.0 and 2.0 µg/L, respectively [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 still in use in some countries such as North America and China. 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 [5]. 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	$C_8H_{14}N_5Cl$
Water Solubility	33 mg/L at pH 7
Vapor Pressure	$2.89*10^{-7}$ mm Hg @ 25 °C
Solubility in organic solvent	18000 mg/L in methanol
Log K_{ow}	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 oxidants in oxidation process. Fenton process has been known as one of the most effective methods in all AOP 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 which was changed to 0.1 mg/L from 100 mg/L was treated with H_2O_2 (5-50 mg/L) and iron 1-55 mg/L [6]. Unfortunately, there are some disadvantages in classic Fenton process: first of all, ferric ions 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-like or heterogeneous Fenton process, in which soluble ferric or ferrous ions are changed by Fe-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 $\cdot OH$ radical. In some studies, heterogeneous Photo-Fenton method was more useful and effective than heterogeneous photo-catalysis to degrade and mineralize the pesticide [7]-[9]. The hydroxyl radical formation ($\cdot OH$) has been demonstrated to be H_2O_2 and magnetite. The significant advantage of heterogeneous Fenton-like process over the classic Fenton oxidation is that heterogeneous Fenton-like 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 accelerates the rate of formation $\cdot OH$ [10].

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-like process. Magnetite (Fe_3O_4) has cubic inverse spinal structure. Its chemical formula can be written as Fe_3O_4 [11]. Chemical structure of magnetite is given in Figure 1.
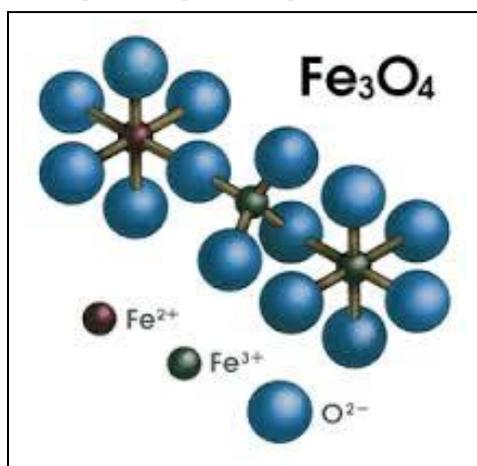
Figure 1: Magnetite structure.

In the Fenton process, magnetite shows some 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 both Fe^{2+} and Fe^{3+}, ferric and ferrous ions can be reversibly react with pollutants to oxidize; and (3) Fe_3O_4 has peroxides-like 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 concentrations 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 ($C_8H_{14}N_5Cl$) was purchased from TCI. Atrazine analyses were done by Thermo Scientific TSQ Quantum MAX LC MSMS. Reaction conditions of LC/MS/MS; Injection Volume:25 ul, MS Acquire Time:15 min, İyon source ESI (+). Mobile Phase of atrazine analyses using LC/MS/MS; Mobile Phase A: %95 H_2O %5 MeOH ,4mM Amonnium Formate, %0.1 Formic Acid. Mobile Phase B: %95 MeOH %5 H_2O,4mM Amonnium Formate, %0.1 Formic Acid. Atrazine concentrations between 25 ppb 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 as a 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±2 °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.

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 set-up

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 placed on a magnetic stirrer to provide a proper mixing with a stirring bar.

UV lamp was axially centered and placed in a quartz tube. UV lamp properties are a 16 W low-pressure mercury vapor lamp and maximum emission at 254 nm. The UV radiation intensity was determined as $4.98*10^{-6}$ einstein/s via ferrioxalate actinometry method. The UV 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.
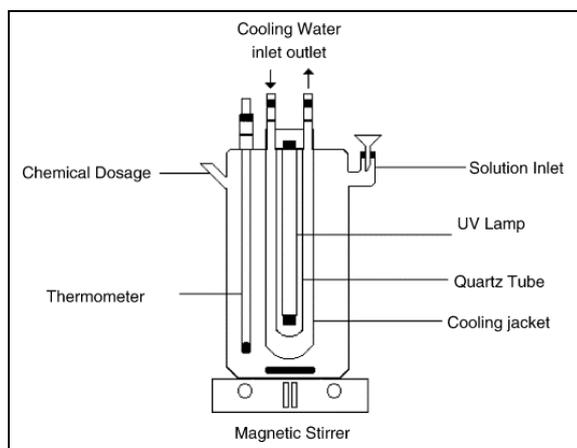
Figure 2: Schematic diagram of UV reactor.

3 Results and discussion

Atrazine (X_1), H_2O_2 (X_2) and magnetite (X_3) as the independent variables were chosen in design. In addition, percent atrazine removal (Y_1) as a dependent variable (or objective function) was chosen in Box-Behnken design. The low (-1), center (0) and high (+1) levels of each variable determined by statically approach were shown in Table 2.

Table 2: Levels of variables in Box-Behnken design.

Variable	Symbol	Low (-1)	Center (0)	High (+1)
Atrazine (mg/L)	X_1	0.1	0.55	1
H_2O_2 (mg/L)	X_2	0	5	10
Magnetite (mg/L)	X_3	0	2.5	5

While initial atrazine concentration (X_1) varied between 0.1 and 1 mg/L, hydrogen peroxide concentration (X_2) altered

between 0 and 10 mg/L. The magnetite concentration (X_3) was ranged 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_1). Heterogeneous Photo-Fenton like oxidation experiments, designed by Box-Behnken design are given in Table 3. Atrazine removal efficiencies as observed and estimated results via statically design are also given in Table 4.

3.1 The regression model

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

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

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

$$Y_1=47.91+149.02X_1+1.43X_2-6.97X_3+2.46X_1X_2+3.91X_1X_3+0.20X_2X_3-135.91X_1^2-0.26X_2^2 +0.70X_3^2 \text{ (R-Squared = 0.992} \tag{2}$$

According to the coefficients in Equations (2), it can be that percent ATZ removal efficiency decreases with high amount of magnetite concentrations (X_2) especially low initial atrazine concentration. The H_2O_2 variable has a more significantly 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^2) is larger than 0.99. In addition, the computed F value is much greater than that of the tabular $F_{0.01 (14. 14)}$ 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 all independent variables to determine effectiveness of variables.

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 from statically design. Initial atrazine concentration effects on atrazine removal efficiencies at different H_2O_2 concentrations during 60 min of reaction time are shown in Figure 3.

At these reaction conditions, initial magnetite concentration was selected as 5 mg/L.

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

Run No	Atrazine (mg/L)	H_2O_2 (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_2O_2 (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_2O_2	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^2	2796.54	1	2796.54	285.40	< 0.0001
B^2	152.22	1	152.22	15.53	0.0109
C^2	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).

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 decrease. High oxidant concentrations give to low atrazine removal efficiency due to excess oxidant and catalyst usage. In other words, high H_2O_2/Fe molar ratio produced insufficient removal efficiencies. Free-radical scavenger can be produced by using high H_2O_2 concentrations. In addition, probably H_2O_2 behavior as an inhibitor for itself reduces the hydroxyl radical.

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$

$$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$$
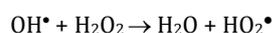
Same situation observed in other studies [17], [18]. In one study, pesticide removal efficiencies decreased at high H_2O_2 concentrations because of the adverse effects of excess H_2O_2.
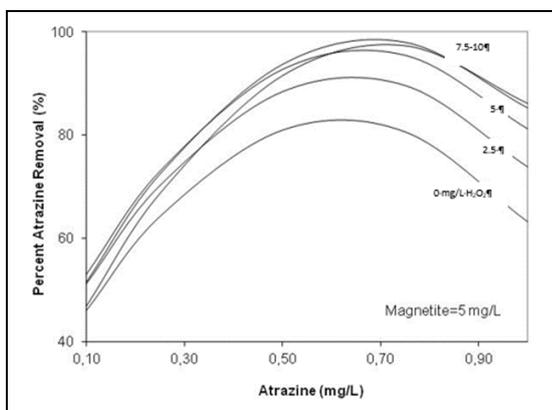
Figure 3: Atrazine removal efficiencies achieved with different atrazine and H_2O_2 concentrations (Magnetite: 5 mg/L. Reaction. Reaction time:60 min. pH:3.5).
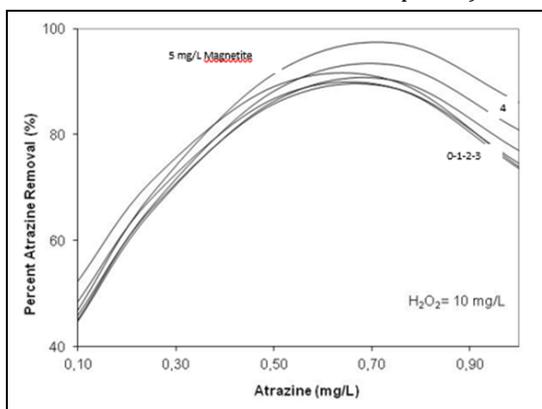
Figure 4: Atrazine removal efficiencies achieved with different atrazine and Magnetite concentrations (H_2O_2:10 mg/L. Reaction time:60 min. pH:3.5).

Atrazine degradation was completely achieved with H_2O_2 concentration of 7.5 mg/L and magnetite concentration of 5 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, at H_2O_2 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_2O_2 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 in sufficient. When inadequate amount of H_2O_2 or magnetite are used, complete atrazine degradation did not observe 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. So,

optimum reaction conditions should be arranged by means of statically design approach according to initial atrazine concentration.

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 1mg/L respectively at a magnetite concentration of 5 mg/L and at a H_2O_2 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_2O_2 concentration due to insufficient concentration of oxidant and catalyst to produce •OH radicals.

Results of atrazine removal by means of different oxidant and catalyst dose are given in Figure 5 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_2O_2/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 a high atrazine dose of 1 mg/L.

The analysis of variance showed that all variables (atrazine, H_2O_2 and magnetite) and the interactions (X_1X_2, X_1X_3, X_2X_3, X_1^2, X_2^2) 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_2O_2 concentration is increased to 5 mg/L from 0 mg/L, oxidation process is converted to UV/H_2O_2/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_2O_2/Magnetite process which is a modification of two processes instead of using UV/H_2O_2 process or UV/Magnetite process, is found to be more effective.
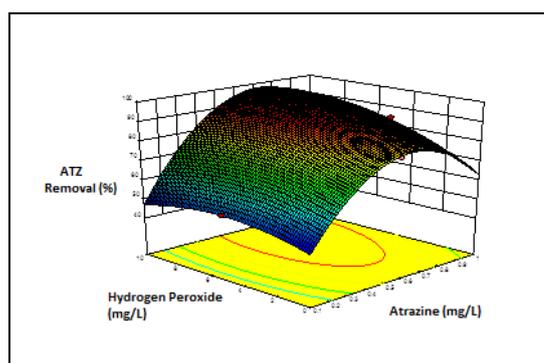
Figure 5: Atrazine removal efficiencies achieved with different atrazine and H_2O_2 concentrations (Magnetite: 5 mg/L, Reaction time: 60 min, pH:3.5).

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 useful response surface methodology is Box-Behnken statistical design which was used for this aim. Atrazine, H_2O_2 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_1) while increasing with the H_2O_2 concentration (X_2) and magnetite concentrations (X_3). The H_2O_2 variable has a more significant effect on atrazine removal efficiency when compared to magnetite independent variables. 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_2O_2/Magnetite/Atrazine ratio of 10/5/0.7 mg/L. The 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/H_2O_2/Magnetite process, which is a modification of two processes instead of using UV/H_2O_2 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 operating costs may be calculated and compared each other.

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