PESTİSİT ATIK SULARININ $CoFe_2O_4$/ULTRASONİK/PERSÜLFAT YÖNTEMİYLE OKSİDASYONU VE CEVAP YÜZEY YÖNTEMİ İLE OPTİMİZASYONU

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ÖZET

Pestisitler çok farklı tarımsal amaçlar için yaygın kullanıma sahip bileşiklerdir. Pestisit üretim tesislerinde, kazanların yıkanması sonrası önemli miktarda atıksu oluşmaktadır. Konvansiyonel atıksu arıtım yöntemleri pek çok pestisitin arıtımında etkili değildir. Persülfat tek başına etkili bir oksidant değildir, ancak çeşitli yöntemlerle aktivasyonu sonucu oldukça reaktif sülfat radikallerinin ($SO_4^{\cdot -}$) oluşumu gerçekleşir. Aktivasyon yöntemleri olarak ısı, metal iyonları (M^{n+}), ultrasonik sistem (US) ve ultraviyole ışıması (UV) sayılabilir.

Bu çalışmada, yüksek toplam organik karbon içeriğine sahip pestisit atık suyunun heterojen katalizör $CoFe_2O_4$ ve persülfat kullanılarak ultrasonik destekli oksidasyonu incelendi. Heterojen ve manyetik özellikli $CoFe_2O_4$ katalizörü sol-jel yöntemi ile sentezlendi ve sonra 600 °C de kalsine edildi. Kobalt ferrit ($CoFe_2O_4$) iyi bilinen bir sert manyetik malzemedir. Ferrit spinel yapısı, tetrahedral ve oktahedral denilen açıklıkların katyonlar tarafından işgal edildiği kapalı bir oksijen kafesi üzerine kuruludur. Ters spinel yapıda (oktahedral bölgelerde iki değerli iyonlar yer alır) tüm Co^{2+} iyonları kafes yapısının oktahedral bölgelerini kaplar, Fe^{3+} iyonlarının yarısı da aynı bölgeleri işgal eder ve Fe^{3+} iyonlarının geri kalanı tetrahedral bölgelerde yer alır.

Katalizörün karakterizasyonu FTIR, XRD ve SEM-EDS analizleri ile gerçekleştirildi. Cevap yüzey yöntemi ve Box-Behnken dizayn (BBD) kullanılarak pestisit atıksu giderimine seyreltme oranı (x_1, 0-2:1, wastewater/water, v/v), katalizör miktarı (x_2, 0,5-2,0 g/L), persülfat derişimi (x_3, 100-200 mM), ve zamanın (x_4, 3-5 saat) etkisi incelendi. Cevap yüzey metodolojisi, istatistiksel ve matematiksel tekniklerin geliştirme ve optimizasyon işlemleri için birlikte kullanıldığı bir yöntem olarak tanımlanmaktadır. BDD, kuadratik model parametrelerinin tahmininde kullanılan, tamamlanmamış çoklu faktör tasarımlarından elde edilen bir çeşit dönebilir tasarımdır. Sonuçların istatistiksel analizi varyans analizi (ANOVA) temel alınarak değerlendirildi. Sonuçlar, modelin ikinci dereceden modele uygun olduğunu gösterdi. Mineralizasyon etkinliği için modelin F değeri 38,87 olarak elde edilmiştir. Elde edilen % 0,01 şans değeri, gürültüden dolayı bu F değerinin ortaya çıkabileceğini gösterdi. Elde edilen modelin F değerinin, tablo F değerinden ($F_{0.05}$, df, (n- (df + 1)) daha yüksek olması modelin uygunluğunun kanıtıdır. Modele uyumun diğer göstergeleri, mineralizasyon verimliliği için 0,9749 (0,9498) olarak elde edilen yüksek R^2 (düzeltilmiş R^2) katsayılarıdır. TOC giderim yüzdesi için uygun model denklemi aşağıda verilmiştir: $\%\, TOC\ giderimi = +68{,}18 + 20{,}72x_1 + 1{,}79x_2 + 21{,}11x_3 + 1{,}77x_4 - 0{,}93x_1x_2 + 5{,}12\, x_1x_3 - 0{,}72x_1x_4 + 3{,}10x_2x_3 - 0{,}66x_2x_4 + 0{,}42x_1x_2 - 9{,}03x_1^2 - 5{,}91x_2^2 - 8{,}25x_3^2 + 0{,}69x_4^2$

Maksimum Toplam Organik Karbon giderim yüzdesi için en uygun koşullarda % 90.58 olarak belirlenmiştir.

Anahtar Kelimeler: Pestisit, katalizör, optimizasyon, mineralizasyon

TREATMENT OF PESTICIDE WASTEWATER USING $CoFe_2O_4$/ULTRASONIC/PERSULPHATE OXIDATION METHOD AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

ABSTRACT

Pesticides are widely used compounds for a wide range of agricultural purposes. A significant amount of wastewater is produced in the pesticide production facilities after washing the cauldrons. Conventional wastewater treatment methods are not effective in the treatment of many pesticides. Persulphate alone is not an effective oxidant, but activation of various methods results in the formation of highly reactive sulfate radicals ($SO_4^{\cdot-}$). Activation methods include heat, metal ions (M^{n+}), ultrasonic system (US), and ultraviolet radiation (UV).

In this study, ultrasonic assisted oxidation of pesticide waste water with high total organic carbon content using heterogeneous catalyst $CoFe_2O_4$ and persulfate was investigated. $CoFe_2O_4$ catalyst which has heterogeneous and magnetic properties was synthesized by sol-gel method and then calcined at 600 °C. Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material. The ferrite spinel structure is based on a closed-packed oxygen lattice, in which tetrahedral and octahedral interstices are occupied by the cations. In the inverse spinel structure (the divalent ions in the octahedral sites) all the Co^{2+} ions occupy the octahedral sites of lattice structure, half of the Fe^{3+} ions also occupy the same sites and the rest of the Fe^{3+} ions stay in tetrahedral sites.

Characterization of the catalyst was performed by FTIR, XRD and SEM-EDS analyzes. The effect of dilution ratio (x_1, 0-2:1, wastewater/water, v/v), catalyst amount (x_2, 0.5-2.0 g/L), persulfate concentration (x_3,100-300 mM), and time (x_4, 3-5 h) on pesticide wastewater removal was investigated by the response surface method using Box-Behnken design (BBD). Response surface methodology is defined as a method which statistical and mathematical techniques are used together for development and optimization processes. BDD is a variety of rotational designs from incomplete multi-factor designs, which are used in the estimation of quadratic model parameters. The statistical analysis of the results was evaluated based on the analysis of variance (ANOVA). The results showed that the model fit quadratic model. The F value of the model for mineralization efficiency was obtained as 38.87. The obtained 0.01 % chance values revealed that F-values of this order could occur due to noise in each case. The fact that the F value of the obtained model was higher than the tabulated F value ($F_{0.05}$, df, (n-(df+1)) of the table is a proof of the model fit. Other indicators of the model fit were high R^2 (adjusted R^2) coefficients, which were obtained as 0.9749 (0.9498) for mineralization efficiency. The fit model equation was shown below for TOC removal percent: $TOC\ removal\ \% = +68.18 + 20.72x_1 + 1.79x_2 + 21.11x_3 + 1.77x_4 - 0.93x_1x_2 + 5.12x_1x_3 - 0.72x_1x_4 + 3.10x_2x_3 - 0.66x_2x_4 + 0.42x_1x_2 - 9.03x_1^2 - 5.91x_2^2 - 8.25x_3^2 + 0.69x_4^2$

The optimal conditions for maximum TOC removal percent are determined as 90.58%.

Keywords: Pesticide, catalyst, optimization, mineralization

1.INTRODUCTION

In recent years, the agricultural industry has been working intensely to increase agricultural yield. Pesticides are the primary chemicals used for this purpose. Pesticides are any chemical substance or a mixture of substances chemical substance which are used to protect agricultural products from all kinds of harmful organisms and plants. However, excessive and unconsciously use of pesticides have made these substances as priority pollutants of natural water resources and soils. Also, many studies that are shown negative effects of pesticides on human and animal health have been published. Due to all these negative effects, the treatment of wastewater containing pesticides is one of the most important issues to be solved (Papazlatani et al., 2019; Yabalak et al., 2018; Zhang et al., 2011).

There are many available conventional methods for the treatment of wastewater polluted with harmful compounds like pesticides. The most commonly used methods like activated carbon adsorption, chemical oxidation, photochemical oxidation, enzymatic transformation, bioremediation may be not effective for the removal of pesticides. Therefore, new technologies are needed for the treatment of wastewater containing harmful organic chemicals (Raschitor et al., 2019; Yabalak et al., 2018) .

One of the wastewater treatment methods used in recent years is oxidation with persulfate. Persulphate is a powerful oxidant which mostly used in the oxidation process as oxidant. It has high solubility, good stability, and high reactivity. Persulphate alone is not an effective oxidant, but activation of various methods results in the formation of highly reactive sulfate radicals ($SO_4^{\cdot -}$). Activation methods include heat, metal ions (M^{n+}), ultrasonic system (US), and ultraviolet radiation (UV) (Bashir et al., 2017; Vicente et al. 2011).

Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material. The ferrite spinel structure is based on a closed-packed oxygen lattice, in which tetrahedral and octahedral interstices are occupied by the cations. In the inverse spinel structure (the divalent ions in the octahedral sites) all the Co^{2+} ions occupy the octahedral sites of lattice structure, half of the Fe^{3+} ions also occupy the same sites and the rest of the Fe^{3+} ions stay in tetrahedral sites (Senthil et al., 2018; Kefeni et al., 2017).

Many experimental design methods are used to minimize time and economic loss during experimental studies. One of the most commonly used methods is The response surface methodology (RSM), too. The response surface methodology is an efficient statistical experimental modeling method that is used for studying various factors and their synergetic effects. RSM has many designs and one of the most important is the Box-Behnken model. Box-Behnken Design (BBD) is a quadratic RSM design. BBD ensures to determine the system performance at each experimental condition and the response function at all intermediate levels. In BBD design, each experimental parameter is coded three levels as -1, 0 and +1 (Emgili, et al, 2017; Kayan, B. and Gözmen, B., 2012; Shokri et al., 2020)

In this study, ultrasonic assisted oxidation of pesticide waste water with high total organic carbon content using heterogeneous catalyst $CoFe_2O_4$ and persulfate was investigated. The effect of dilution ratio (x_1, 0-2:1, wastewater/water, v/v), catalyst amount (x_2, 0.5-2.0 g/L), persulfate concentration (x_3,100-300 mM), and time (x_4, 3-5 h) on pesticide wastewater removal was investigated by the response surface method using Box-Behnken design (BBD).

2. MATERIAL AND METHOD

2.1. Ultrasonic oxidation experiments

Before starting the experiments, firstly, the amount of Total Organic Carbon of pesticide wastewater was measured. It was determined that the stock solution contained 90959 ppm organic carbon. As a result of the preliminary experiments, the effects of the 4 parameters shown in Table 1 on the system were investigated. For each experiment shown in Table 1, 100 mL of pesticide solution was taken and after the required dilution rate, persulfate and catalyst ($CoFe_2O_4$) were added and oxidation treatments were carried out according to the schedule using Bandelin Sonorex ultrasonic bath (35 kHz). All experiments were carried out at 50 °C.

At the end of each experiment 40 mL of sample was taken and Total Organic Carbon measurements were made. The results obtained are shown in Table 1.

2.2. Total organic carbon analysis

Total Organic Carbon measurement (TOC) is used to determine organic pollutants (carbons) in water. TOC analysis of samples taken after oxidation was performed with Shimadzu TOC analyzer.

2.3. Synthesis of $CoFe_2O_4$

$CoFe_2O_4$ nanocatalyst was synthesized by Sol-gel method. In the synthesis of $CoFe_2O_4$, $Co(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ were mixed in deionized water with a molar ratio of 2:1. Citric acid solution was dripped to the homogeneous mixture of metals with a molar ratio of 1:1. Then, the prepared mixture waited on a magnetic stirrer for 1 hour at 70 ° C. After removing some of the solvent, the residue was calcined at 600 ° C for 5 hours. The calcined material was washed with distilled water, centrifuged and then dried in the oven for 1 day. Thus, $CoFe_2O_4$ nanocatalyst was prepared. Characterization of the catalyst was performed by FTIR, XRD and SEM-EDS analyzes.

3.RESULTS

3.1. Box-Behnken design of experiments

Box-Behnken Design was used to determine the simple and interactive effects of the experimental variables for the oxidation of pesticide wastewater. Table 1 shows the experimental program designed with box –Behnken design. As seen in Table 1, the highest TOC removal rate was obtained as 90.58% and the lowest TOC removal rate was obtained as 21.21%.

Table 1. Experiments and results of TOC removal percentages.

Run	Dilution F. (x_1) v/v	Catalyst (x_2) g/L	Persulphate Con. (x_3) mM	Time (x_4) h	TOC Removal %
1	1.00	0.50	200.00	3.00	58.45
2	0.00	1.25	200.00	5.00	41.2
3	0.00	0.50	200.00	4.00	28.4
4	0.00	2.00	200.00	4.00	31.83
5	1.00	1.25	100.00	3.00	38.6
6	0.00	1.25	200.00	3.00	35.8
7	1.00	1.25	100.00	5.00	40.7
8	0.00	1.25	300.00	4.00	45.23
9	1.00	1.25	200.00	4.00	74.52
10	1.00	1.25	300.00	3.00	80.78
11	1.00	2.00	300.00	4.00	84.11
12	2.00	1.25	100.00	4.00	46.09
13	2.00	1.25	200.00	5.00	81.6
14	1.00	2.00	100.00	4.00	28.55

15	0.00	1.25	100.00	4.00	21.21
16	1.00	2.00	200.00	3.00	63.48
17	1.00	1.25	200.00	4.00	71.52
18	2.00	1.25	200.00	3.00	79.07
19	2.00	0.50	200.00	4.00	77.59
20	1.00	0.50	200.00	5.00	63.51
21	1.00	1.25	300.00	5.00	84.57
22	2.00	2.00	200.00	4.00	77.32
23	1.00	1.25	200.00	4.00	63.37
24	1.00	0.50	300.00	4.00	72.43
25	1.00	1.25	200.00	4.00	68.25
26	2.00	1.25	300.00	4.00	90.58
27	1.00	2.00	200.00	5.00	65.89
28	1.00	0.50	100.00	4.00	29.26
29	1.00	1.25	200.00	4.00	63.22

3.2. ANOVA results of experimental model

It was determined that the model obtained as a result of the experiments conformed to the quadratic model. ANOVA results of the quadratic model are shown in Table 2. The data in Table 2 can be summarized as follows and all of these data were generated automatically by the Design-Expert Software:

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The model ratio of 25.067 indicates an adequate signal. This model can be used to navigate the design space. The "Pred R-Squared" of 0.8901 is in reasonable agreement with the "Adj R-Squared" of 0.9498; i.e. the difference is less than 0.2.The Model F-value of 38.87 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.Also, standart deviation of model was determined as 4.64. Bu bilgil

Table 2. ANOVA results of the quadratic model.

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Adeq Precision	F Value
Quadratic	4.64	0.9749	0.9498	0.8901	1319.97	25.067	38.87

In addition, the conformity between experimental results and predicted results which are produced by the model, are shown in Figure 1. Each colored point in the graph represents the experiments in Table 1, and the closer these points are to the line seen in the graph, the better the agreement between the predicted and actual values. Thus, our obtained results are quite appropriate to each other.

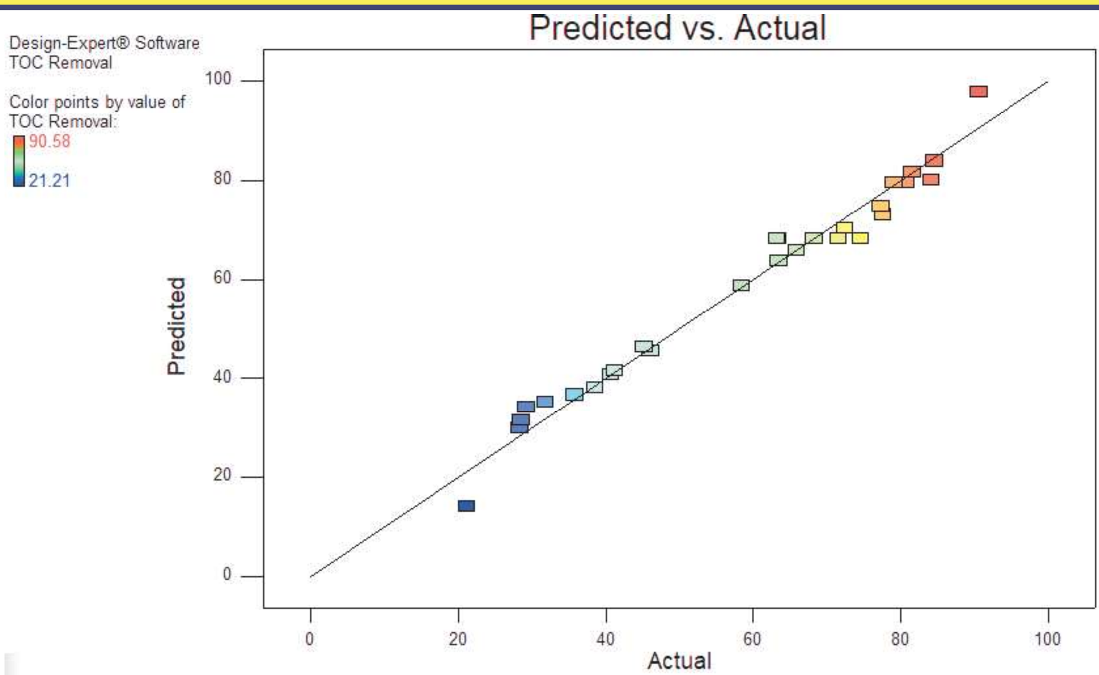

Figure 1. The actual values versus predicted values of TOC removal rate of pesticide wastewater.

3.3. Final equation of experimental model

The fit model equation was shown below for TOC removal percent:

$$\%\,TOC\ giderimi\ = +68{,}18 + 20{,}72x_1 + 1{,}79x_2 + 21{,}11x_3 + 1{,}77x_4 - 0{,}93x_1x_2 + 5{,}12\,x_1x_3 - 0{,}72x_1x_4 + 3{,}10x_2x_3 - 0{,}66x_2x_4 + 0{,}42x_1x_2 - 9{,}03x_1^2 - 5{,}91x_2^2 - 8{,}25x_3^2 + 0{,}69x_4^2$$

This equation can be used to predict the degradation range at different experimental conditions which can be theoretical. This equation can also be used to determine the relative effects of variables by comparing the coefficients of variables. For example, the x_3 (Persulphate Con.) independent variable which is 21.11, is the most effective parameter that effects positively the percentage of TOC removal.

4. CONCLUSION

$CoFe_2O_4$ nanocatalyst was successfully synthesized by sol-gel method. wastewater of pesticides was successfully degraded with the help of the combined $CoFe_2O_4$ / Ultrasonic / Persulphate system. The maximum TOC removal rate was obtained as 90.58%. A mathematical equation of the oxidation process is derived. ANOVA test results of the quadratic model were determined. in particular, the obtained mathematical equation will guide future studies in this context.

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