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**ORIGINAL RESEARCH PAPER**

# Catalytic effect of $Fe@Fe_2O_3$ nanowires and Fenton process on carbamazepine removal from aqueous solutions using response surface methodology

**M.M. Amin[1,2], S. Yousefinejad[3], M. Dehghani[4], S. Rahimi[2,*]**

[1]*Environment Research Center, Research Institute for Primordial Prevention of Non-Communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran*

[2]*Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran*

[3]*Research Center for Health Sciences, Institute of Health, Department of Occupational Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran*

[4]*Research Center for Health Sciences, Institute of Health, Department of Environmental Health, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran*

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**ABSTRACT**

Carbamazepine is one of the hydrophilic compounds identified in aquatic environments. Due to toxicity and bio-stability of this psychotropic pharmaceutical in the environment and humans, its removal efficiency and mineralization are important. In this study, synthesized $Fe@Fe_2O_3$ nanowires were applied to improve Fenton oxidation process using $FeCl_3.6H_2O$ and $NaBH_4$. The effects of different parameters such as initial pH, $H_2O_2$, $FeSO_4.7H_2O$, carbamazepine concentrations, oxidation time, and nanowires dose were evaluated using response surface methodology. After scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffract meter analysis, $Fe@Fe_2O_3$ morphology was synthesized in the form of nanowires with diameters of about 40-80 nm. The optimum oxidation conditions for carbamazepine were established at pH= 4.3, reaction time of 45.9 min, nanowire dose of 179.4 mg/L as well as $H_2O_2$, $FeSO_4.7H_2O$ and carbamazepine concentrations of 22, 52.2 and 7.7 mg/L, respectively. The oxidation efficiency (99.5%) achieved under the optimum condition, which was determined by the model, was consistent with the efficiency predicted by the model. The multi-parameter models showed good calibration and prediction abilities with $R^2_{=}$ 0.922, $R^2_{adj}$= 0.907, $R^2_{pred}$= 0.868. According to the results, the carbamazepine degradation rate increased with the increase of $Fe^{2+}$ due to the synergistic effect between $Fe@Fe_2O_3$ and $Fe^{2+}$ on the catalytic decomposition of $H_2O_2$ and generation of OH•. It was concluded that the Fenton process based on the $Fe@Fe_2O_3$ nanowires can increase the carbamazepine oxidation rate in aqueous solutions. This method can also be used as an effective and pre-treatment process in the conventional treatment plants.

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## INTRODUCTION

Thousands of active chemicals, such as drugs, are annually produced in pharmaceutical plants for control, diagnosis, and treatment of various diseases. These drug compounds are mostly stable or semi-stable, and are not removed during pharmaceutical wastewater treatment processes. Different studies have shown that a large number of drugs are not removed by the conventional treatment methods applied in the wastewater treatment plants and are eventually discharged into the aquatic environment. Such discharges,

*Corresponding Author:
Email: *rahimi.somaye@gmail.com*
Phone: +9891 783 68651
Fax: +9831 366 82509

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especially into surface and underground waters, affect the ecosystem of organisms and threaten human life (Zhang *et al.*, 2008; Lyons, 2014). Carbamazepine is a resistant drug in the environment and its annual consumption is approximately 1,000 tons. Over 30 tons of this drug is discharged into the environment by the wastewater treatment plants (Komtchou *et al.*, 2015). 72% of carbamazepine used to treat seizures is typically absorbed by body and 28% of it is excreted unchanged. After carbamazepine absorption in the body, it is converted into various metabolites in liver and excreted in urine (Zhang *et al.*, 2008). Studies indicate that carbamazepine has a removal rate of 10-30% in the wastewater treatment plant (Zhang *et al.*, 2008). Due to incomplete removal of carbamazepine in wastewater treatment plants, it remains in the treated wastewater and is finally discharged into the environment. There are some evidences that prolonged exposure to low levels of this drug leads to enzymatic activity reduction, biological accumulation in various organisms, morphology changes, and restrained growth in organisms in the environment (Pomati *et al.*, 2006; Braeutigam *et al.*, 2012; De *et al.*, 2016). According to the standards presented by the agency for humans and wildlife protection against harmful chemicals in England, the amount of drug combinations in aqueous solutions, especially surface water and underground water, should be zero (Lyons, 2014). This shows the necessity of an effective technology in wastewater treatment plants to reduce or remove drug compounds such as carbamazepine. Various removal methods, such as biological treatment (activated sludge and sand filter), adsorption by activated carbon, membrane and advanced oxidation processes (AOPs) have been investigated. Meanwhile, conventional biological processes have inadequate efficiency (10-30%), and absorption and nanofiltration processes have low efficiency (10-20%) and lead to fouling and reduction. In contrast, advanced oxidation treatment seems to have a high efficiency due to existence of radical hydroxyl (Zhang *et al.*, 2008; Komtchou *et al.*, 2015). Advanced oxidation processes are widely used for the treatment of organic pollutants by producing strong oxidizing agents such as radical hydroxyl (OH•) which is a non-selective chemical oxidant with a high reactivity and rapid oxidation (Sirés *et al.*, 2014). Among the advanced oxidation processes (AOPs), Fenton reaction ($Fe^{2+}/H_2O_2$) has attracted much attentions due to its high efficiency, ease of use, and environmentally friendly properties (Shi *et al.*, 2014). Typically, hydroxyl radicals are produced in the Fenton process. $Fe^{2+}$ acts as a catalyst in the Fenton process and produces radical hydroxyl and $Fe^{3+}$. Large amount of $Fe^{2+}$ ions can be added to produce high concentrations of OH•. However, high amounts of sludge produced in this process will require proper management and disposal (Kang *et al.*, 2002; Huang *et al.*, 2009). To overcome these constraints, several strategies have been proposed. These strategies are: the use of organic chelators, such as tetra acetate ethylenediamine, to prevent ferric ion precipitation (Chen *et al.*, 2011); the development of heterogeneous Fenton system with iron containing zeolite (Song *et al.*, 2006; Navalon *et al.*, 2011; Rusevova *et al.*, 2014); and the use of core-shell $Fe@Fe_2O_3$ nanowires (Shi *et al.*, 2014). Obviously, addition of organic chelators lead to increased costs, reduced OH• formation, and production of secondary pollutants during environmental applications. Furthermore, heterogeneous Fenton systems have a low efficiency in degradation of pollutants because of their wide pH range and ability to reuse iron reagents and perform oxidation at pH>4 (Shi *et al.*, 2014). The Low oxidation efficacy of Fenton system at pH>4 is mainly due to the formation of insoluble ferric products which block the $Fe^{3+}/Fe^{2+}$ cycle. In addition, the ability of OH• oxidation is very poor at high pH (Babuponnusami and Muthukumar, 2012; Wu *et al.*, 2014). Since change in OH• oxidation ability depends on pH change, the use of core-shell $Fe@Fe_2O_3$ nanowires to improve the efficiency of $Fe^{3+}/Fe^{2+}$ cycle can increase the oxidation efficiency in Fenton systems (Shi *et al.*, 2014). Core-shell $Fe@Fe_2O_3$ nanowires are a special type of zero-valent iron nanoparticles (nZVI) with super synthesized activity performed by reduction of ferric ions with sodium borohydride without mixing (mixing breaks the nanowires) (Ai *et al.*, 2013). These nanowires can stimulate two-electron molecular oxygen activation to produce $H_2O_2$ along with transferring outward electron from the iron core to the surface of the iron oxide shell. They also stimulate the single-electron molecular oxygen activity to produce $\cdot O_2^-$ (pH> 4.8) by ferrous bonding surface on the iron oxide shell (Ai *et al.*, 2013). Obviously, production of $H_2O_2$ and $\cdot O_2^-$ along with activation of molecular oxygen by $Fe@Fe_2O_3$ nanowires not only increases the amount of activated oxygen species but also increases the $Fe^{3+}/Fe^{2+}$ cycle at high pH values because the $H_2O_2$ and $\cdot O_2^-$ produced by this method constantly transform ferric ions to ferrous ions (Brillas *et al.*, 2009; Shi *et al.*, 2014). In addition, core-shell $Fe@Fe_2O_3$ nanowires have two important advantages over other zero-valent iron

nanoparticles. First, the $Fe_2O_3$ covering protects the core-shell Fe@$Fe_2O_3$ nanowires against spontaneous burning in the air. Second, the ferrous ion adsorbed on $Fe_2O_3$ shell can lead to the development of a single-electron reduction process for production of more $\cdot O_2^-$ radicals (Shi *et al.*, 2014). In this study, it has been attempted to investigate the synergistic effect of Fe@$Fe_2O_3$ nanowires on Fenton process for the removal of carbamazepine from aqueous solutions by accelerating the Fe(III)/Fe(II) cycles. Since no study yet has been focused on the removal of carbamazepine using Fenton processes containing Fe@$Fe_2O_3$ nanowires, the aim of this study is to investigate the synergistic effects of Fe@$Fe_2O_3$ nanowires on Fenton process for the removal of carbamazepine from aqueous solutions by accelerating the Fe(III)/Fe(II) cycles. Few studies have reported on adsorption of carbamazepine, which indicates the necessity to study the adsorption of carbamazepine by different adsorbents. This study was conducted in the laboratory of Shiraz University of Medical Sciences in 2017 and approved by Isfahan University of Medical Sciences.

## MATERIALS AND METHODS

*Standards and reagents*

$FeCl_3.6H_2O$, $NaBH_4$, $H_2O_2$ (30% w/w) and $FeSO_4.7H_2O$ (analytic reagent) with high purity were purchased from Sigma Aldrich, USA. All materials were used without any purification. Carbamazepine (CBZ, CAS No. 298-46-4, $C_{15}H_{12}N_2O$, and 236.67 g/mol) was bought from Sigma Aldrich. The acetonitrile and water (HPLC grade) were obtained from Merck Company (Germany) and Sigma Aldrich (USA), respectively. Carbamazepine stock solution was prepared in a glass container in a concentration of 100 mg/L (500 rpm) at room temperature (25 °C) over a 24-hour period. The solutions were prepared by diluting the carbamazepine stock solution at desired concentrations for each working day.

*Synthesis of Fe@$Fe_2O_3$ nanowires*

Fe@$Fe_2O_3$ nanowires were synthesized according to the method developed by (Zhu *et al.*, 2013). Accordingly, 0.15 g $FeCl_3.6H_2O$ and 0.3 g $NaBH_4$ were dissolved in 50 mL (solution No. 1) and 20 mL (solution No. 2) distilled water, respectively. Then, solution No. 2 was added to solution No. 1 at a rate of 0.5 mL/s to synthesize nanowires. The addition process was carried out at room temperature. During the addition, mixing was done by hand but not a magnetic stirrer to avoid accumulation of iron particles and formation of the nanowires. During the addition of $NaBH_4$, a large amount of gas or bubble along with a black and white sediment appeared on the surface. This black and white sediment was washed using distilled water and ethanol and then dried under nitrogen flow. In preparing Fe@$Fe_2O_3$ nanowires, the physical and structural properties of the nanoparticles were determined using the standard methods of scanning electron microscopy (Tescan SEM Mira 3, USA) and X-Ray dispersion device (D8 Advance, Bruker, Germany).

*Batch reactor for carbamazepine removal*

Batch experiments were performed using a 100 mL glass flask. The desired amount of Fe@$Fe_2O_3$ nanowires was added to a solution containing carbamazepine. Hydrochloric acid and sodium hydroxide (0.1 M) were used to adjust pH. After adding nanocatalysts, mixing of hydrogen peroxide and $FeSO_4.7H_2O$ in solution was performed by a magnetic stirrer to obtain complete homogeneity. The samples were removed at different time periods, filtered through a membrane filter with a pore size 0.22 µm, and kept in the refrigerator for analysis by a high performance liquid chromatography (HPLC) instrument.

*Measurements and chromatographic analysis*

Concentration of carbamazepine was determined using an HPLC instrument (Azura, Knauer, Berlin, Germany) equipped with a C18 column and a diode array UV detector which was set up at a wavelength of 270 nm in isocratic elution mode. A mixture of acetonitrile/water (35: 65 v/v) was used as mobile phase at a flow rate of 1 mL/min. The samples were filtered on a PTFE filter and then injected using a 20-µL injection loop. Some samples detected by HPLC instrument did not need to be extracted, but the samples which were normally lower than the detection limit were extracted and re-injected into the HPLC instrument after the extraction process. The dispersive liquid-liquid microextraction (DLLME) technique was applied for extraction. For this purpose, 1 mL of methanol as a dispersing solution and 100 µl of chloroform as an extraction solution were injected into the sample. The cloud-formed solution was centrifuged for 5 min at 5000 rpm. 30 µl of the sediment obtained from DLLME was injected into the device. Notably, two calibration curves were prepared for high concentration range without extraction and for low concentration range after applying DLLME procedure. Total organic carbon (TOC) was

measured by a Shimadzu TOC-VCPH analyzer (Japan) after filtration through a 0.22-µm filter. In addition, the value of TOC removal in optimal conditions for Fenton was studied. The pH was measured by means of a Metrohm pH-meter 827 (Switzerland) equipped with a pH-combined electrode.

*Optimization and modeling of response level*

Response surface methodology **(**RSM) is a statistical method for designing the experiments and optimizing the chemical reactions and industrial processes (Dean *et al*., 2017; Khamparia and Jaspal, 2017). When multiple variables affect the outputs of the system, RSM can be used to evaluate the relationship between dependent and independent variables (experimental conditions) and to optimize the relevant processes. In addition, the process optimization by RSM to collect empirical research results is much faster than conventional methods. In the present study, carbamazepine removal efficiency was considered as dependent variable (response) and six experimental conditions were assumed as independent variables. Central Composite Design (CCD), a well-known form of RSM, was used to optimize carbamazepine treatment by Fenton process. In this study, 81 runs were defined for experiments with respect to six factors in a five-level full factorial and in a single block. Among them, five experiments were designed as center points. Initial pH, $H_2O_2$ concentration, $FeSO_4.7H_2O$ concentration, carbamazepine concentration, oxidation time, and nanowires dose were the six independent variables. The values of independent variables and variation ranges were determined according to other studies (Table 1). Using Design-Expert 7 software (Stat Ease Inc., Minneapolis, USA), the table of experiments was designed and analyzed on a personal computer under Windows 7 operating system. A multiple linear regression (MLR) quadratic equation was used to calculate the interaction between the dependent and independent variables. For example, a quadratic model for two independent variables ($x_1$ and $x_2$) can be expressed as Eq. 1.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \varepsilon \quad (1)$$

Where, y is the efficiency of carbamazepine removal (dependent variable), $\beta_0$ is the intercept of MLR equation, $\beta_1$ is the coefficient of factor $x_1$, $\beta_{11}$ and $\beta_{22}$ are coefficients of the self-interactions of factor $x_1$ and $x_2$, respectively *(i.e. $x_1^2$ and $x_2^2$)*, and $\beta_{12}$ is the coefficient of interaction of the factors $x_1$ and $x_2$. It is emphasized that six independent factors were used in the current study to optimize the removal of carbamazepine from aqueous media.

## RESULTS AND DISCUSSION

*Characterization of Fe@$Fe_2O_3$*

After synthesis of Fe@$Fe_2O_3$ nanowires, X-ray diffraction (XRD) was used to determine the product phases (Fig. 1). The nanowire XRD analysis showed that the phases occur more in 2Θ= 35.6° and 44.7°, indicating the presence of $Fe_2O_3$ phase (Hematite) and Fe phase. These results are consistent with the findings of previous studies (Zhu *et al*., 2013). SEM images of Fe@$Fe_2O_3$ morphology were in the form of a nanowire in the range of 40-80 nm, and chain clusters were formed through chemical interactions. $NaBH_4$ addition to the solution at a rate of 0.5 mL/s resulted in formation of wire structure (Fig. 2a). In addition, the energy-dispersive X-ray (EDX) peaks shown in Fig. 2b confirmed the presence of $Fe_2O_3$ in oxygen and iron species. These results are consistent with the results of other studies (Ai *et al*., 2013; Zhu *et al*., 2013; Wu *et al*., 2014; Shen *et al*., 2017).

*Application of synthesized Fe@$Fe_2O_3$ nanowires in carbamazepine oxidation*

As already mentioned, the parameters such as pH,

Table 1. Range of variables for the central composite design technique used to study the removal of carbamazepine in the proposed catalyst-Fenton process

| Independent variable | Code name | Star low (-α) (-2) | Low (-1) | Center (0) | High (+1) | Star high (+α) (2) |
|---|---|---|---|---|---|---|
| pH | A | 2.5 | 4 | 5.5 | 7 | 8.5 |
| $H_2O_2$ Conc. (mg/ L)* | B | 3.3 | 9.9 | 16.49 | 23 | 29.68 |
| $FeSO_4.7H_2O$ Conc. (mg/L) | C | 1 | 3 | 5 | 7 | 9 |
| Carbamazepine Conc. (mg/L) | D | 3 | 7 | 11 | 15 | 19 |
| Nanowires dose (mg/L) | E | 0 | 75 | 150 | 225 | 300 |
| Oxidation time (min.) | F | 5 | 20 | 35 | 50 | 65 |

* The $H_2O_2$ volumes used for these concentrations in the removal reactor at +α, +1, 0, 1, and -α levels were 9, 7, 5, 3, and 1 µl, respectively.

$H_2O_2$, $FeSO_4.7H_2O$, carbamazepine concentrations, contact time, and nanowires dose were changed in five levels to optimize the conditions for the removal of carbamazepine (Table 1) and eventually 81 runs were designed. Each experiment was carried out under the designed conditions in the presence of certain amount of $Fe@Fe_2O_3$ nanowires, and the efficiency of carbamazepine removal was calculated according to the initial and final concentrations of carbamazepine through HPLC analysis. For instance, chromatogram related to one of the runes, before and after treatment with $Fe@Fe_2O_3$ nanowires and Fenton process, is shown in Fig. 3. In order to achieve the linear model related to the data, multiple linear regression and analysis of variance (ANOVA) were done. The related results are discussed in the following parts.

Analysis of variance (ANOVA) and linear model of the experimental design For choosing the best model, different models such as linear relationship, 2-factor interaction (2FI), and quadratic model were checked, and the best results were obtained from the quadratic model according to Eq. 2.

$$Y= b_0+ b_1A+ b_2B+ b_3C+ b_4D+ b_5E+ b_6F+ b_{12}AB+ b_{13}AC+ b_{14}AD+ b_{15}AE+ b_{16}AF+ b_{11}A^2+ b_{22}B^2+ b_{33}C^2+ b_{44}D^2+ b_{55}E^2+ b_{66}F^2 \quad (2)$$

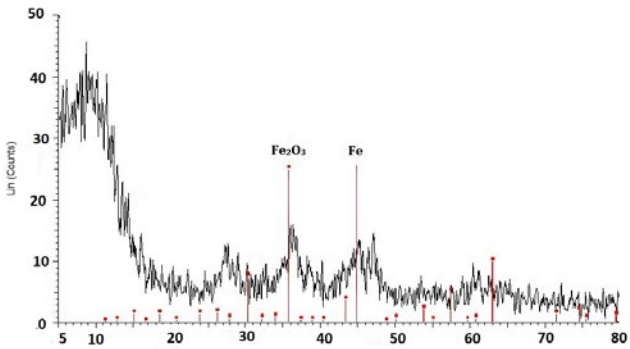



Fig. 1. XRD patterns of the $Fe@Fe_2O_3$ nanowires synthesis

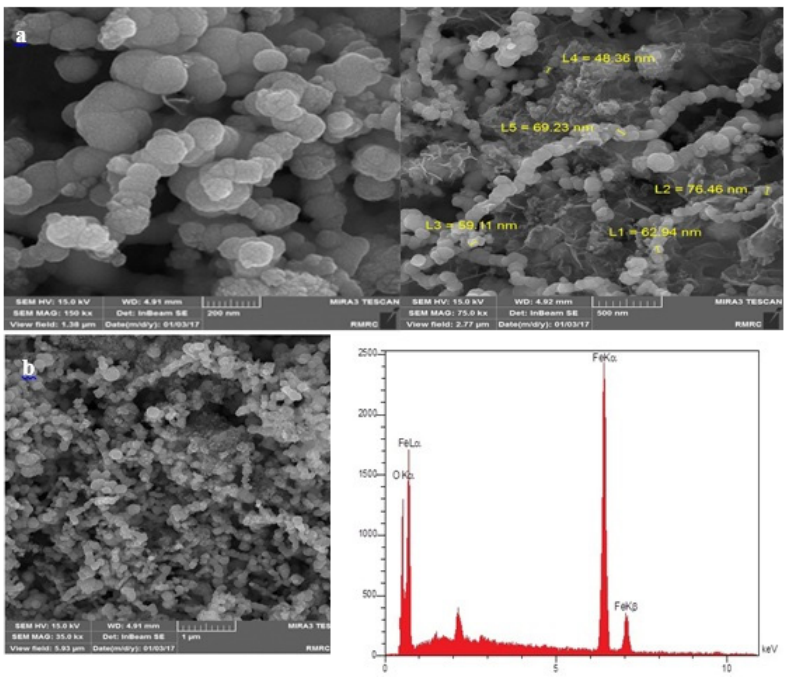



Fig. 2. (a) SEM images of the synthesized $Fe@Fe_2O_3$ nanowires; (b) SEM-EDX images of the $Fe@Fe_2O_3$ nanowires synthesis

Considering the suitable number of experiments (81 cases), use of this model seems logical. However, it should be noted that the use of a model with a large number of parameters can lead to overfitting and consequently good results during the construction of regression model and poor results in the prediction step. For this reason, a variable selection strategy was performed using backward elimination and the variables with p values greater than 0.1 were eliminated. Finally, Eq. 3 was obtained from the CCD as below:

$$\text{Efficiency, \%} = 84.34 - 7.91A + 2.56B + 4.92C - 5.92D + 5.62 + 0.80F - 1.33AB + 1.3AE + 1.23BE + 0.88CD - 1.28CE - 2.68A^2 - 4.22E^2 \quad (3)$$

According to this MLR equation, the positive sign of the one-factor coefficient implies that the removal efficiency is improved with the factor level increase, and the negative sign of the one-factor coefficient indicates that removal efficiency decreases with the factor level increase. The p value of the proposed model for carbamazepine and the involved variables (factors) such as initial pH, $H_2O_2$ concentration, $FeSO_4.7H_2O$ concentration, carbamazepine concentration, reaction time, and nanowire dose are listed in Table 2. The regression coefficient for interactions of the response model, F value, and sum of squares for the independent and dependent variables are given in Table 2 as well. The high F values for coefficients and the model imply their significance in expression of experimental conditions for the removal of contaminant. P value is used to show that F is large enough to represent the statistical significance. P values less than 0.05 indicate that the model conditions are significant at 95% confidence level or more. Specifically, the amount of F-value of

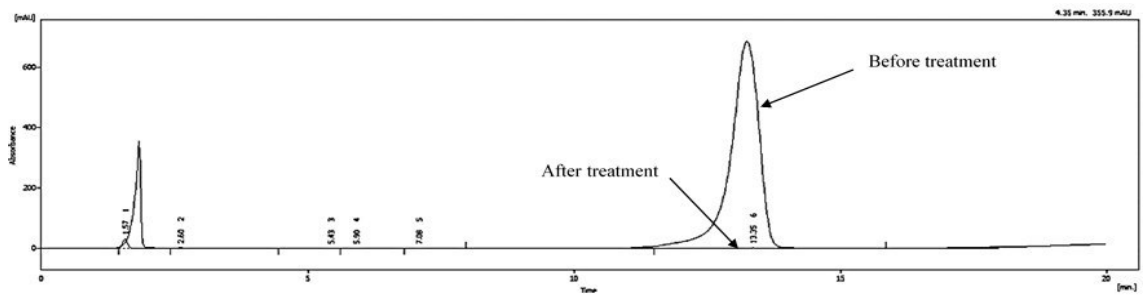



Fig. 3. Two typical chromatogram peaks of carbamazepine before and after treatment with the $Fe@Fe_2O_3$ nanowire and Fenton process

Table 2. ANOVA results from the second-order carbamazepine oxidation by Fenton process

| Source | Sum of squares | df | Mean square | F value | p-value prob >F | Contribution (%) | |
|---|---|---|---|---|---|---|---|
| Model | 12832.5 | 13 | 987.1158 | 60.89736 | < 0.0001 | | Significant |
| A-pH | 4500.317 | 1 | 4500.317 | 277.6345 | < 0.0001 | 35.07 | |
| B- $H_2O_2$ | 473.0375 | 1 | 473.0375 | 29.18274 | < 0.0001 | 3.69 | |
| C- $FeSO_4.7H_2O$ | 1742.369 | 1 | 1742.369 | 107.4906 | < 0.0001 | 13.58 | |
| D-carbamazepine Con.* | 2523.933 | 1 | 2523.933 | 155.707 | < 0.0001 | 19.67 | |
| E-Nano Dose ** | 2272.391 | 1 | 2272.391 | 140.1889 | < 0.0001 | 17.71 | |
| F-exposure time | 45.55351 | 1 | 45.55351 | 2.810297 | 0.0983 | 0.35 | |
| AB | 113.7156 | 1 | 113.7156 | 7.015366 | 0.0101 | 0.89 | |
| AE | 108.9675 | 1 | 108.9675 | 6.722447 | 0.0117 | 0.85 | |
| BE | 96.26063 | 1 | 96.26063 | 5.938532 | 0.0175 | 0.75 | |
| CD | 49.72013 | 1 | 49.72013 | 3.067345 | 0.0845 | 0.39 | |
| CE | 104.9856 | 1 | 104.9856 | 6.476797 | 0.0132 | 0.82 | |
| $A^2$ | 230.4387 | 1 | 230.4387 | 14.21628 | 0.0003 | 1.80 | |
| $E^2$ | 570.8163 | 1 | 570.8163 | 35.21493 | < 0.0001 | 4.45 | |
| Residuals | 1086.036 | 67 | 16.2095 | | | | |
| Lack-of-fit | 1068.599 | 63 | 16.96188 | 3.890813 | 0.0957 | | Insignificant |
| Pure error | 17.43788 | 4 | 4.35947 | | | | |
| Total | 13918.54 | 80 | | | | | |
| $R^2_{fit}$ | 0.9219 | | | | | | |
| $R^2_{pred}$ | 0.8679 | | | | | | |

*Concentration of carbamazepine
** Dose of utilized nanowires

the model (=60.89 and p-value<0.0001) indicate that the proposed model is statistically significant and can be used for obtaining the optimum conditions for the removal of carbamazepine. As can be seen, all the main factors, including pH, $H_2O_2$ concentration, $FeSO_4.7H_2O$ concentration, carbamazepine concentration, dose of nanowires, and reaction time remained in the model after selection of the variables. However, among the main factors, exposure time had the lowest percentage of contribution in the model (coefficient=0.35 and F =2.81), and pH had the highest effect (coefficient=35.07 and F =277.63). Among the binary interactions, only AB, AE, BE, CD, and CE were preserved in the model. On the other hand, the binary interactions, including factor F (exposure time), were not significant and were excluded from the final model. Considering the absolute amount of coefficients in the model (Eq. 3), the CD factor (interaction of $FeSO_4.7H_2O$ concentration and carbamazepine concentration) has the lowest participation in the model among the binary interactions. Totally, the effect of interactions was less than the effect of main factors. It should be noted that among the second-order interactions, only self-interaction of pH with pH ($A^2$) and concentration of nanowire with itself ($E^2$) remained in the model after selection of the variables. It should be noted that the significance of a model will not be valuable if the lack-of-fit of the model is not considered. A small F-value (lower than 0.1) for lack-of-fit indicates the suitability of the mode. The graph of carbamazepine actual removal efficiency versus it predicted efficiency expressed by Eq. 3 is shown in Fig. 4a. As can be seen in Fig. 4a, there is an acceptable agreement between the actual oxidation rate of carbamazepine and its predicted rate. The squared correlation coefficient of fitting ($R^2_{fit}$) (0.9219) and the $R^2$ of prediction ($R^2_{pred}$) (0.868) suggest good fitting and prediction ability of the model. Finally, it was concluded that the proposed model is suitable for explaining the relationship between oxidation efficiency and operator factors for degradation of carbamazepine by Fenton process. An important point which should be considered in establishing a suitable model for extracting optimized conditions is excluding pair-correlation and multi-correlation. In this study, in addition to pair correlation, multi-correlation was checked using the variance inflation factor (VIF) (Honarasa *et al.*, 2015). The VIF of all factors in Eq. 3 were not greater than 1.0 as they were significantly lower than 5.0 (the cut of VIF value) (Yousefinejad *et al.*, 2016). Thus, it can be inferred that no significant dependency was presented in the model and the results can be used for optimizing the experimental conditions for the removal of carbamazepine. A proper approach to check the accuracy of the model extracted from CCD is study of the plot of normal probability of residuals versus internally studentized residuals. Fig. 4b indicates the normal probability plot of the residuals in which residual points almost lie on a straight line without high deviations and confirms the normal distribution of errors.

*Effect of factors on carbamazepine oxidation*

To investigate the effect of each variable on the oxidation efficiency, 3D diagram and interaction diagrams were used to explain the effect of interactions between two parameters and on removal

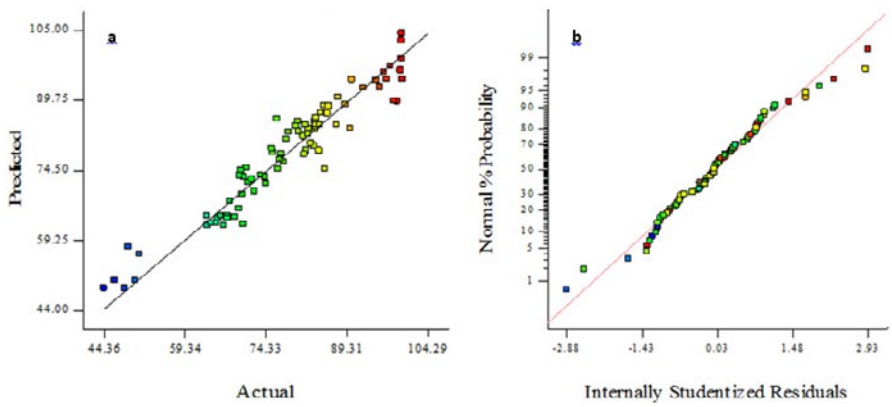



Fig. 4. (a) Relationship among the predicted oxidation efficiencies of carbamazepine; (b) Normal probability plot of studentized residuals for the suggested quadratic model in terms of removal efficiency

of carbamazepine. Fig. 5a shows the interaction between pH and $H_2O_2$ concentration at a constant reaction time of 35 min, when nanowires and carbamazepine concentrations were 150 mg/L and 11 mg/L respectively. Obviously, the carbamazepine removal efficiency decreased with the increase of initial pH and the highest removal rate occurred at pH=4. The increased removal rate at pH=4 can be due to the formation of large amounts of radical hydroxyl and reduction of the reaction between OH• and $H^+$ ions (Babuponnusami and Muthukumar, 2014; Dehghani *et al*., 2016). According to Ding *et al*. (2016), Fenton oxidation of carbamazepine by $CuFeO_2$ will be recyclable if hydroxylamine is used. Some studies have shown that the potential of radical hydroxyl oxidation changes with the change of pH (Babuponnusami and Muthukumar, 2014). At lower pH values (< 3-4), existence of complex spices $[Fe(H_2O)_6]^{2+}$ and high amount of $H^+$ ions reduce the amount of radical hydroxyl production through the formation of stable oxonium ions ($[H_3O_2]^+$) (Kwon *et al*., 1999; Kavitha and Palanivelu, 2005; Xu *et al*., 2009). Reduction of carbamazepine degradation rate at high pH values can be due to formation of $Fe(OH)_3$ and $HO_2^{2-}$ ions which decrease the potential for radical hydroxyl production (Dehghani *et al*., 2016). In addition, the efficiency of carbamazepine degradation significantly increased with the increase of $H_2O_2$ concentration. The increase of drug degradation by increase of $H_2O_2$ concentration can be due to formation of higher hydroxyl radicals at high concentrations of $H_2O_2$ in the studied range (Sun *et al*., 2014). According to the 3D diagram illustrated in Fig. 5a, the maximum degradation efficiency for carbamazepine (over 98%) was obtained at pH=4 and $H_2O_2$ concentration of 23 mg/L. These results are consistent with the results reported in previous studies concerning the effect of pH and $H_2O_2$ on the removal of pollutants (Basturk *et al*., 2014; Arshadi *et al*., 2016; Saini *et al*., 2016). Fig. 5b shows the effect of Fe@$Fe_2O_3$ nanowires concentration and their interaction with $H_2O_2$ concentration at pH=5.5, carbamazepine concentration of 11 mg/L, $FeSO_4.7H_2O$ concentration of 5 mg/L, and oxidation time of 35 min. According to Fig. 5b, by increasing the dose of

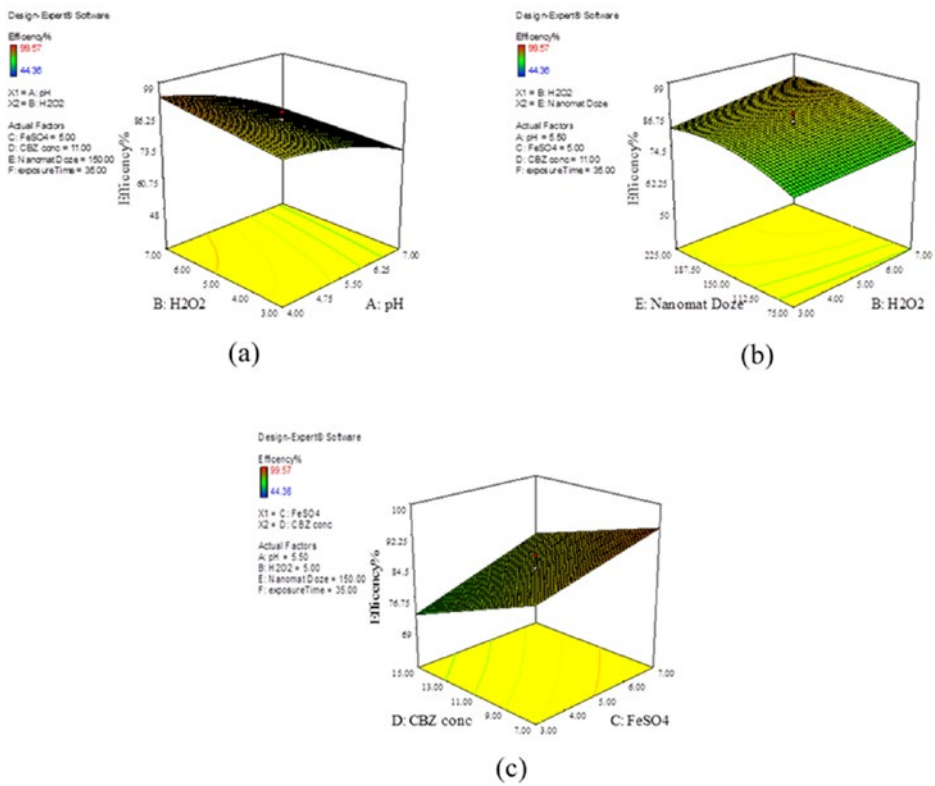



Fig. 5. (a) Effect of pH and initial concentration of $H_2O_2$ interaction on the efficiency of carbamazepine degradation; (b) Effect of initial $H_2O_2$ concentration and Fe@$Fe_2O_3$ nanowires dose interaction on the efficiency of carbamazepine degradation; and (c) Effect of initial $FeSO_4.7H_2O$ concentration and drug concentration interaction on the efficiency of carbamazepine degradation

$Fe@Fe_2O_3$ nanowires from 75 mg/L to 150 mg/L, carbamazepine oxidation first increased and then remained constant. The increase of removal rate can be due to the reaction between the nanowires and molecular oxygen to produce reactive oxygen species (ROSs) such as $\cdot O_2^-$, $H_2O_2$, and OH• according to Eqs. 4 to 7 (Shi *et al.,* 2014; Sirés *et al.,* 2014).

$$Fe + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (4)$$
$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + {}^{\circ}\cdot O_2^- \quad (5)$$
$$2H^+ + {}^{\circ}\cdot O_2^- \rightarrow H_2O_2 \quad (6)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\circ}OH \quad (7)$$

Typically, the produced oxygen species have the ability to oxidize or reduce carbamazepine in the Fenton process. These results are in agreement with the results obtained by Shen *et al*. (2017) on the bromate removal by $Fe@Fe_2O_3$ nanowires. Increase of carbamazepine degradation efficiency was observed by increasing the concentration of $H_2O_2$ in different amounts of nanowires. This can be attributed to the production of more radical hydroxyls in the presence of both variables. According to the results obtained from the interaction of $Fe@Fe_2O_3$ nanowires and $H_2O_2$ concentration, the maximum degradation efficiency was achieved at 90% when the dose of nanowires was 225 mg/L and $H_2O_2$ concentration was 23 mg/L. These results are consistent with the results reported in previous studies concerning the effect of interactions between the catalyst and $H_2O_2$ (Chen *et al*., 2014; Saldaña-Robles *et al*., 2014; Shi *et al*., 2014). The effects of interaction between the initial concentration of $FeSO_4.7H_2O$ and the initial concentration of carbamazepine on degradation efficiency at pH=5.5, $H_2O_2$ concentration of 16.49 mg/L, nanowires dose of 150 mg/L, and reaction time of 35 min are shown in Fig. 5c. Obviously, the efficiency of carbamazepine degradation increased with the increase of $Fe^{2+}$ levels. This was due to the synergistic effect of $Fe@Fe_2O_3$ and $Fe^{2+}$ on the catalytic decomposition of $H_2O_2$ for rapid degradation of carbamazepine (Shi *et al*., 2014). In addition, the increase of ferrous-ion ($Fe^{2+}$) concentration in the $Fe@Fe_2O_3/Fe^{2+}/H_2O_2$ system led to generation of ROSs according to Eqs. 4-7. Shi *et al.* (2014) in their study, investigated the effect of $Fe^{2+}$ on degradation of Rhodamine B by $Fe@Fe_2O_3$ nanowires and concluded that addition of $Fe^{2+}$ can increase $H_2O_2$ degradation and ROSs production(Shi et al., 2014). As can be seen in Fig 5c, the rate of degradation decreased with the increase of carbamazepine initial concentration. The reduced carbamazepine removal can be explained by the need for more radical hydroxyls to degrade the drug and its derivatives at high concentrations of carbamazepine (Shen *et al*., 2017). Sun *et al.* (2014) showed that the efficiency of carbamazepine degradation by $Fe_3O_4/H_2O_2$ decreases with the increase of carbamazepine initial concentration. They attributed this reduction to the fact that in a steady state, the amount of radical hydroxyl production is constant and limited. Ertugay and Acar. (2017) revealed that in Fenton process the oxidation rate decreases with the increase of Azo concentration. In a study by Youssef *et al.* (2016), it was shown that efficiency of color degradation by Fenton catalytic reaction decreased with the increase of methyl orange color concentration. They related the reduction of color concentrations to a low concentration of hydroxyl radicals. After fitting the experimental data obtained by RSM into Eq. 3, the simplex strategy was used to find optimum conditions (the maximum efficiency of carbamazepine degradation). Finally, it was concluded that an efficiency of about 99.83% can be obtained at pH =4.3, $H_2O_2$ concentration of 22 mg/L, $FeSO_4.7H_2O$ concentration of 52.2 mg/L, carbamazepine concentration of 7.7 mg/L, nanowire dose of 179.4 mg/L, and reaction time of 45.9 min. Moreover, the adsorption capacity of $Fe@Fe_2O_3$ was 41.17 mg/g under the mentioned conditions. The obtained results were confirmed with more experimental studies on the predicted values of factors. In fact, the optimum values suggested for the factors were used in the experimental runs (three replicates) and efficiencies of over 99% were obtained in agreement with the predictions. The successful removal of carbamazepine in the proposed optimized conditions implies that optimization of drug degradation and maximum degradation efficiency can be achieved by application of RSM for oxidation of carbamazepine by $Fe@Fe_2O_3/Fe^{2+}/H_2O_2$. Under optimum conditions (pH =4.3, $H_2O_2$ concentration of 22 mg/L, $FeSO_4.7H_2O$ concentration of 52.2 mg/L, carbamazepine concentration of 7.7 mg/L, nanowire dose of 179.4 mg/L, and reaction time of 45.9 min), the obtained TOC removal efficiency was 39.12%. The decreased TOC removal efficiency may be related to the conversion of carbamazepine compounds into intermediate products during Fenton oxidation. The potencies of $Fe@Fe_2O_3$ and various adsorbents used for the removal of carbamazepine have been compared in Table 3.

Table 3. The removal of carbamazepine from aqueous solutions using various adsorbents

| Adsorbents | | qe (mg/g) | References |
|---|---|---|---|
| fly ash-amended soil | | 0% fly ash= 0.07636<br>5% fly ash=0.09396<br>10% fly ash= 0.11124<br>30% fly ash= 0.1542 | Swarcewicz *et al.*, 2013 |
| Regenerable granular carbon-nanotubes/alumina hybrid | | 37.21 | Wei *et al.*, 2013 |
| functionalized silica-based porous materials | | HMS:0.04<br>A-HMS:0.006<br>M-HMS:0.05 | Suriyanon *et al.*, 2013 |
| Sludge/ fish waste | | 37.2 | Nielsen *et al.*, 2014 |
| Multi-walled carbon nanotubes (MWCNTs) | | MWNT10 = 30<br>MWNT20 = 4<br>MWNT40 = 3<br>MWNT60 = 2.5 MWNT100 = 2 | Oleszczuk *et al.*, 2009 |
| $Fe@Fe_2O_3$ | $Fe@Fe_2O_3$ nanowires and Fenton process | 41.17 | The present work |

## CONCLUSION

In this study, an effective model was presented synthesize $Fe@Fe_2O_3$ nanowires. The efficiency of $Fe@Fe_2O_3$ nanowires in the carbamazepine synergistic removal process was also investigated using $Fe^{2+}/Fe@Fe_2O_3/H_2O_2$. The results showed that $Fe@Fe_2O_3$ nanowires were synthesized with a wire-like structure, a suitable diameter distribution, and high purity. The RSM based on CCD was used to evaluate and optimize the effect of 6 main factors on the carbamazepine oxidation efficiency. The results of analysis of variance (p value <0.0001 and F =60.89) showed that the regression model has a statistically significant relationship and can be used to predict the removal of carbamazepine from aqueous solutions. Based on prediction, the maximum efficiency for carbamazepine degradation by oxidation (99.83%) occurred in pH value of 4.3, 22 mg/L $H_2O_2$ , 52.2 mg/L $FeSO_4.7H_2O$, 7.7 mg/L carbamazepine, nanowires dose of 179.4 mg/L, and reaction time of 45.9 min. The obtained results were confirmed with further experimental studies under the predicted optimized conditions. Statistical analysis showed that CCD-based RSM is a reliable tool for optimizing Fenton oxidation of carbamazepine.

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## CONFLICT OF INTERESTS

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

## ABBREVIATIONS

| | |
|---|---|
| *ANOVA* | Analysis of variance |
| *AOPs* | Advanced oxidation processes |
| *CBZ* | Carbamazepine |
| *CCD* | Central Composite Design |
| *°C* | Degree centigrade |
| *DLLME* | Dispersive liquid-liquid microextraction |
| *EDX* | Energy-dispersive X-ray |
| $Fe^{2+}/H_2O_2$ | Fenton reaction |
| $Fe^{2+}$ | Ferrous-ion |
| $Fe@Fe_2O_3$ | Nanowire |
| $FeCl_3.6H_2O$ | Ferric Chloride Hexahydrate, Iron (III) Chloride Hexahydrate |
| $FeSO_4.7H_2O$ | Ferrous Sulfate Heptahydrate, Iron (II) Sulfate |
| *g* | Gram |
| *g/mol* | Gram/mol |
| $H_2O_2$ | Hydrogen peroxide |

| | |
|---|---|
| *HPLC* | High performance liquid chromatography |
| *mg/g* | Milligram per gram |
| *mg/L* | Milligram/liter |
| *min* | Minute |
| *ML* | Milliliter |
| *ML/s* | Milliliter/second |
| *M* | Molar |
| *ML/min* | Milliliter/minute |
| *µm* | Micrometer |
| *µL* | Microliter |
| *MLR* | Multiple linear regression |
| *$NaBH_4$* | Sodium borohydride |
| *nm* | Nanometer |
| *nZVI* | Zero-valent iron nanoparticles |
| *OH•* | Radical hydroxyl |
| *$[H3O2]^+$* | Oxonium ions |
| *pH* | Potential of hydrogen |
| *RSM* | Response surface methodology |
| *ROSs* | Reactive oxygen species |
| *$R^2_{pred}$* | $R^2$ of prediction |
| *$R^2_{fit}$* | $R^2$ of fitting |
| *rpm* | Revolutions per minute |
| *TOC* | Total organic carbon |
| *VIF* | Variance inflation factor |
| *v/v* | Volume/ Volume |
| *w/w* | Weight/ Weight |
| *XRD* | X-ray diffraction |

## REFERENCES


Ai, Z.; Gao, Z.; Zhang, L.; He, W.; Yin, J.J., (2013). Core–shell structure dependent reactivity of Fe@$Fe_2O_3$ nanowires on aerobic degradation of 4-chlorophenol. Environ. Sci. Technol., 47: 5344–5352 (**9 pages**).

Arshadi, M.; Abdolmaleki, M. K.; Mousavinia, F.; Khalafi- Nezhad, A.; Firouzabadi, H.; Gil, A., (2016). Degradation of methyl orange by heterogeneous Fenton-like oxidation on a nano-organometallic compound in the presence of multi-walled carbon nanotubes. Chem Eng Res Des., 112: 113–121 **(9 pages).**

Babuponnusami, A.; Muthukumar, K., (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Eng., 2: 557–572 (**16 pages**).

Babuponnusami, A.; Muthukumar, K., (2012). Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes. Chem. Eng. J., 183: 1–9 **(9 pages).**

Basturk, E.; Karatas, M., (2014). Advanced oxidation of Reactive Blue 181 solution: A comparison between Fenton and Sono-Fenton process. Ultrason Sonochem., 21: 1881–1885 **(5 pages).**

Braeutigam, P.; Franke, M.; Schneider, R. J.; Lehmann, A.; Stolle, A.; Ondruschka, B., (2012). Degradation of carbamazepine in environmentally relevant concentrations in water by Hydrodynamic-Acoustic-Cavitation (HAC). Water Res., 46: 2469–2477 (**9 pages**).

Brillas, E.; Sirés, I.; Oturan, M.A., (2009). Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. Chem. Rev., 109: 6570–6631 (**62 pages**).

Chen, K.; Wang, G.H.; Li, W.B.; Wan, D.; Hu, Q.; Lu, L.L., (2014). Application of response surface methodology for optimization of Orange II removal by heterogeneous Fenton-like process using Fe3O4 nanoparticles. Chinese Chem. Lett., 25: 1455–1460 (**6 pages**).

Chen, L.; Ma, J.; Li, X.; Zhang, J.; Fang, J.; Guan, Y.; Xie, P., (2011). Strong Enhancement on Fenton Oxidation by Addition of Hydroxylamine to Accelerate the Ferric and Ferrous Iron Cycles. Environ. Sci. Technol., 45: 3925–3930 (**6 pages**).

De, S.; Maiti, S.; Hazra, T.; Debsarkar, A.; Dutta, A., (2016). Leachate characterization and identification of dominant pollutants using leachate pollution index for an uncontrolled landfill site. Global J. Environ. Sci. Manage., 2(2): 177-186 **(10 pages).**

Dean, A.; Voss, D.; Dragulјić, D., (2017). Response Surface Methodology. in: Springer, Cham, 565–614 (**50 pages**).

Dehghani, M.; Behzadi, S.; Sekhavatjou, M. S., (2016). Optimizing Fenton process for the removal of amoxicillin from the aqueous phase using Taguchi method. Desalination Water Treat., 57: 6604–6613 (**10 pages**).

Ding, Y.; Huang, W.; Ding, Z.; Nie, G.; Tang, H., (2016). Dramatically enhanced Fenton oxidation of carbamazepine with easily recyclable microscaled CuFeO 2 by hydroxylamine: Kinetic and mechanism study. Sep. Purif. Technol., 168: 223–231 (**9 pages**).

Ertugay, N.; Acar, F. N., (2017). Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study. Arab. J. Chem., 10: S1158–S1163 (**6 pages**).

Honarasa, F.; Yousefinejad, S.; Nasr, S.; Nekoeinia, M., (2015). Structure–electrochemistry relationship in non-aqueous solutions: Predicting the reduction potential of anthraquinones derivatives in some organic solvents. J. Mol. Liq., 212: 52–57 (**6 pages**).

Huang, Y.H.; Su, H.T.; Lin, L.W., (2009). Removal of citrate and hypophosphite binary components using Fenton, photo-Fenton and electro-Fenton processes. J. Environ. Sci (China)., 21: 35–40 (**6 pages**).

Kang, N.; Lee, D. S.; Yoon, J., (2002). Kinetic modeling of Fenton oxidation of phenol and monochlorophenols. Chemosphere., 47: 915–924 (**10 pages**).

Kavitha, V.; Palanivelu, K., (2005). Destruction of cresols by Fenton oxidation process. Water Res., 39:3062–3072 (**11 pages**).

Khamparia, S.; Jaspal, D., (2017). Study of decolorisation of binary dye mixture by response surface methodology. J. Environ. Manage., 201: 316–326 (**11 pages**).

Komtchou, S.; Dirany, A.; Drogui, P.; Bermond, A., (2015). Removal of carbamazepine from spiked municipal wastewater using electro-Fenton process. Environ. Sci. Pollut. Res., 22: 11513–11525 (**13 pages**).

Kwon, B.G.; Lee, D.S.; Kang, N.; Yoon, J., (1999). Characteristics of p-chlorophenol oxidation by Fenton's reagent. Water Res., 33: 2110–2118 (**9 pages**).

Lyons, G., (2014). Pharmaceuticals in the environment: A growing threat to our tap water and wildlife. In CHEM Trust.

Navalon, S.; de Miguel, M.; Martin, R.; Alvaro, M.; Garcia, H., (2011). Enhancement of the Catalytic Activity of Supported Gold Nanoparticles for the Fenton Reaction by Light. J. Am. Chem. Soc., 133: 2218–2226 ( **9 pages**).

Nielsen, L.; Zhang, P.; Bandosz, T. J., (2015). Adsorption of carbamazepine on sludge / fish waste derived adsorbents : Effect of surface chemistry and texture. Chem. Eng. J., 267: 170–181 (**12 pages**).

Oleszczuk, P.; Pan, B.; Xing, B., (2009). Adsorption and Desorption of Oxytetracycline and Carbamazepine by Multiwalled Carbon Nanotubes. Environ. Sci. Technol., 43: 9167–9173 (**7 pages**).

Pomati, F.; Castiglioni, S.; Zuccato, E.; Fanelli, R.; Vigetti, D.; Rossetti, C.; Calamari, D., (2006). Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. Environ. Sci. Technol., 40: 2442–2447 (**6 pages**).

Rusevova, K.; Köferstein, R.; Rosell, M.; Richnow, H.H .; Kopinke, F. D.; Georgi, A., (2014). LaFeO3 and BiFeO3 perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions. Chem. Eng. J., 239: 322-331 (**10 pages**).

Saini, R.; Kumar, P., (2016). Optimization of chlorpyrifos degradation by Fenton oxidation using CCD and ANFIS computing technique. J. Environ. Chem. Eng ., 4: 2952–2963 (**12 pages**).

Saldaña-Robles, A.; Guerra-Sánchez, R.; Maldonado-Rubio, M.I.; Peralta-Hernández, J.M., (2014). Optimization of the operating parameters using RSM for the Fenton oxidation process and adsorption on vegetal carbon of MO solutions. J. Ind. Eng. Chem., 20: 848-857 (**10 pages**).

Shen, W.; Lin, F.; Jiang, X.; Li, H.; Ai, Z.; Zhang, L., (2017). Efficient removal of bromate with core-shell Fe@Fe 2 O 3 nanowires. Chem. Eng. J., 308: 880–888 (**9 pages**).

Shi, J.; Ai, Z.; Zhang, L., (2014). Fe@Fe2O3 core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles. Water Res., 59: 145–153 (**9 pages**).

Sirés, I.; Brillas, E.; Oturan, M.A.; Rodrigo, M. A.; Panizza, M., (2014). Electrochemical advanced oxidation processes: today and tomorrow. A review. Environ. Sci. Pollut. Res., 21: 8336-8367 (**32 pages**).

Song, W.; Cheng, M.;Ma, J.; Ma, W.; Chen, C.; Zhao, J., (2006). Decomposition of hydrogen peroxide driven by photochemical cycling of iron species in clay. Environ. Sci. Technol., 40: 4782–4787 (**6 pages**).

Sun, S.P.; Zeng, X.; Li, C.; T.Lemley, A., (2014). Enhanced heterogeneous and homogeneous Fenton-like degradation of carbamazepine by nano-Fe3O4/H2O2 with nitrilotriacetic acid. Chem. Eng. J., 244: 44–49 (**6 pages**).

Suriyanon, N.; Punyapalakul, P.; Ngamcharussrivichai, C., (2013). Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials. Chem. Eng. J., 214: 208–218 (**11 pages**).

Swarcewicz, M. K.; Sobczak, J.; Paz´dzioch, W., (2013). Removal of carbamazepine from aqueous solution by adsorption on fly ash-amended soil. Water Sci. Technol., 67: 1396–1402 (**7 pages**).

Wei, H.; Deng, S.; Huang, Q.; Nie, Y.; Wang, B., (2013). Regenerable granular carbon nanotubes / alumina hybrid adsorbents for diclofenac sodium and carbamazepine removal from aqueous solution. Water Res., 47: 4139–4147 (**9 pages**).

Wu, C.; Zhang, H.; Wu, Y.X.; Zhuang, Q.C.; Tian, L.L.; Zhang, X.X., (2014). Synthesis and characterization of Fe@Fe2O3 core-shell nanoparticles/graphene anode material for lithium-ion batteries. Electrochim. Acta., 134: 18–27 (**10 pages**).

Wu, H.; Ai, Z.; Zhang, L., (2014). Anoxic and oxic removal of humic acids with Fe@Fe2O3 core-shell nanowires: a comparative study. Water Res., 52: 92–100 (**9 pages**).

Xu, X.R.; Li, X.Y.; Li, X.Z.; Li, H.B., (2009). Degradation of melatonin by UV, UV/H2O2, Fe2+/H2O2 and UV/Fe2+/H2O2 processes. Sep. Purif. Technol., 68: 261–266 (**6 pages**).

Yousefinejad, S.; Honarasa, F.; Chaabi, M., (2016). New relationship models for solvent–pyrene solubility based on molecular structure and empirical properties. New. J. Chem., 40: 10197–10207 (**11 pages**).

Youssef, N.A.; Shaban, S.A.; Ibrahim, F.A.; Mahmoud, A.S., (2016). Degradation of methyl orange using Fenton catalytic reaction. Egypt. J. Pet., 25: 317–321 (**5 pages**).

Zhang, Y.; Geißen, S.U.; Gal, C., (2008). Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies. Chemosphere., 73: 1151-1161 (**11 pages**).

Zhu, L.; Ai, Z.; Ho, W.; Zhang, L., (2013). Core–shell Fe–Fe2O3 nanostructures as effective persulfate activator for degradation of methyl orange. Sep. Purif. Technol., 108: 159–165 (**7 pages**).

**AUTHOR (S) BIOSKETCHES**

**Amin, M.M.,** Ph.D., Professor, Environment Research Center, Research Institute for Primordial Prevention of Non-Communicable Disease, Isfahan University of Medical Sciences, and Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran. Email: *amin@hlth.mui.ac.ir*

**Yousefinejad, S.,** Ph.D., Assistant Professor, Research Center for Health Sciences, Institute of Health, Department of Occupational Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran. Email: *yousefisa@sums.ac.ir*

**Dehghani, M.,** Ph.D., Professor, Research Center for Health Sciences, Institute of Health, Department of Environmental Health, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran. Email: *mdehghany@sums.ac.ir*

**Rahimi, S.,** Ph.D. Candidate, Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran. Email: *rahimi.somaye@gmail.com*

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