Removal of Bromocresol Green from aqueous solution by electro-Fenton and electro-Fenton-like processes with different catalysts: laboratory and kinetic model investigation

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ABSTRACT

This study presents the removal of triarylmethane dye Bromocresol Green from aqueous solution by the electro-Fenton process. As catalysts five different cations were used: Fe^{2+}, Ce^{3+}, Ni^{2+}, Mn^{2+}, and Co^{2+}. They play crucial roles in the whole process because they react with H_{2}O_{2} producing hydroxyl radicals that are capable of breaking down dye molecules. Based on this, a comparison of catalytic activity of these cations in the electro-Fenton process is made for Bromocresol Green degradation. A simple and universal kinetic model is also applied to study the catalytic activity of investigated catalysts. Due to its multidimensionality it is fitted to experimental data using a genetic algorithm. The procedure of fitting using a genetic algorithm is thoroughly described and demonstrated. The activity of utilized catalysts is compared based on both experimental and model data revealing that for Bromocresol Green removal all alternative catalysts (Ni^{2+}, Co^{2+}, Ce^{3+}, Mn^{2+}) are better than the typical one (Fe^{2+}, 51.83% degradation). The best catalyst is Co^{2+} with 78.35% degradation efficiency. Moreover, the adopted kinetic model proved its universality and outlined different interactions between catalysts and dye molecules.

Key words: Bromocresol Green, decolorization, electro-Fenton process, genetic algorithm, kinetic model

HIGHLIGHTS

- Bromocresol Green was degraded in an electro-Fenton process with different catalysts.
- Five different catalysts were compared in terms of their catalytic activity.
- A simplified kinetic model was used to simulate experimental data.
- A genetic algorithm fits the kinetic model to experimental data very well.
- Both experimental and model data show that the best catalyst is Co^{2+}.

GRAPHICAL ABSTRACT

INTRODUCTION

Synthetic dyes are often used to color many different products, for example textiles, cosmetics, food, paper and chemicals (El-Desoky et al. (2010), Panizza & Oturan (2011)). Likewise they are used as pH indicators in organic analytics. Despite being widely used in industry, synthetic dyes have many disadvantages. Aromatic rings, which dyes usually contain, makes
these colored compounds chemically durable and biologically recalcitrant (Rosales et al. (2009)). Therefore their presence in water causes non-aesthetic pollution and danger for the environment.

Conventional physico-chemical treatment of dyeing wastewater usually results in generation of secondary waste products, such as sludge (El-Desoky et al. (2010)), so the majority of these pollutants cannot be degraded. Advanced oxidation processes such as Fenton’s reaction (2), are a more effective removal alternative. The electro-Fenton method is based on oxidation, due to intensive production of hydroxyl radicals, which attack dye molecules (Panizza & Oturan (2011)). Dissolved molecular O₂ is continuously reduced to hydrogen peroxide (1) (Rosales et al. (2009), El-Desoky et al. (2010)) at the cathode, under control of applied current. Fenton’s reaction is coupled with iron oxidation, but in order to remove highly reactive and iron sludge productive Fe³⁺ ions from the solution (Rosales et al. (2009)), it is rapidly regenerated at the cathode (3). Reactions are conducted in acidic medium:

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
Fe^{2+} + H_2O_2 + H^+ & \rightarrow Fe^{3+} + H_2O + OH^- \\
Fe^{3+} + e^- & \rightarrow Fe^{2+}
\end{align*}
\]

(1) (2) (3)

The molecular oxygen that is necessary for the production of H₂O₂ is generated by oxidizing water in the anodic process (4) (Brillas & Martinez-Huitle (2015)). Oxygen can also be supplied from external sources (e. g. air) by continuously passing through a reaction mixture:

\[
2H_2O \rightarrow 4H^+ + O_2 + 4e^-
\]

(4)

Adding up the processes occurring at the electrodes and in the solution (1–4) we get following summary reaction of the electro-Fenton process (5):

\[
\frac{1}{2}O_2 + H_2O \rightarrow 2OH
\]

(5)

In situ generation of H₂O₂ avoids the need for transport and storage of this hazardous substance, offers safer operation by virtue of providing diluted H₂O₂ solutions and enhances the mixing of solutions (Rosales et al. (2009)). Therefore the electro-Fenton process is environmentally friendly. Moreover this method is efficient in degrading organic molecules and easy to implement (for example 95% removal of Alizarin Red S (Panizza & Oturan (2011))).

Modifications of the electro-Fenton process were investigated in terms of the applied catalyst. It turned out that efficiency of degradation can be enhanced by using catalysts alternative to Fe²⁺, such as Cu⁺, Mn²⁺ and Co²⁺ cations (Leonard et al. (1998), Bokare & Choi (2014)). Moreover, recently novel, two-electron type, catalysts (Sn²⁺, Bi³⁺) have been reported (Matyszczak et al. (2020b)). Use of cations of other metals gives the possibility for increasing performance of the electro-Fenton process due to differences in interplay of catalyst cations with dye molecules.

The electro-Fenton process is a complex system of many reactions, therefore the most suitable way to investigate kinetics of this process is the kinetic model. Such an approach has been found to be very useful and many times leads to results being in good agreement with experimental data (Liu et al. (2007), Mousset et al. (2016), Nakagawa et al. (2016)). Many so far presented kinetic models of the electro-Fenton process include specific pathways and intermediate compounds, thus they are limited to types of pollutants for which they were constructed. Organic molecules of different types are expected to have distinct pathways of degradation. Matyszczak et al. (2020a) considered only the most important reactions in the process and proposed a simple kinetic model based on the rate-limiting step approximation that is independent of the type of pollutant molecule. This model has been validated for azo dye Metanil Yellow.

Kinetic models may include many parameters and therefore, due to their multidimensionality, they are hard to fit to experimental data using conventional methods. Luckily, there exist global optimization methods, such as genetic algorithms. For example, they are able to solve NP-hard problems (a problem is NP-hard if an algorithm for solving it can be translated into one for solving any NP problem (nondeterministic polynomial time) problem) like the traveling salesman problem – finding the shortest and the most moneymaking way for the salesman through certain cities knowing prices of goods in each city and distances between them (Vikhar (2017), Hussain et al. (2017)). More interestingly, they proved their utility in a variety of
chemical problems like determining the optimal reaction mechanism, parameter estimation, crystal structure prediction (together with new unexpected crystal phases) and more (Tsuchiya & Ross (2001), Elliott et al. (2004), Katare et al. (2004), Montgomery et al. (2006), Organov et al. (2007), Rahimi et al. (2010), Szilágyi & Bódis (2018)).

This paper investigates the removal of triarylmethane dye Bromocresol Green from aqueous solution using five different catalysts: Fe$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Ce$^{3+}$ in the electro-Fenton process. A simplified kinetic model proposed by Matyszczak et al. (2020a) is adopted and its universality is verified. The catalytic activity of distinct catalysts is compared based on experimental and model results. The kinetic model, due to its multidimensionality, is fitted to experimental data using a genetic algorithm. The application of a genetic algorithm for kinetic modeling of degradation of model triarylmethane dye is demonstrated step by step. The applied catalysts have not been used for degradation of Bromocresole Green and adopted kinetic model has not been verified for triarylmethane dye previously. Also, it is the first time that a genetic algorithm has been used for fitting the adopted model.

**METHODS**

**Material and reagents**

A commercial Bromocresol Green triarylmethane dye (Figure 1) was used in the present study without further purification. Solutions of H$_2$SO$_4$ (1 M) and NaOH (1 M) were used. FeSO$_4$·7H$_2$O, MnSO$_4$·4H$_2$O, CoSO$_4$·7H$_2$O, NiSO$_4$·7H$_2$O, Ce$_2$(SO$_4$)$_3$·8H$_2$O were used as catalysts and Na$_2$SO$_4$·10 H$_2$O was used to make supporting electrolyte. All reagents were pure for analysis (producer: POCH).

**Electrochemical apparatus**

The electrochemical apparatus used in this study was the same as in the Matyszczak et al. (2020a) investigation. A potentiostat Model EP 20, graphite roller cathode, platinum plate anode, pH-meter (CP-505, Elmetron), pH electrode (ERH-13, Hydromet), and saturated calomel electrode (RU-10, Hydromet) were used.

**Procedure for the electro-Fenton process**

The experimental setup (Figure 2) and procedure for the electro-Fenton process were adopted from the Matyszczak et al. (2020a) study.

**Monitoring of oxidation reaction**

To monitor the degradation of Bromocresol Green in aqueous solution by the electro-Fenton oxidation a procedure from the Matyszczak et al. (2020a) study was applied. It included recording the absorbance spectra, making its derivative and construction of a calibration curve. See Figures S1–S3 in supplemental materials.

![Figure 1](image1.png) | Chemical structure of the Bromocresol Green molecule.
THEORY

The kinetic model

In this study we use a simplified and universal kinetic model proposed previously by Matyszczak et al. (2020a). We will recall and shortly describe it for clarity. This model views the whole electro-Fenton process as the interplay of five reactions:

\[
\begin{align*}
O_2 + 2H^+ + 2e^- &\rightarrow H_2O_2 \quad (6) \\
M^{n+} + H_2O_2 + H^+ &\rightarrow M^{(n+1)+} + H_2O + OH \quad (7) \\
M^{(n+1)+} + e^- &\rightarrow M^{n+} \quad (8) \\
\text{Bromocresol Green} + X OH &\rightarrow CO_2 + H_2O \quad (9) \\
2H_2O &\rightarrow 4H^+ + O_2 + 4e^- \quad (10)
\end{align*}
\]

The symbol of the catalyst is denoted by M (in this study: Fe, Co, Mn, Ni, Ce) and its charge is denoted by n. X is the number of hydroxyl radicals needed to break down one molecule of dye. It does not have to be integer value, because the break down of a molecule of Bromocresol Green can occur in many ways as this molecule is big (Figure 1) and has many sides (e.g. carbon atoms) which hydroxyl radical may attack, this contributes to many possible detailed pathways of degradation of molecules of this pollutant.

Based on reactions in the model and assumptions underlying it, following differential equations the rates of changes in the domain of time of different chemicals during the electro-Fenton process were expressed:

\[
\begin{align*}
\frac{d}[O_2]{dt} &\approx 0 \\
\frac{d}[H^+]{dt} &\approx 0 \\
\frac{d}[M^{n+}]{dt} &= k_8[M^{(n+1)+}][M^{(n+1)+}] + [H^+] - k_7[M^{n+}][H_2O_2] = -\frac{d}[M^{(n+1)+}]{dt} \\
\frac{d}[H_2O_2]{dt} &= \frac{l_0}{2} \cdot \frac{[H^+]}{[H^+] + [M^{(n+1)+}]} - k_7[M^{n+}][H_2O_2] \\
\frac{d}[\text{Bromocresol}]{dt} &= -\frac{k_7}{X}[M^{n+}][H_2O_2]
\end{align*}
\]
Kinetic constants of reactions (7) and (8), \( k_7 \) and \( k_8 \), together with \( X \) are parameters of this model. See Matyszczak et al. (2020a) for detailed derivation and justification of this kinetic model.

**Genetic algorithm**

To fit the parameters of the kinetic model to experimental data we used the genetic algorithm. As a global optimization method it is efficient for multidimensional problems (Vikhar (2017)). Our problem is three-dimensional because there are three parameters in the model. Compared to local optimization methods (such as: simplex method, interior point, iterative least squares etc.), a genetic algorithm is less likely to find the local minima and is far more independent of initial guess of parameters values (i.e. starting point). At the same time, it shares the desirable properties of local methods due to usage of the information collected in the process of sampling of the parameter space. It merges the advantages of both fully local and fully random (e.g. Monte Carlo) optimization methods (Gallagher & Sambridge (1994), Mirjalili et al. (2019), Katoch et al. (2021)).

During the action of the genetic algorithm the solutions are referred to as ‘genotypes’. In each generation there is a certain number of genotypes characterized by their quality as a solution to the problem. Each next generation is formed from previous generation using operations of reproduction, mutations, and crossing-over. The probability of passing of a certain genotype to the next generation is proportional to its quality. Additionally, during the action of an elitist genetic algorithm, a pre-established number of the best genotypes (referred to as ‘elites’) is passed to the next generation without any modifications. After meeting the desired termination conditions the algorithm stops.

In this study we used Python 3 library ‘geneticalgorithm’ (version 1.0.1) as a implementation of genetic algorithms, simultaneously applying the default setup for the genetic algorithm: population size was 100, no boundaries were set for number of iterations, probability of mutation was 0.1, probability of crossing-over was 0.5, portion of members from previous generation passed to the next generation was 0.3, number of elites in each generation was 1. To solve the system of ordinary differential equations we used Python 3 library ‘scipy’ (version 1.5.2) with method ‘odeint’ from module ‘integrate’ exploiting ‘lsoda’ algorithm with relative error tolerances \( 10^{-6} \). The objective function for the genetic algorithm was defined by following equation:

\[
f(x) = \sum_t ((x_{m,t} - x_{e,t})^2)
\]  

where:

- \( x_{m,t} \) – value determined at moment in time ‘\( t \)’ obtained by solving the set of differential equations
- \( x_{e,t} \) – experimental value at moment in time ‘\( t \)’
- \( t \) – time.

The values of parameters were bound to certain ranges. At the start, regions for specific parameters were the same for each catalyst:

- \( k_7 \) – min: 500; max: 600000
- \( k_8 \) – min: 0; max: 5
- \( X \) – min: 0; max: 50

This allowed us to obtain approximate values for each parameter and then the boundaries for their values were narrowed (Table 1). For each catalyst, the algorithm was run five times and the results differed slightly in values of parameters and objective function due to the stochastic nature of the algorithm. Each time for the best result (in terms of value of objective function) was selected.

**RESULTS AND DISCUSSION**

Concentrations of Bromocresol Green divided by respective concentrations at the start of reaction are shown on Figure 3. For most reactions the initial current was about 6.6 mA. After the start of the reaction, the current momentarily decreased and then it returned to near initial value and remained almost constant for most reactions.

The efficiencies of degradation of Bromocresol Green in the electro-Fenton process with different catalysts after 110 minutes may be easily calculated based on normalized concentrations. A comparison of the study catalysts is presented in Figure 4.
Kinetic model study
The genetic algorithm converged each time it was run with no problems. Figure 5 presents a typical convergence plot for the elitist genetic algorithm (i.e. the value of objective function is non-increasing).

Parameters of the adopted model for each investigated catalyst were fitted by minimizing the difference between the experimental data and the numerical solution of the system of differential equations. Initial current of 6.6 mA value is taken as

Table 1 | The detailed and final boundaries for each parameter

| Catalyst | $k_7$ [M$^{-1}$·min$^{-1}$] | $k_8$ [min$^{-1}$] | $X$ [-] |
|----------|-----------------|-----------------|--------|
|          | min. | max. | min. | max. | min. | max. |
| Mn$^{2+}$ | 30,000 | 50,000 | 0 | $10^{-13}$ | 0 | 10 |
| Co$^{2+}$ | 580,000 | 610,000 | 0 | $10^{-14}$ | 0 | 10 |
| Ni$^{2+}$ | 350,000 | 370,000 | 0 | $10^{-13}$ | 0 | 10 |
| Ce$^{3+}$ | 500 | 5,000 | 0 | $10^{-15}$ | 0 | 10 |
| Fe$^{2+}$ | 350,000 | 370,000 | 0 | $10^{-18}$ | 0 | 30 |

Figure 3 | Plot of concentrations of Bromocresol Green divided by initial concentrations for reactions with different catalysts.

Figure 4 | Comparison of experimental degradation efficiency for five different catalysts.
current of cathodic generation of H$_2$O$_2$. It is the only process that can occur on this electrode at beginning of the reaction. Due to the continuous flow of oxygen through the reaction mixture, the rate of the generation of hydrogen peroxide at the cathode is assumed to be constant during the whole process. The value of this rate determined under such conditions is in qualitative agreement with value found previously at pH = 3.0 by Qiu et al. (2015) (4.27 · 10$^{-8}$ Ms$^{-1}$ at pH = 2.5 in this study versus 5.9 · 10$^{-9}$ Ms$^{-1}$ at pH = 3.0). For reactions involving Co$^{2+}$, Ce$^{3+}$, Ni$^{2+}$ and Mn$^{2+}$ cations it was found that the mean number of hydroxyl radicals needed to destroy one molecule of Bromocresol Green is much lesser than the value of that same parameter for reaction with Fe$^{2+}$. A summary of fitted values of parameters of the kinetic model, as well as the objective function values for the investigated catalysts is shown in Table 2.

Plots of experimental data with comparison with data simulated numerically applying the adopted kinetic model and using values of parameters determined by the genetic algorithm are presented in Figure 6.

Taking exactly the same initial concentration of Bromocresol Green (3·10$^{-5}$ mol/L) across reactions with different catalysts, we simulated the efficiencies of degradation for each used catalyst. The concentration of catalysts used in numerical simulations was 1.5·10$^{-4}$ mol/L. The results are presented in Figure 7.

Despite the simplified nature of the adopted kinetic model results obtained by numerical solution of the system of model differential equations are overall in very good agreement with experimental data, as presented in Figure 6. Mean number of hydroxyl radicals OH$^·$ needed to destroy one molecule of Bromocresol Green is determined to be in the range 6.30–8.05 for catalysts: Co$^{2+}$, Ce$^{3+}$, Ni$^{2+}$ and Mn$^{2+}$ and 18.99 (≈19) for Fe$^{2+}$ catalyst. The molecule of Bromocresol Green has three benzene rings and four atoms of bromine. Thus the found values of X parameter look reasonable. It seems that Fe$^{2+}$ cations in some way protect the molecule of Bromocresol Green from destruction by hydroxyl radicals in comparison with other studied catalysts because of the much larger value of the X parameter. Moreover Figure 6 shows that the model fits various experimental data across different catalysts. For cations Fe$^{2+}$, Ce$^{3+}$ and Mn$^{2+}$ the fitness is good over the whole range of time. For Co$^{2+}$ and Ni$^{2+}$ catalysts, the kinetic model best fits experimental data at the beginning and the end of the reaction.

| Catalyst | k$_7$ [M$^{-1}$·min$^{-1}$] | k$_8$ [min$^{-1}$] | X | Objective function |
|----------|---------------------------|----------------|---|-------------------|
| Ni$^{2+}$ | 358,779 | 4.778·10$^{-14}$ | 7.30 | 1.229·10$^{-10}$ |
| Mn$^{2+}$ | 40,917 | 8.691·10$^{-14}$ | 8.05 | 1.548·10$^{-11}$ |
| Co$^{2+}$ | 593,410 | 4.415·10$^{-15}$ | 6.31 | 7.124·10$^{-11}$ |
| Fe$^{2+}$ | 358,778 | 5.050·10$^{-19}$ | 18.99 | 9.287·10$^{-12}$ |
| Ce$^{3+}$ | 2,925 | 7.811·10$^{-16}$ | 7.69 | 1.598·10$^{-11}$ |
Figure 6 | Comparison of experimental and kinetic model data for each catalyst.

Figure 7 | Comparison of simulated degradation efficiency for five different catalysts at initial concentration of dye $3 \times 10^{-5}$ mol/L and catalyst concentration $1.5 \times 10^{-4}$ mol/L.
This led to a conclusion that electro-Fenton process with cations Co\textsuperscript{2+} and Ni\textsuperscript{2+} as catalysts may have more complicated mechanisms in comparison with cases of remaining cations. It should be emphasized that the genetic algorithm proved to be capable of efficient fitting of the model to the experimental data.

It was shown that all alternative catalysts used in this study improved the performance of the electro-Fenton process in comparison to the Fe\textsuperscript{2+} catalyst (Figure 4). The model study additionally supports this conclusion (Figure 7). Both model and experimental data showed that the best enhancement takes place when using Co\textsuperscript{2+} cations as the catalyst. Cations Ni\textsuperscript{2+}, Ce\textsuperscript{3+} and Mn\textsuperscript{2+} gave approximately the same degradation efficiency for Bromocresol Green. Previously, George et al. (2014) showed that Ni\textsuperscript{2+} and Mn\textsuperscript{2+} cations did not improve the performance of the electro-Fenton process during salicylic acid degradation, while for Metanil Yellow Matyszczak et al. (2020a) observed an increase in efficiency only for Ni\textsuperscript{2+} and Co\textsuperscript{2+} cations in comparison to Fe\textsuperscript{2+} cations (amongst the same applied catalysts as in this study). Bromocresol Green, salicylic acid, and Metanil Yellow represent three distinct types of organic molecules – triarylmethane dye, aromatic hydrocarboxylic acid, and azo dye, respectively. It seems that the interaction of the catalyst’s cation with pollutant compounds may be different across different pollutant molecules and is crucial for the overall efficiency of the electro-Fenton process. A catalyst that is good for breaking down one pollutant does not need to be effective for another pollutant.

CONCLUSIONS

In the removal of Bromocresol Green from aqueous solution by the electro-Fenton process it is possible to enhance the performance of whole process by substituting Fe\textsuperscript{2+} catalyst cations with Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Ce\textsuperscript{3+} and Mn\textsuperscript{2+} cations. It was found that Co\textsuperscript{2+} catalyst cations are the best to increase the performance of degradation of Bromocresol Green in the electro-Fenton process. Both experimental and model results confirmed this finding.

The adopted kinetic model is in very good agreement with the experimental model and it proved its utility for triarylmethane dye. Moreover, the genetic algorithm turned out to be efficient in fitting the multidimensional kinetic model to the experimental data. Mathematical modeling revealed that Fe\textsuperscript{2+} cations protected the molecule of Bromocresol Green from being broken down by hydroxyl radicals (greater value of X parameter) in contrast to other investigated catalysts. Furthermore, comparison of model and experimental data for five different catalysts suggested the existence of differences in interactions of cations with dye molecules during the electro-Fenton process.

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DECLARATIONS OF INTEREST

None.

COMPETING INTERESTS

Authors have no competing interests to declare.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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