Usage of green synthesized nZVI for degradation of three different dye molecules

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Abstract The aim of this study was to optimize decolourization of synthetic solution containing dye molecule, using nano zero valent iron, synthesized by an oak leaves extract (OAK-nZVI), in Fenton process. Same process conditions were applied on three structurally different dye molecules: azo, antraquinone and triphenylmethane dye. The study included process optimization of dye solution decolourization, wherein the optimal conditions were determined (concentration of OAK-nZVI, the dose of hydrogen peroxide, pH and initial dye concentration) at which the significant percentage of decolourization were achieved. Optimization was performed by the response surface methodology (RSM). RSM enabled identification of the key variables and their impact on each process. Further testing included characterization of the obtained effluents, indicating that there is a degradation of the whole dye molecules. All results confirmed that OAK-nZVI is an efficient catalyst and the source of iron in the Fenton process, and that these particles are inexpensive and environmentally friendly material for this type of treatment.

Keywords: nZVI, green synthesis, dyes, Fenton process

1. Introduction

Dyes are one of the most important sources of water pollution. Great percent of dyes is discharged from manufacturing as well as from dying process (Sievers, 2011, Carneiro *et al*., 2007). Advanced oxidation processes (AOPs) are the most attractive technology for waste effluents containing dyes, because it can quickly oxidize a wide variety of contaminants. Fenton process is particularly suitable for the degradation of wide range of dye molecules. Its main characteristics are that it is relatively easy to perform and it is inexpensive in comparison with other AOPs processes. Fenton process is based on the addition of Fenton's reagent which requires the addition of iron ions and hydrogen peroxide, wherein the iron acts as a catalyst in the production of hydroxyl radicals. Fenton's reagent is generally very efficient for the oxidation of different pollutants in wastewater.

In recent years, Fenton system with nano particles of zero-valent iron (nZVI) is increasingly used in degradation processes for dyes, due to nZVI low cost, low impact on the environment, ease of use and due to the fact that they do not burden the waste effluent with high concentrations of iron (Choi and Lee, 2012, Fu *et al*., 2010). In the last few years, more environmentally preferable mode of nZVI production has been developed. This approach is based on the use of natural products (usually the plant leaves) that have high content of polyphenol components and large natural antioxidant capacity (Martins *et al*., 2013, Chrysochoou *et al*., 2012).

The aim of this study was to evaluate and optimize the dye decolourization process of synthetic dye solutions of Reactive Red 120 – RR120 (azo dye), Reactive Blue 4 – RB4 (anthraquinone dye) and Brilliant Blue R – BBR (triphenylmethane dye) using nano zero valent iron synthesized with the oak leaf extract (OAK-nZVI) in Fenton process. Optimization is performed by the response surface methodology, RSM. This is a simple and widely used method of examining the relationship between the independent process parameters and different characteristics of the obtained product.

Also investigation included the characterization of the obtained effluents in order to assess the effectiveness of the applied, and the possibility of further treatment.

2. Materials and methods

All chemicals used in the experiment were the purity of *pro analisy* and were further used without additional purification. OAK-nZVI was synthetized according to Machado *et al*., 2013.

2.1. Optimization of operating conditions for dye decolourization process

In order to reduce the number of analysis, response surface methodology, RSM, was applied as an instrument for testing the decolourization efficacy of synthetic dye solutions with the use of OAK-nZVI as a source of iron in the Fenton process. Minitab 15 software was used for generating three factors with Box-Behnken model. By using this model the number of experiments is optimized (in this case the number of necessary experiments on the Jar Test apparatus is reduced to 16) and further information are obtained, stating the error of the procedure since the replicates are performed in the central point. Tests were conducted, for each dye, in a 4 series of experiments on the Jar Test apparatus (FC6S Velp scientific, Italy). Dye solutions, 0.25 l of volume, were mixed in one hour time intervals, at 150 rpm. Upon completion of mixing solutions were filtered through a membrane filter. After filtration absorbance were measured (A) at the wavelengths for the RR120 λ_{max}= 512 nm, for RB4 λ_{max}= 595 nm and for BBR λ_{max}= 551 nm. Determination of the absorption maximum (λ_{max}), recording of the dye solution spectrum as well as monitoring the change in the absorbance during the experiments was carried out using a UV-VIS spectrophotometer UV-1800 PG Instruments Ltd T80 + UV/VIS, Model: UV-1800 (Shimadzu, Japan). The series of experiments included testing of the following operating parameters on the decolourization efficiency: OAK-nZVI concentration, H_2O_2 concentration, pH value, and the effect of the initial dye concentration in the solution. Measurement of pH value was performed using the pH-meter inoLabpH/ION 735 (WTW GmbH, Germany).

2.2. Characterization of the obtained effluents after treatment

Characterization included the determination of the mineralization degree of obtained effluents, by determining the chemical oxygen demand, using the standard method ISO 6060: 1994. The potential toxicity of the effluents after the treatment was examined by inhibitory effect on the light emission of luminescent bacteria *Vibrio fischeri* (LANGE LUMI Stherm, LUMIStox, Germany) according to Method ISO 11348-1:2007.

3. Results and discussion

3.1. Optimization of decolourization of dye solutions

Optimization of the dye decolourization process of RR120, RB4 and BBR was performed in blocks at different initial dye concentrations, different pH values and different concentrations of hydrogen-peroxide and OAK-nZVI. By applying the RSM procedure it was possible to simultaneously evaluate the effects of these parameters on the decolourization efficiency.

The initial dye concentrations were 50 and 300 mg/l. Initial concentrations of the OAK-nZVI was 0.75 and 42.5 mg/l (expressed as Fe^0 content), a concentration of hydrogen-peroxide of 1 and 10 mM. Investigation of the effect pH of the solution was carried out at values of 2 and 8. If it is taken into consideration that it is not possible to draw a graph to display a response to all four of the studied variables, each figure presents the results which shows a response (decolourization efficiency) in comparison to two variables. To show the response surface changes between two variables, the third variable has been fixed. Each graph is drawn to all fixed tested levels to demonstrate whether a variable value that is not visible on the axis, has an impact on the response surface (Figure 1). In addition, to determine whether and how the examined parameters interact, Pareto graphs of variables effects that influence decolourization are designed (Figure 2). Pareto graphs represent the type of graphics that contain bars and lines, where individual values are presented in descending order with the help of the bars, and the cumulative value of effects is represented by the line. The purpose of the Pareto graphics is to highlight the most important factors, if there are multiple factors present. According to the obtained graphs pH value is a parameter which had the largest impact on the whole process. The results indicate that Fenton process with the use of nanomaterials, similar to the conventional Fenton processes, shows the highest efficiency for the lower pH value, as well as the downward trend in the decolourization efficiency with increasing pH values (Alaton and Teksoy, 2007). The acidity of the nanomaterial suspension added contributes to pH reduction even for two pH units so that the correction of the pH value is minimal, and even can be omitted. This is a very important conclusion regarding the economic viability of the process. OAK-nZVI concentration has also a great influence on decolourization, as increase in iron ions content influenced greater production of HO• radicals (Daud and Hameed, 2010). In terms of testing the concentration of hydrogen peroxide solutions, results differed between dyes. Namely, regarding Pareto diagrams, compared to other variables H_2O_2 had the biggest influence during the decolourization process of BBR dye, followed by RR120 and RB4. This sequence is the same regarding initial dye concentration. Low dosage of hydrogen-peroxide can be insufficient to effectively decolorize the

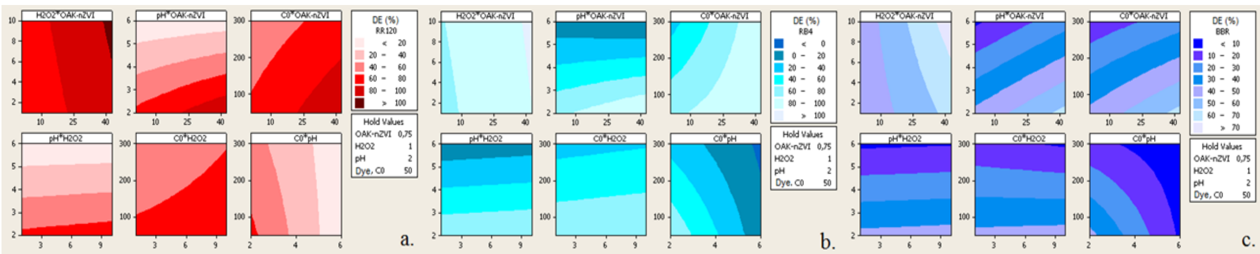

Figure 1. Contour plots of examined parameters onto decolourization efficiency of dye solution a) RR120, b) RB4 and c) BBR

solution, and at higher concentrations the molecules of H_2O_2 exerts effects "scavenging" towards HO• and lead to the formation of less reactive species, such as HO_2• (Hassan and Hameed, 2011). It is noted that with the increase of dye concentration there is decolourization decrease. Namely, the increase in the dye concentration implies an increase in the number of dye molecules while the number of OH• radicals stays the same which causes this effect. Overall, interaction of different parameters is much more pronounced regarding BBR, which indicates that this process is more sensitive and more complex with respect to the RB4 and RR120 where only few variables determine the efficiency of the whole process. The analysis of all RSM obtained results indicated on the optimal conditions, at which the highest decolourization efficiences were achieved (Table 1). Under these conditions the efficiency for RR120 and RB4 was ~ 99 %, and for BBR ~ 75%. For each dye a set of 16 experiments was performed and spectra recorded. The spectra analysis of each experiment lead to the conclusion that when process conditions are approaching the optimum it leads not only to the decrease of the selected maximum absorbance in the visible region, but also in the UV region. This indicates that not only the destruction of chromophore group occurs, but also the degradation of the aromatic structures which dye molecule is predominantly made of. Absorbance decrease is evident at wavelengths of 254, 256 and 310 nm corresponding to the absorption peaks of the components that include a benzene ring, aromatic and dichlorotriazine groups and naphthalene compounds, respectively (Chang *et al*., 2009).

Table 1. Optimal conditions for effective dye decolourization

Parameter	RR120	RB4	BBR
OAK-nZVI (mg/l)	42.5	42.5	42.5
H_2O_2 (mM)	9.9	2.3	10
pH	2.07	2	2
Initial dye concentration (mg/l)	50	50	50

3.2. Mineralization of treated effluents

The mineralization degree of the treated effluent before and after the Fenton process with OAK-nZVI is determined by the measurement of the chemical oxygen demand (COD). Removal of COD depends on the complete mineralization of color. This parameter was measured in the initial solutions of the tested dyes and the effluents after the Fenton process applied at optimal conditions. The values of the examined parameters are shown in Table 2.

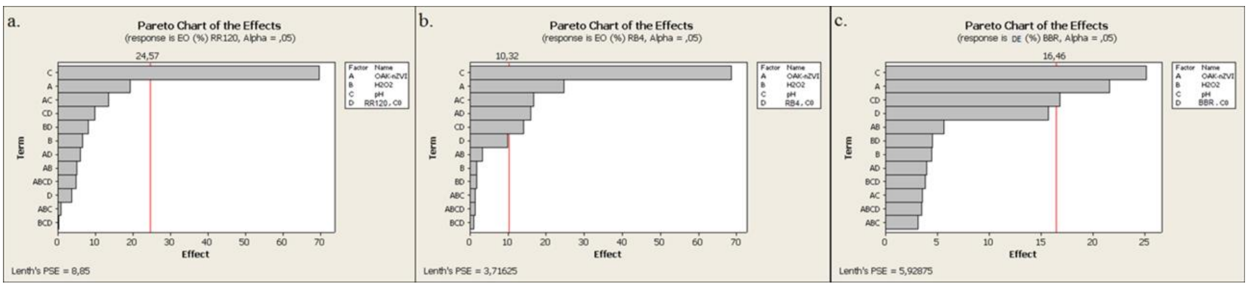

Figure 2. Interaction of two or more examined parameters in relation to decolourization efficiency for dye solution a) RR120, b) RB4 and c) BBR

Table 2. COD values and mineralization degree of tested effluents

Dye	$COD_{before\ treatment}$	$COD_{after\ treatment}$	Mineralization
	mg/l		%
RR120	210.8	163.5	22.4
RB4	271.2	103.4	61.9
BBR	456.4	181.9	60.2

Table 3. The toxicity results of the effluents after treatment tested on organisms *Vibrio fischeri*

Effluent after treatment	EC	Concentration (mg/l)	GL
RR120		184	3
RB4	50	61.0	9
BBR		6.24	64

During the Fenton process, decolorizing of the solution is caused by the destruction of the chromophore group, while the COD decrease is dependent on the level of mineralization of the entire molecule. Differences in the degree of mineralization of tested dyes are the result of differences in molecular weights, the complexity of the structure of the molecules. Mineralization degree is descending in order RR4> BBR> RR120 which is in a good correlation with corresponding molecular weights 637, 825 and 1470 g/mol respectively. Decolourization rapidly followed by a slower COD decrease is an indication of formation of a stable intermediate in the reaction medium, which contributes to a higher value of this parameter (Kusvuran *et al*., 2004). To increase efficiency in terms of mineralization it is necessary to extend the treatment time and Fenton reagents concentration (Arslan-Alaton *et al*., 2008).

3.3. Toxicity test on organisms Vibrio fischeri

Further characterization of the obtained effluents after treatment, under optimal conditions, involved the assessment of their toxicity. Also, blank probe was tested (it contained all chemical components of the investigated process except dye molecules). Toxicity is measured based on a bioluminescence inhibition test of marine gram-with obtained spectra analysis (Zheng *et al*, 2016).

3. Conclusion

Generally, all the results show that the OAK-nZVI is efficient catalyst and a source of iron in the Fenton process for decolourization of synthetic solutions for different dye

negative bacteria *Vibrio fischeri* (Parvez *et al*., 2009). Blank probe showed that the reaction mixture (especially regarding nanomaterial added) is not toxic to the used organisms. This result is of great importance since the nanomaterial is used in suspension form right after its synthesis. In this way it is proved that residual leaf extract, also possibly subjected to Fenton treatment, does not constitute a problem regarding potential contribution in overall effluent toxicity. In order to simplify the data presentation, from the results obtained GL value was calculated for the effluents after treatment. This value represents the dilution level at which the investigated effluent causes less than 20% inhibition of the test organisms. On the basis of the GL value effluents are divided into three categories (i) a highly toxic samples, GL> 100; (ii) moderately toxic ≥10 to 100; and (iii) low toxicity, GL <10 (Wang *et al*., 2002). Toxicity of obtained effluents increased in order RR120< RB4< BBR. End effluents of azo and antraquinone dye is considered low toxic while the end effluent of triphenylmethane dye is moderately toxic and needs extended treatment. Half maximal effective concentrations (EC50) show also great difference between obtained effluents as EC50 for BBR is 30 times lower that EC50 for RR120. These results can be explained with higher toxicity of degradation products between effluents, and also with toxicity decrease with the disappearance of aromatics which is in a good correlation

groups. Applied RSM methodology, which was efficient in process optimization, indicated the need for quite low concentrations of nanomaterials and hydrogen-peroxide to achieve satisfactory results in terms of decolourization efficiency. Further characterization of the resulting effluents proved that there is no only the chromophore group destruction but entire dye molecule degradation with the formation of simpler fragments. Sum of results pointed out that OAK-nZVI particles are inexpensive and environmentally friendly material for this type of treatment.

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