Sewage sludge biochar-supported nano zerovalent iron (nZVI) as an effective catalyst in Fenton process of decolorization

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Abstract
Purpose: The main focus of this study is exploring possibility of beneficially using solid wastes in heterogeneous Fenton treatment of coloured wastewaters. Such application is an alternative to landfill disposal and promotes industrial symbiosis. **Methods:** The experiments included: nano zero valent iron/biochar (nZVI-BC) synthesis and characterization, *Definitive Screening Design* (DSD) model evaluation and process optimisation and effluent characterization under optimal conditions. **Results:** In order to characterize the system under the influence of different process conditions, DSD statistical analysis was applied. pH correction was not performed because the process took place at pH=3.2. The statistical model within the Fenton process proposes a high dye removal efficiency of 95.02% under the following optimal conditions: [RB4]=50 mg/L, [nZVI]=200 mg/L, [H_2O_2] =10 mM. **Conclusions:** nZVI-BC is an efficient catalyst and source of iron in the Fenton process. The applied DSD methodology indicated that very low concentrations of the obtained nano-biochar and hydrogen peroxide were required to achieve satisfactory results in terms of decolourization efficiency. The results are promising from the aspect of overcoming the limiting factors of the homogeneous Fenton process, such as the need to maintain the operating pH value within the narrow range 2.8 - 3.5 in order to achieve maximum catalytic activity of iron as a catalyst and prevent its deposition as hydroxide. Usage of sewage sludge for biochar production for reuse in Fenton process aims to reduce costs, while providing a solution for waste management. It also contributes to the application of the circular economy concept in practice.

Keywords: wastewater sludge, nZVI-biochar, Fenton catalyst, dye.

1. Introduction

With the accelerated industrialization, increased sewage sludge (SS) needs to be treated properly. The conversion of sludge into harmless biochar material with dual utilization value of adsorption and catalysis by pyrolysis is in line with the concept of sustainable development. However, the reaction mechanisms of pristine sludge biochar and its composites in adsorption and Fenton-like advanced oxidation processes (AOPs) are very closely related to its adsorption performance and catalytic efficiency. The disposal of SS has emerged as one of the most acute issues facing society today. Fortunately, thermal processing offers an efficient and environmentally friendly way to recover sludge by transforming sludge waste into functional biochar. Pyrolysis is a technique that treats sludge at elevated temperatures under anoxic or inert atmosphere. This technology not only removes hazardous compounds from sludge, but also converts organic matters into bio-oil and biogas that can be used as fuel, and the residual solid remains (biochar) can be utilized as an adsorbent or catalytic material [1]. Recent research has revealed the potential of biochar in hydroxyl radical based AOPs besides its use as an adsorbent in the water treatment industry. Biochar with its enormous surface area, porous structure, active functional groups and conduct nature owe its potential in AOPs to activate hydrogen peroxide and support metals and metal oxide composites [2, 3]. Transition metals have been widely applied to activate oxidants for the degradation of organic compounds. Among these transition metals, iron-based catalysts have received widespread attention due to their advantages of high efficiency, non-toxicity and environmentally friendly characteristics [4, 5]. Nanoscale zero valent iron (nZVI) as a potential alternative source of Fe has been successfully used to activate peroxide for the degradation of various pollutants. However, due to its high surface energy and strong magnetic interaction, nZVI tends to aggregate into forming microscale particles, resulting in diminished reactivity. Considering its large surface area, porous structure and cost-effectiveness, BC has been used as a supporting material to stabilize nZVI and enhance its catalytic ability [6]. The usage of plant leaves to generate nanoparticles is based on the reduction of ferric or ferrous iron to zero valent iron (Fe^0) using biologically-active substances from plant extracts. In addition to the reduction of Fe^{2+}/ Fe^{3+}, polyphenols, flavonoids and other reducing substances effectively prevent nanoparticles from agglomeration, and cap the metal protecting it from oxidation [7, 8]. One of high demanding industries in terms of water and chemical usage is the textile industry. Only in wet process of cotton dying more than 100 L of water is spent per kg of textile. Also, unfixed dyes are a known problem in textile effluents, whose chemical structures widely differentiate [9]. Worldwide legislation is forcing industries to treat wastewater to the level without any negative influence on the environment and aquatic organisms. Among biological and physicochemical treatments, Fenton process stands out between advanced oxidation processes as efficient in dye degradation Literature research points out to a few efficiency determining factors, such as pH value, initial oxidant concentration, catalyst concentration, dye concentration, reaction time and temperature [9]. A powerful tool for the system characterization under different conditions and further process optimization, design of experiment (DOE), takes into account the variable interactions, while the number of experiments is limited. To overcome the problem of a limited number of operating variables, caused by the fact that the number of experiments increases quickly when more variables are included in the experimental design, authors [7, 10, 11] suggest it is necessary to employ statistical screening methods that will identify the significant variables and eliminate the irrelevant ones. Accordingly, a new generation of experimental design, Definitive Screening Design (DSD) was introduced in 2011 by Jones and Nachtsheim [12]. The principle of the DSD statistical method is based on the application of a numerical algorithm that maximizes the matrix determinant of the main effect model. The analysis conceived in this way is used to determine significant factors and to predict their two-factor interactions, but also to estimate the coefficient of the equation model that describes the total number of performed experiments. The main focus of this study is on sewage sludge based biochar supported with "green" syntesized nZVI that can be used beneficially in a heterogeneous Fenton treatment of colored wastewaters. Such application is an alternative to landfill disposal and promotes industrial symbiosis. Also, cost reduction of handling solid waste is reinforced and further value addition is boosted. Synthetic anthraquinone dye solution (Reactive Blue 4 - RB 4) was effectively treated by a promising technology based on degradation reaction catalysed by "green" nano zero valent iron supported biochar (nZVI-BC) in this work. The experiments included 3 phases: (1) nZVI-BC synthesis, (2) *definitive screening design* (DSD) model evaluation and process optimisation and (3) effluent characterization under optimal conditions.

2. Materials and methods

2.1. Sludge sampling and treatment

The sewage sludge originated from the wastewater treatment plant in a small settlement, 3.500 ES. The procedure of biochar preparation was performed according to the work of Chen *et al.* [13] Sludge was delivered to the laboratory and dried in an oven at 105°C and then combusted in furnace under inert atmosphere (Nabertherm, Germany) at 400°C. Biochar yield after combustion was 57.53%.

2.2. Materials and chemicals

All sample analyzes were carried out directly, without pretreatment, and the chemicals used during the laboratory tests were of analytical grade. Hydrogen peroxide (30%), NaOH (>98.8%), $FeCl_3$ was obtained from Sigma Aldrich, while cc H_2SO_4 (>96%) was produced by J.T. Baker. Deionized water was used for the preparation of all working solutions within the desired concentrations. Commercial anthraquinone dye reactive Blue 4 (RB4) (CAS no. 13324-20-4, molecular weight, MW= 697.43 g/mol), was obtained from Sigma-Aldrich. Fig. 1 presents the structure of the dye investigated.

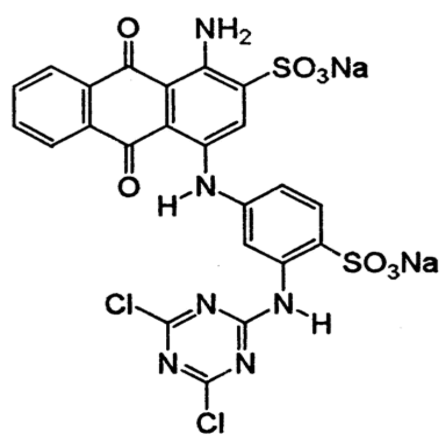

Fig 1 Structure of RB4 dye

2.3. Synthesis of nZVI-BC catalyst

’’Green’’ synthesis method of nZVI particles was conducted using fallen leaves from oak trees (Quercus Peatrea) growing in the National Park of Fruska Gora, in Vojvodina, Serbia. The leaves were milled by using a kitchen chopper, then sieved by using a 2 mm sieve and pre-dried at 50 °C in an oven for 48 h. The amount of 3.7 g of the oak leaves was measured and carried to a 300 mL Erlenmeyer flask, to which 100 mL of water was added. Then the flask was put in a shaker bath at 80 °C for 20 min. The extraction procedure was given according to Machado et al. (2013). Further preparation of nZVI-BC was done according to Mortazavian et al. [14]. The oak leaf extract was mixed with 0.1 M Fe (III) and biochar in a ratio of 3: 1: 1. The material thus prepared was stirred for 60 minutes at ambient temperature in an ultrasonic bath. The material was stored in the refrigerator until further use.

2.4. Characterization of nanomaterial

The morphology of synthesized nanomaterial was examined by using scanning electron microscopy (SEM) (TM3030 (Hitachi High-Technologies, S-4700 Type II Japan)) followed with energy-dispersive X-ray spectroscopy (EDS). EDS mapped the present elements on the nanomaterial surface at 15 kV acceleration (Brucker Quantax 70 X-ray detector system, Brucker Nano, GmbH Germany).

2.5. Physico-chemical analysis of RB 4 before and after treatment

pH value, conductivity and temperature were measured using SenTix®21 electrode. Chemical Oxygen Demand (COD) was determined from potassium dichromate volumetric method - SRPS ISO 6060: 1994 [15]. Determination of biological oxygen demand (BOD) after 5 days at 20 C was performed with manometric method - H1.002, by using the instrument Velp Scientifica Italia, Lowibond and WTW. Determination of total organic carbon (TOC) inwaterwas performed by LiquiTOC II (Elementar, Germany), with the method SRPS ISO 8245:2007 [16]. The FTIR spectra of RB4 obtained with a Fourier transform infrared spectra Thermo-Nicolet Nexus 670. The spectrum was recorded in the range of 4000-6000 cm^{-1} in diffuse reflection mode, at a resolution of 4 cm^{-1}.

2.6. Definitive screening design

The efficiency of the applied treatment depends on several process parameters, which requires optimization of the entire process. To overcome the problem with a limited number of operational variables (caused by the fact that the number of experiments increases sharply when more variables are included in the experimental design) it is necessary to use statistical screening methods that will identify significant variables and eliminate irrelevant ones. For this purpose, it is possible to use a set of empirical statistical methods based on the application of quantitative data of appropriately designed experiments in order to determine the optimal conditions. Accordingly, a new generation of experimental design, Definitive Screening Design (DSD) was introduced in 2011 by Jones and Nachtsheim. The principle of the DSD statistical method is based on the application of a numerical algorithm that maximizes the matrix determinant of the main effect model. The analysis conceived in this way is used to determine significant factors and to predict their two-factor interactions, but also to estimate the coefficient of the equation model that describes the total number of performed experiments. This statistical method enables the application of a significantly reduced number of performed experiments with maximum precision. The basic scheme of the DSD experiment with three numerical factors consists of 13 experiments, which with replication and two additional central points makes a total of 28 experiments. The tests were conducted by a series of experiments on JAR test apparatus (FC6S Velp scientific, Italy). Dye solutions with a volume of 0.25 L, were mixed in laboratory beakers at intervals of one hour, at 150 rpm. After mixing, the solutions were filtered through a membrane filter. After filtration, the absorbance (A) was measured at the wavelength for RB4 λ_{max} = 595 nm. Determination of absorption maxima (λ_{max}) by recording the spectrum of the dye solution, as well as monitoring the change in absorbance during the experiments was performed using a UV-VIS spectrophotometer. The series of experiments included the examination of the following operational conditions on the efficiency of color degradation: nZVI concentrations, hydrogen peroxide concentrations, pH, as well as the influence of the initial dye concentration in solutions.
Decolorization efficiency of aqueous solution was obtained based on the following equation (1):

$$\text{Removal efficiency } [\%] = ((A_0-A_t)/A_0) * 100\% \quad (1)$$

where A_0 is initial absorbance of aqueous solution before Fenton treatment, whereas A represents absorbance of aqueous solution after treatment.

3. Results and discussion

3.1. Characterization of nZVI-BC catalyst

The morphologies of BC and nZVI-BC were analyzed by SEM and are presented in Fig 2. BC was characterized by a smooth surface and porous structure. There are many tiny pores in the interior and surface of the original biochar, which provide sites for the adsorption of nZVI particles. The particle size of BC is differentiated ranging from 600 nm to 2.15 µm (Fig 2a). In the absence of BC, the "green" synthesized nZVI particles were spherical and sized from 30 to 825 nm (published in [7]). When introduced to BC, the nZVI particles were randomly located and roughened the BC surface. nZVI-NBC particles are irregular lumps. Particle size ranged from 68 to 521 nm. Initial Fe^{3+} concentration, initial substrate concentration, temperature, pH and stirring rate of reaction medium are depending factor for control nanoparticle size and size distributions according to Turabik and Simsek [17].They established that Fe^{3+} concentration lower than the stoichiometric requirement contributes to the larger nanoparticles synthesis. Similar effect had the temperature increase, as well as increase of stirring rate over 400 rpm. The phenolic content of plant extract is also a significant factor for nZVI synthesis. Polyphenols are extremely important components of plants, because of their antioxidant capacity, antimicrobial, antiviral, and anti-inflammatory properties. Therefore, to fully understand what defines the size of green nZVIs, a more detailed study on the chemical composition of the extracts, namely the polyphenol profile, is required [18].

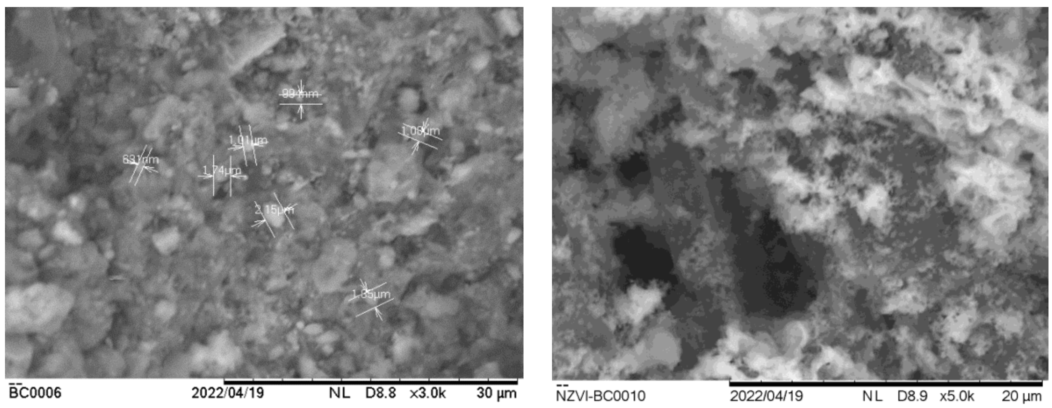

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Fig 2 SEM images of bare BC and nZVI-BC

EDS results (Table 1) shows the results of the elemental qualitative chemical analysis, which confirmed the presence of carbon, oxygen, chlorine, calcium and phosphorous atoms in addition to iron, on the surface of synthesized nanomaterial, based on the obtained intense peaks of detected atoms. The C signals originate predominantly from the biochar itself and from polyphenol groups and other C-containing molecules in the oak extract. Moreover, $FeCl_3$ utilized in the synthesis of OAK-nZVI must be accountable for the appearance of the Cl element, whereas Ca element is attributed to the oak extracts because, Ca is vital to plant growth and exists in every living plant cell. The Fe peak in the EDS spectra (figure not shown in the paper) and the uniform Fe distribution in the SEM element mapping (Fig. 2b) further verified the nZVI synthesis on BC. The phosphorus element originates from sewage sludge.

Table 1. Results of EDS analysis

Element, %	**BC**	**nZVI-BC**
C	37	28
O	29	22
Fe	4	25
Cl	-	19
P	6	2
Ca	7	2

3.2. DSD model evaluation and Fenton process optimization

In order to characterize the system under the influence of different process conditions: initial dye concentrations, initial catalyst concentrations and initial hydrogen peroxide concentrations on the decolorization efficiency of Reactive Blue 4 synthetic dye solution, DSD statistical analysis was applied. As explained in Chapter 2.6, the basic scheme of the DSD experiment with three numerical factors consists of 13 experiments, which with replication and two additional central points makes a total of 28 experiments (Table 2). The results of removal efficiencies of RB4 are shown in Table 2, where the range of decolorization efficiency of 5.03 - 92.96% was established. Achieving maximum and minimum decolorization efficiency in the Fenton process is observed a different set of process conditions, confirming the assumption that RB4 removal process itself largely depends on the applied experimental conditions. In order to select the regression model that best approximates the obtained results, JMP stepwise regression analysis was applied, which generates a large number of regression models with different number of parameters, taking into account the main factors and their two-factor interactions. From a large set of regression models, a small set of candidate models with different numbers of members was selected, all of which provide good data approximation. The final selection of the final model is based on the standard selection criteria: BIC (Bayesian Information Criterion), AIC (Akaike Information Criterion) and RMSE (Root Mean Square Error) indicators (Table 3) [19]. AIC and BIC indicators are very similar in form, but derive from different assumptions. The AIC indicator is presented as an indicator of the relative quality of statistical models for a given data set and its role is to select the model that produces the probability distribution with the smallest deviation from the true distribution. In other words, AIC evaluates the quality of an individual model in relation to all observed models, relying on good approximation and simplicity of the model. On the other hand, the role of the BIC parameter is to remove inadequate data fitting. Lower values of BIC and AIC indicators indicate a better ability to predict the regression model. RMSE represents the standard deviation of residuals (prediction errors) and provides insight into how much data is concentrated around the line of best fit [20].

Table 2. Matrix of experiment with achieved decolorization efficiencies

Sample	c(H2O2) (mM)	c(nZVI-BC) (mg/L)	c(RB4) (mg/L)	Removal efficiency (%)
1	5,5	200	150	75,77
2	5,5	5	50	18,28
3	10	102,5	50	64,64
4	1	102,5	150	39,37
5	10	5	100	21,62
6	1	200	100	73,97
7	10	200	50	90,05
8	1	5	150	14,77
9	10	200	150	85,35
10	1	5	50	15,78
11	10	5	150	20,47
12	1	200	50	77,81
13	5,5	102,5	100	52,58
14	5,5	200	150	77,9
15	5,5	5	50	14,62
16	10	102,5	50	66,12
17	1	102,5	150	39,74
18	10	5	100	17,05
19	1	200	100	72,01
20	10	200	50	92,96
21	1	5	150	6,00
22	10	200	150	88,06
23	1	5	50	5,03
24	10	5	150	19,35
25	1	200	50	69,86
26	5,5	102,5	100	50,97
27	5,5	102,5	100	47,91
28	5,5	102,5	100	53,45

Table 3. Selected regression model (all interactions included)

Descriptive factor	Value
R^2	0,986522
R^2_{adj}	0.982671
AIC	170.1597
BIC	173.2384
RMSE (Root Mean Square Error)	3.828282

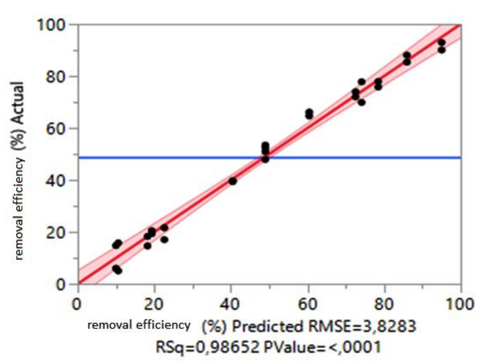
In addition to the standard selection criteria for the appropriate model, an additional technological criterion is that the models must contain a dye concentration factor, but also all other tested input parameters, which is extremely important from an engineering point of view in solving the observed problem. A summary of the descriptive factors of the adopted regression models, the results of the variance analysis test (ANOVA), as well as the estimated regression coefficients of significant main parameters and their two-factor interactions for the obtained models are shown in Tables 4 and 5. Therefore, the final model selection is based on the lowest values of BIC, AIC and RMSE indicators, respecting the simplicity of the model as an additional criterion. High values of the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adj}) are observed in all applied Fenton processes (Table 4), which implies a good approximation of the experimental data with the selected model, ie. indicates the absence of over-adaptation of the model to the data. The obtained values of descriptive factors R^2 and R^2_{adj} represent the percentage of data closest to the best fit line, and indicate the fact that 98-99% of the variance for RB4 dye removal efficiency is explained by an independent variable, while the remaining 1-2% of the total variance is not covered by the model. Based on the results of the ANOVA test, shown in Table 3, the significance of the regression model was confirmed since the value of the probability parameter Prob> F <0.0001. In addition, the validity of the selected model was confirmed by the value of the parameter that describes the insignificance of the "lack of fit" test (Prob> F> 0.05).

Table 4. Analysis of variance (ANOVA)

Source	**[a]DF**	**[b]SS**	**[c]MS**	**F parametar**
Model	6	22527,522	3754,59	256,1854
Error	21	307,771	14,66	**Prob>F**
C. Total	27	22835,292	-	**<0,0001***
Lack of Fit	6	131,06432	21,8441	1,8543
Pure Error	15	176,70627	11,7804	**Prob>F**
Total Error	21	307,7706	-	**0,1554**

[a]Number of degrees of freedom, [b]Sum of squares, [c]Variance (mean value of squares)

Additional confirmation of the ANOVA test and the significance of the model is reflected in the diagnostic diagrams (a. ratio of experimental and model-predicted decolorization efficiencies and b. Diagram of normal distribution)



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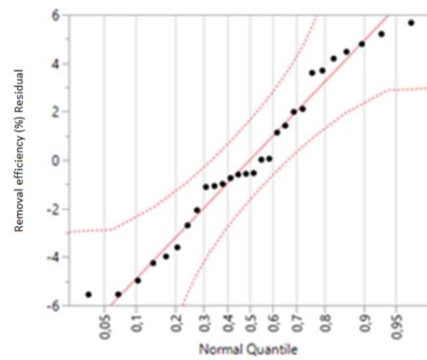

b

Fig 3 (a) Diagram of normal distribution, (b) Relationship between experimental and model-predicted decolorization efficiencies

Figure 3a shows that the residues follow the right of normal distribution and are within the confidence interval. Adequate approximation is confirmed by the diagnostic graph of real dependence, ie. experimental values in relation to the predicted values of decolorization efficiency, which are in good correlation (Figure 3b).

Based on the approximated parameter values and standard error, the factors with statistical significance shown in Table 5 (bold values) were singled out, which mostly contribute to the efficiency of RB4 removal in the Fenton process. It can be noticed that the main (linear) factors have the most significant influence on the response of the Fenton process, among which the initial concentration of RB4 dye has a slightly lower value compared to the oxidant and catalyst used.

Table 5. Statistical comparison of DSD model factors

Term	Estimate	Std Error	t ratio	Prob>|t|
Intercept	48,981786	0,723477	67,70	**<,0001***
c(H_2O_2) (mM)(1,10)	7,5665	0,85603	8,84	**<,0001***
c(nZVI-BC) (mg/L)(5,200)	32,5385	0,85603	38,01	**<,0001***
c(RB4) (mg/L)(50,150)	-2,4185	0,85603	-2,83	**0,0101***
c(H_2O_2) (mM)*c(nZVI-BC) (mg/L)	1,403	1,048418	1,34	0,1951
c(H_2O_2) (mM)*c(RB4) (mg/L)	-1,487	1,048418	-1,42	0,1708
c(nZVI-BC) (mg/L)*c(RB4) (mg/L)	-0,634	1,048418	-0,60	0,5518

It can be noticed that in Fenton treatment the parameters of catalyst concentrations are statistically significant, nZVI-BC and H_2O_2 value, while the catalyst concentration has a greater positive effect on the paint removal process.
Figure 4 shows the diagrams of the response surfaces of the examined two-factor interactions. In the first place, it is important to note that reaction medium was acidic (pH = 3.45), which can positively affect the Fenton reaction, resulting in the formation of highly reactive hydroxyl radicals [7]. It should be noted that no pH correction was performed. Comparing the effect of variation in the initial concentration of hydrogen peroxide and catalyst (Figure 4a), an increase in decolorization efficiency is observed with an increase in both factors.

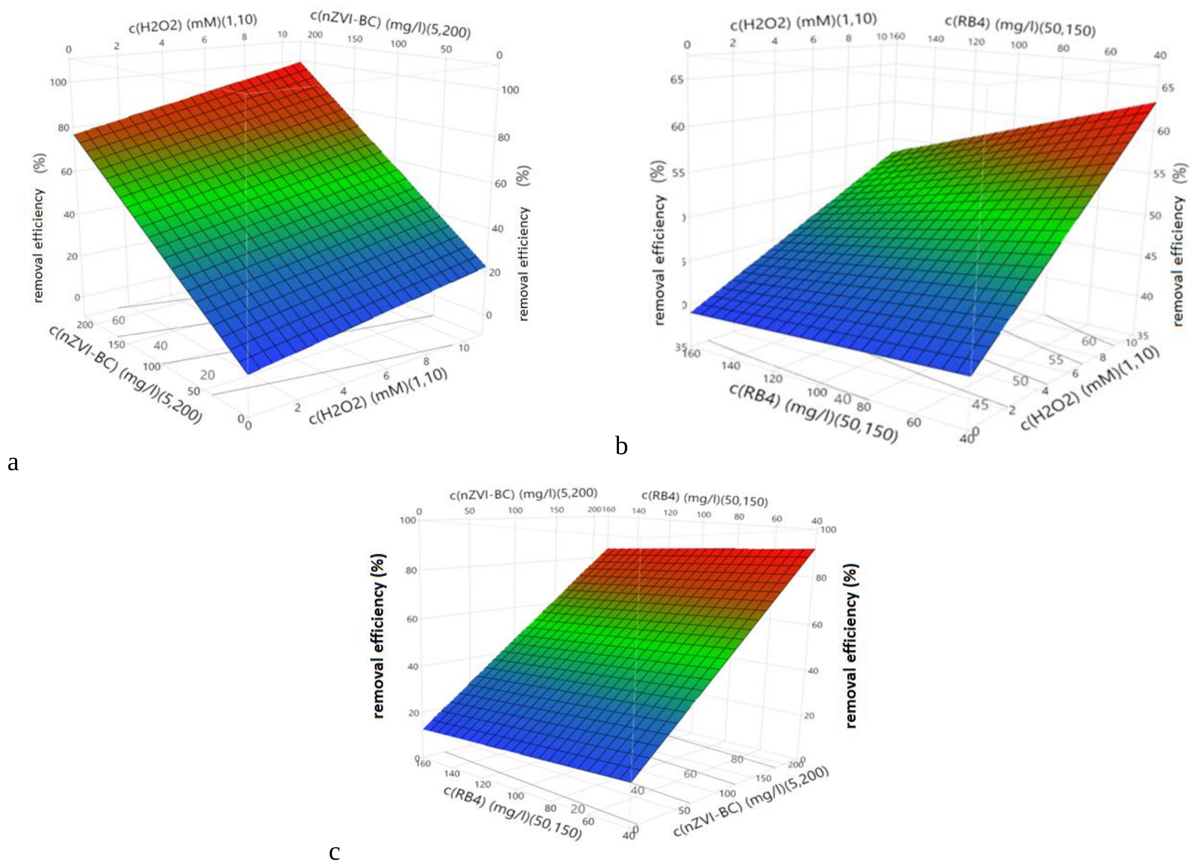

Fig 4 3D graphics of response surfaces

It is considered that the highest concentration of nZVI-BC catalysts provides sufficient active sites for hydrogen peroxide decomposition and production of desired radicals [21], as indicated by the results of tests 7 and 20 (Table 2) with achieved efficiencies of 90, 05 and 92.96%. When observing the influence of the initial concentration of hydrogen peroxide and pollutant (Figure 4b), a difference between the upper and lower tested dose of oxidant is noticeable. Namely, at 10 mM H_2O_2, a significant decolorization of the aqueous solution is achieved with a decrease in the concentration of RB4 dye. This trend of declining efficiency of the Fenton process has been observed in the

[22, 23] and this phenomenon is due to possible competitive adsorption of dye molecules on the surface of the solid catalyst, thus masking available sites for reaction with hydrogen –peroxide [24]. Figure 4c shows the influence of the initial concentration of catalyst and RB4 dye, where a significant increase in treatment efficiency is observed, which can be assisted by the development of reactions between RB4 dye molecules and nZVI-BC. However, as previous tests have shown the efficiency of RB4 dye removal by sorption (35% and 70% for 20 mg/L and 100 mg/L, respectively), it can be concluded that both processes (oxidation and sorption) can take place simultaneously, which in optimal conditions leads to high treatment efficiency. The Fenton process optimization diagram is shown in Figure 5 and gives a clear insight into how the three process parameters affect the dependent variable, i.e. RB4 dye decolorization efficiency. The statistical model within the Fenton process proposes a high dye removal efficiency of 95.02% under the following optimal conditions: dye concentration of 50 mg/L, catalyst concentration of 200 mg/L, and hydrogen peroxide concentration of 10 mM. The mean value of the obtained efficiencies is 98.48%, with a standard deviation of 0.24. The obtained results are promising from the aspect of overcoming the limiting factors of the homogeneous Fenton process, such as the need to maintain the operating pH value within the narrow range 2.8 - 3.5 in order to achieve maximum catalytic activity of iron as a catalyst and prevent its deposition as hydroxide.

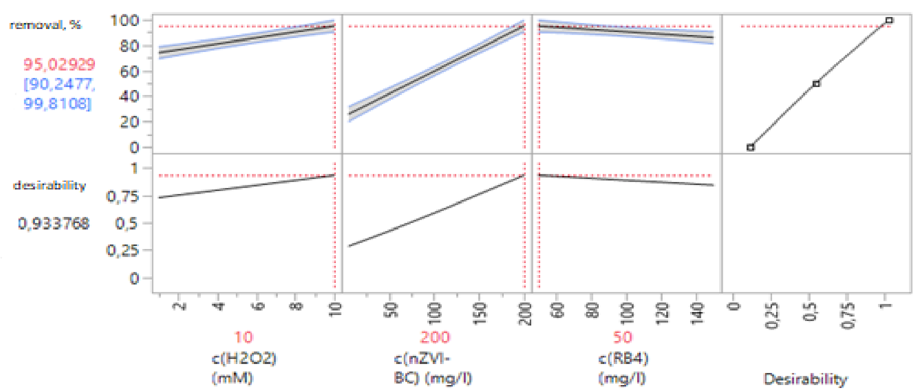

Fig 5 Fenton process optimization diagram

3.3. Treatment and characterization of real effluent of RB4 color under optimal conditions of Fenton process

After the performed treatments, the characterization of the treated effluent was performed. The results of physico-chemical characterization of the effluent before and after treatment are shown in Table 6.

Table 6. Results of physico-chemical characterization of the effluent before and after treatment

Parameter	Before treatment	After treatment	Mineralization, %
pH	6,4	3,4	-
Conductivity (μS/c)	72	280,6	-
BOD (mgO_2/L)	0	16	-
COD (mgO_2/L)	280	105	62,5%
TOC (mgC/L)	16	10,15	36,6%

Increased conductivity after the treatment indicates the formation of degradation products and the release of certain inorganic ions, which can originate from the dye molecule itself. It is these inorganic ions that compete with Fenton catalysts, since they can act as traps for hydroxyl radicals and thus contribute to the reduced efficiency of the applied Fenton treatment.

The BOD value of real effluent is below the detection limit, which confirms the fact that real effluent is non-biodegradable, and it is not possible to apply biological treatment in order to achieve high efficiency of color degradation. The increased value of BOD after treatment in the treated samples indicates the fact that a number of degradation products were formed, which confirms the assumption that removing dye from solution and decomposition of the chromophore group does not necessarily mean its complete oxidation to CO_2 and H_2O.

The derived conclusion is in accordance with the results of determining TOC and COD values. Namely, the degree of mineralization of RB4 after homogeneous Fenton process was determined by measuring the degree of removal of TOC value (93.7%) and the degree of reduction of COD value (62.5%) under optimal process conditions of the decolorization reaction. For a set of 5 samples under optimal conditions, the spectra of the final effluents after decolorization were recorded (Figure 6).

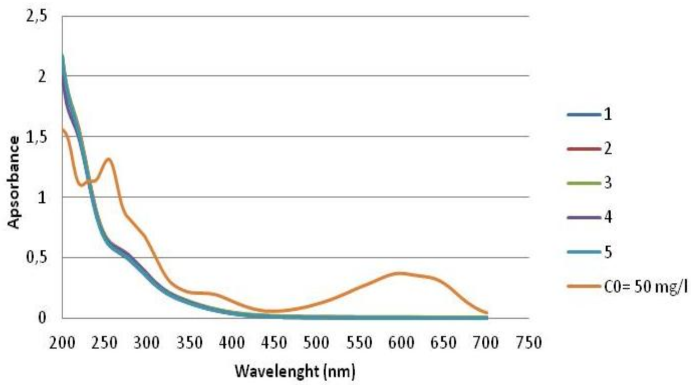

Fig 6 Spectra of final effluents after decolorization

Spectrum analysis concludes that converging the conditions to the optimal ones reduces the absorbance not only in the selected visible region, but also in the UV region. This indicates that not only the chromophore group is destroyed, but also the degradation of aromatic structures, which are predominantly color molecules. There is a noticeable decrease in the absorption at wavelengths in the range of 250-300 nm, which corresponds to the absorption maxima of the components containing the benzene ring, aromatic and dichlorotriazine groups and naphthalene compounds [25]. However, below 250 nm, the appearance of new degradation products is observed, which is indicated by the increase in conductivity after paint treatment in optimal conditions.

3.4. FTIR analysis of effluents

The results of the FTIR analysis are shown in Figure 7. This analysis was performed for the synthetic dye solution before treatment as well as for the effluent after treatment.

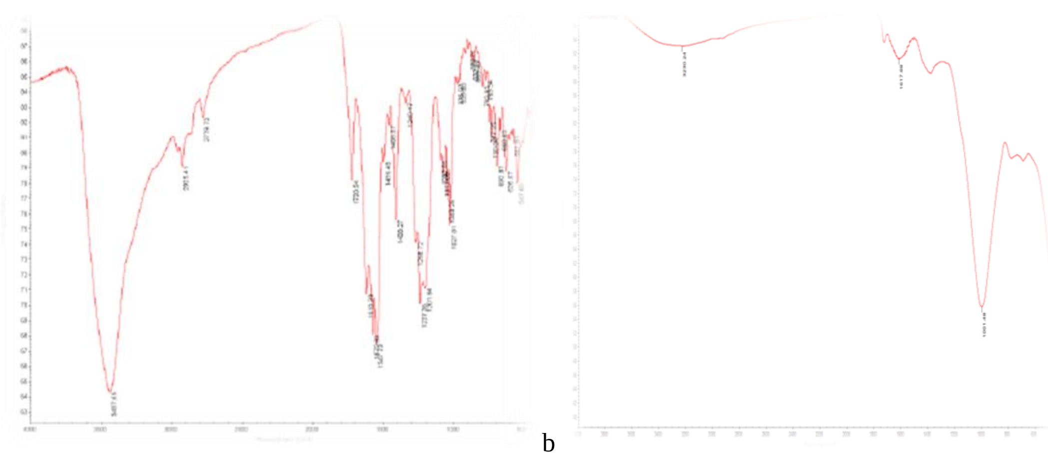

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Fig 7 FTIR spectra a) RB4 solution after treatment, b) RB4 effluent after treatment

For the color RB4 the initial effluent indicated the presence of expected groups such as groups with double bonds primarily carbonyl groups with oscillation at 1720 cm^{-1} with oscillation type ν (C = O), then different aromatic structures with halogen atom (in this case it is Cl) with the frequency of the absorption band at 680-725 and 750-810 cm-1 δ (CH) out of the plane, as the aromatic ring frequency at 1450 ± 10 cm^{-1} with the type of oscillations ν (C = C) and ν (C-C) skeletal. Amino groups with an aryl residue in the frequency range 1280-1350 cm^{-1}, ν (C-N), as well as aromatics containing nitrogen in the structure (pyridine type structure) with a frequency of 1200-1300 cm^{-1}, ν (N-O) were also identified. [26]. After the treatment, the recorded spectra show significantly lower frequency maxima, which indicates the mineralization of the solution as well as the degradation that took place in the direction of creating smaller molecules and reducing aromatic structures. Peaks in the range of 1000-3300 cm^{-1} are attributed to vibrations of O-H bond stretching in carboxylic acid molecules. The second maximum at 1617 cm^{-1} corresponds to the tensile vibrations of the C = C bond of the polyphenolic components. The maximum at 1031 cm-1 indicates the presence of C-C tensile vibrations, as well as C = C, C-O-C and O-H vibrations. The maximum at 441 cm^{-1} is attributed to -S-S- tensile vibrations. The identified peaks of characteristic functional groups have also been confirmed by the author [27].

4. Conclusion

One can conclude that nZVI-BC is an efficient catalyst and source of iron in the Fenton process. The applied DSD methodology, which was efficient in process optimization, indicated that very low concentrations of the obtained nano-biochar and hydrogen peroxide were required to achieve satisfactory results in terms of decolorization efficiency. Further characterization of the resulting effluents proved that in addition to the destruction of chromophore groups, the degradation of the entire dye molecule also occurs. In addition to, results are promising from the aspect of overcoming the limiting factors of the homogeneous Fenton process, such as the need to maintain the operating pH value within the narrow range 2.8 - 3.5 in order to achieve maximum catalytic activity of iron as a catalyst and prevent its deposition as hydroxide. On the other hand, the use of sewage sludge in the production of biochar for reuse in Fenton process is a proposal that aims to reduce costs, while providing a solution for waste management. It also contributes to the application of the circular economy concept in practice.

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