Photocatalytic degradation of azo dye using nanocomposite catalyst based on zinc oxide and zeolite

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Abstract
Purpose: To improve the applicability of metal oxide nanoparticles for water treatment, nanocomposite materials have emerged as a suitable alternative to overcome the limitations of nanoparticle growth, with the use of porous materials to support large areas. Among the various matrices, zeolites are considered to be promising hosts and stabilizers due to their unique characteristics such as: large surface area, high ion exchange capacity cavities, hydrophilicity, environmentally friendly nature, easily adjustable chemical properties and high thermal stability. **Methods:** Statistical processing of the obtained results (Box-Behnken statistical analysis) of the Reactive Red 120 dye removal efficiency test using a photocatalytic process, with ZnO/Zeolite as catalyst, included a study of the influence of the main process factors and their interactions. The dye concentration, pH value and catalyst dose were varied to provide optimal decolourization conditions. **Results:** The highest decolourization efficiency (85.6%) was observed at pH 3, after 30 minutes. Dye degradation percentage decreases as pH value increases. It was confirmed that individual parameters to some extent contribute to the efficiency of the photocatalytic process. At the lowest pH value and at the highest mass of catalyst (at the longest reaction time), statistical software suggests a decolourization efficiency of synthetic dye solution of ~89%. **Conclusion:** According to the obtained experimental data, it can be concluded that this type of catalyst has a great potential in photocatalytic reactions in order to decompose complex organic molecules.

Keywords: photocatalytic process, reactive azo dyes, degradation, composite catalysts

1. Introduction

Water on Earth is a valuable but limited resource. It is estimated that by 2050, the number of people living in scarce water areas will increase to 5.7 billion. In this way, reducing freshwater consumption and conserving natural resources largely depends on wastewater treatment and reuse [1]. The rapid development of various industries at the beginning of the 21st century has led to an increase in the rate of wastewater generation compared to the past. Globally, it is estimated that 2212 km^3/year of wastewater is returned to the environment (municipal and industrial wastewater, agricultural and drainage water), and over 80% is probably without adequate treatment. The toxic and harmful effects that wastewater discharges can cause are worrying, given that domestic and industrial effluents can have high rates of chemical oxygen demand (HPK), turbidity, alkaline pH, intense colour, and complex chemical composition. These characteristics occur due to the presence of detergents, waxes and mineral oils, dissolved solids, dye mixtures and many others. Several methods of wastewater treatment have been investigated to reduce the concentration of organic pollutants, in order to reduce freshwater scarcity problems [2, 3]. In the twentieth century, a large number of natural dyes used to change the colour of the fabric were replaced by synthetic dyes that have longer durability and lower cost. Hundreds of new synthetic dyes are produced every year, which are used for various purposes. Due to the widespread use of paints in many industries, huge amounts of wastewater are contaminated with paints that adversely affect the environment and human health and are difficult to remove by conventional methods. The textile industry is one of the biggest polluters of the environment, because it produces a large amount of dyed wastewater during its processes. The textile industry alone uses over five hundred thousand tons of dyes a year. In addition to dyes, these waters may also contain other harmful substances. When it comes to the correctness of wastewater before discharge into waste streams, residual paint is a very important factor. The biggest problem when it comes to dyes, in addition to aesthetics, is the reflection of sunlight and absorption. These processes interfere with the process of photosynthesis in aquatic ecosystems, which results in disturbance of the ecological balance and an increase in the number of bacteria. Dyes can have acute or chronic effects on organisms, depending on the time of exposure and the concentration of the dye. They exhibit mutagenic, carcinogenic and teratogenic properties, and are therefore undesirable in the environment.

In addition to the textile industry, the printing industry is also a significant source of dyes in the environment. Inks used for printing in this industry may contain traces of heavy metals. By cleaning printing machines, a large part of these compounds is dissolved and transferred to wastewater. Risks associated with heavy metals are related to toxicity and bioaccumulation in living organisms. One of the side effects of the presence of dyes is a reduced level of dissolved oxygen in the water, as a consequence of blocking sunlight and resistance to photochemical reactions. Chemical and biological needs for oxygen increase in the presence of dyes. Various conventional methods have been used for the treatment of industrial wastewater depending on the type and composition of wastewater (primarily due to the increased organic load of the effluent). The most commonly used are: chemical coagulation and flocculation, photocatalytic processes, adsorption processes, electrodialysis, distillation as well as biological treatments such as anaerobic and aerobic degradation. The application of these treatments resulted in incomplete degradation due to low biodegradability of treated dyes, significant amount of sludge, high cost of waste disposal, difficulties in the process of regeneration of applied materials and the need for large amounts of coagulant, which generally leads to reduced efficiency. For this reason, it is important to apply modern methods for removing dye that could be based on natural or waste materials. In order to solve this problem, advanced oxidation processes (AOP) have been developed that serve to remove various types of specific pollutants. Heterogeneous photocatalysis is a promising process, as it combines the use of semiconductor materials, which are usually cheap and efficient photocatalysts under solar radiation. Mechanism of these processes are shown in Figure 1. The advantages of photocatalysis compared to other oxidation processes are reflected in the following: It is based on the application of low-energy ultraviolet radiation for the excitation/activation of phototclaysts; Allows complete mineralization of many organic compounds, including compounds with limited biodegradability; Work in mild conditions, mainly at room temperature and atmospheric pressure [4]. Photocatalytic processes are considered modern techniques that in combination with traditional methods can give the desired results in terms of efficiency and safety (treatment of a wide range of organic pollution in water and wastewater). Heterogeneous photocatalytic processes using nanometer semiconductor photocatalysts have become an important technology that leads to complete demineralization of organic pollutants (without undesirable products), and is therefore environmentally friendly. Due to its thermal and chemical stability, ZnO is a material that is successfully used in photocatalysis as a catalyst for extensive application is in the form of nanoparticles [5, 6]. To improve the applicability of metal oxide nanoparticles for water treatment, nanocomposite materials have emerged as a suitable alternative to overcome the limitations of nanoparticle growth, with the use of porous materials to support large areas (matrices or stabilizers). Among the various matrices, zeolites are considered to be promising hosts and stabilizers due to their unique characteristics such as: large surface area, high ion exchange capacity cavities, hydrophilicity, environmentally friendly nature, easily adjustable chemical properties and high thermal stability [7].

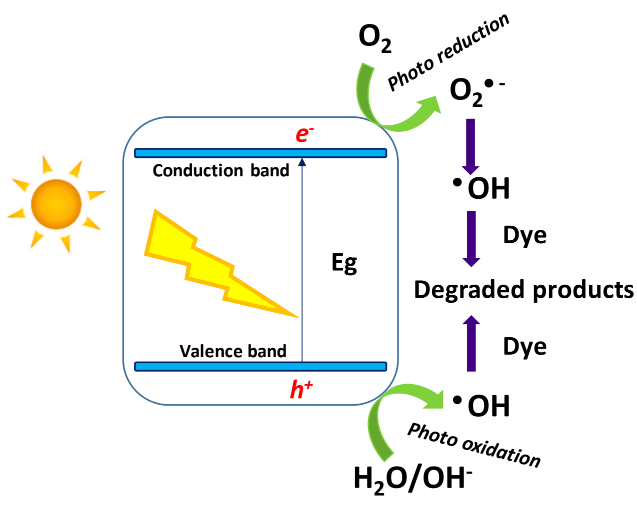

Fig. 1 Photocatalytic mechanism

In this paper, the possibility of Reactive Red 120 dye removal using a photocatalytic process was investigated, using ZnO/Zeolite nanocomposites as a catalyst in a photocatalytic reactor.

2. Materials and methods

The efficiency of Reactive Red 120 dye removal (Figure 2) efficiency was investigated using photocatalytic processes. ZnO/Zeolite nanocomposite was used as a catalyst. The use of nanocomposite material to improve the applicability of metal oxide nanoparticles (in this case ZnO) has proven to be a promising solution. In this test, the nanocomposite material is a combination of ZnO nanoparticles incorporated into the zeolite structure as a porous material to support a large surface area.

2.1. Synthesis of nanocomposite ZnO/Zeolite catalyst

5 g of zeolite was dissolved in 100 ml of deionized water, in a volume of a flask with a round bottom of 250 ml. An equivalent amount of 5% by weight of ZnO/Zeolite from Zn $(Ac)_2$•$2H_2O$ was added to the suspension. The suspension was stirred under reflux at 80°C for 5h to ion exchange to give Zn^{2+} altered zeolite. 0.1M NaOH was added to the suspension until pH 11 was reached. After 2h, the product was filtered and washed with deionized water to remove residual acetate before drying overnight at 60°C. Finally, the final product was calcined for 2h at 450°C.

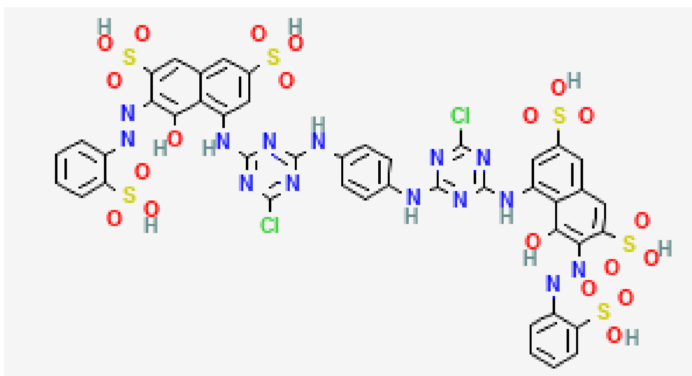

Fig. 2 Structure of Reactive Red 120

2.2. Experimental procedure

Several consecutive trials were performed. Different concentrations of dye solution (in the range of 20-180 mg/l) were made and the predicted catalyst mass was measured for each sample. Solutions of a certain dye concentration are made by dissolving the measured mass of dye in a beaker and quantitatively transferring it to a normal vessel (volume 1l), which is then topped up to the line. 250 ml of contents from a normal vessel are measured in a beaker, and then it is poured into the reactor. The pH of the dye solution in the reactor was then adjusted with NaOH and H_2SO_4 (in the range of 3-10) and checked with a pH meter. The measured mass of catalyst is then added to the dye solution and magnetic stirring is turned on to homogenize the reaction mixture. The previously installed lamp is lowered inside the reactor (immersed in the dye solution) and switched on. The reactor is then covered to prevent external influences on the dye solution and allow only the light effect of the lamp (254 nm). Also, water is released into the water jacket on the reactor for cooling. After 30 minutes, sample of the reaction mixture is withdrawn (using a pipette) and transferred to measurement. The sample is further analyzed in a spectrophotometer (quartz cuvettes are used), the absorbance of the colored solution was measured at 512 nm and then the results were read. Decolorization efficiency of aqueous solution was obtained based on the following equation (1):

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

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

3. Results and discussion

Statistical processing of the obtained results (Box-Behnken statistical analysis) of the Reactive Red 120 dye removal efficiency test using a photocatalytic process included a study of the influence of the main process factors and their interactions. It included 14 runs.

Table 1 shows the process parameters for each individual experiment, as well as the corresponding decolourization efficiency. The obtained results indicate that the achieved decolourization efficiency is in the range of 25 - 85.6%. Process efficiency depends on the relationship between process parameters. The highest process efficiency (85.6%) was obtained at pH 3, and the lowest process efficiency (25%) was obtained at pH 10.

Table 1 Experimental setup and efficiency of the photocatalytic decolourization process

	20-180	**3-10**	**0.02-0.4**	
Probe	**X1 – Dye (mg/l)**	**X2 – pH**	**X3 – Catalyst (g/l)**	**Decolourization efficiency (%)**
1	20	3	0.21	75
2	20	10	0.21	55.7
3	180	3	0.21	85.6
4	180	10	0.21	38
5	100	3	0.02	62.3
6	100	3	0.4	78
7	100	10	0.02	25
8	100	10	0.4	35.6
9	20	6.5	0.02	30
10	180	6.5	0.02	28
11	20	6.5	0.4	60
12	180	6.5	0.4	40
13	100	6.5	0.21	54.3
14	100	6.5	0.21	56.8
15	100	6.5	0.21	55

The selection of an adequate regression model is based on standard selection criteria, such as: AIC (*Akaike Information Criterion*), RMSE (*Root Mean Square Error*) and BIC (*Bayesian Information Criterion*) parameters.

Descriptive factors of the selected statistical model for the applied photocatalytic process are shown in Table 2, where high values of the coefficient of determination (R2) and adjusted coefficient of determination (R2 adj), as well as approximate values of AIC and BIC parameters imply a good approximation of experimental data.

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 parameter F <0.0001. In addition, the validity of the selected model was confirmed by the value of the F parameter that describes the insignificance of the "*lack of fit*" test (F> 0.05).

Table 2 Selected regression model (all interactions included)

Descriptive factor	**Value**
R^2	0.98337
R^2 adj	0.953436
AIC	178.1156
BIC	97.90412
RMSE	4.058797

Table 3 Analysis of variance and Lack of fit test (all interactions included)

Source	**^{a}DF**	**^{b}SS**	**^{c}MS**	**F parameter**
Model	9	4870.6282	541.181	32.8509
Error	5	82.3692	16.478	**Prob>F**
C. Total	14	4952.9973	-	**0,0006***
Lack of Fit	3	79.042500	26.3475	15.8402
Pure Error	2	3.326667	1.6633	**Prob>F**
Total Error	5	82.369167	-	**0.0600**

^{a}Number of degrees of freedom, ^{b}Squares sum, ^{c}Variance (mean square)

The adequacy of the adopted model was examined using diagnostic diagrams (Figures 3 – 5) which include a diagram of the dependence of the actual in relation to the predicted values of paint removal efficiency, a diagram of deviations of standardized residuals relative to the zero line, and a normal distribution diagram. Adequate approximation is confirmed by the diagnostic graph of the dependence of the real ones, ie. experimental values in relation to the predicted values of decolourization efficiency, which are in good correlation (Figure 3). From the diagram of deviations of standardized residuals in relation to the zero line (Figure 4), there is no tendency to scatter values, but the points are randomized in space, which means that the regression model describes the examined problem well. Figure 5 shows that the residues follow the right of normal distribution and are within the confidence interval.

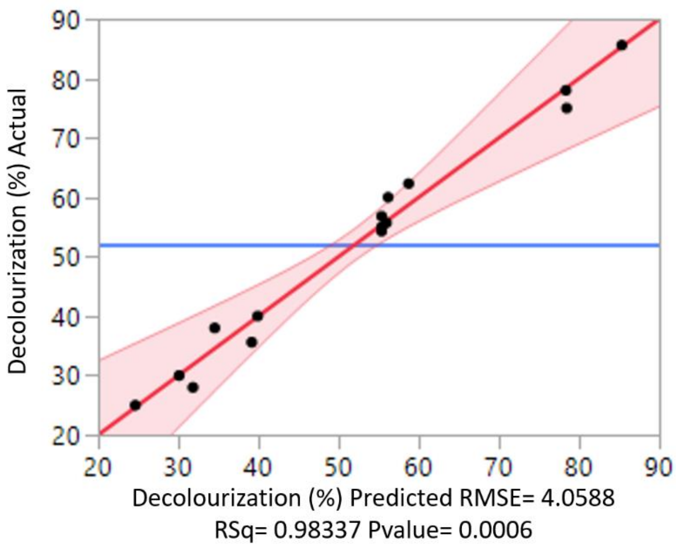

Fig. 3 Diagram of the dependence of the actual in relation to the predicted values of the discoloration efficiency of the dye removal (all interactions included)

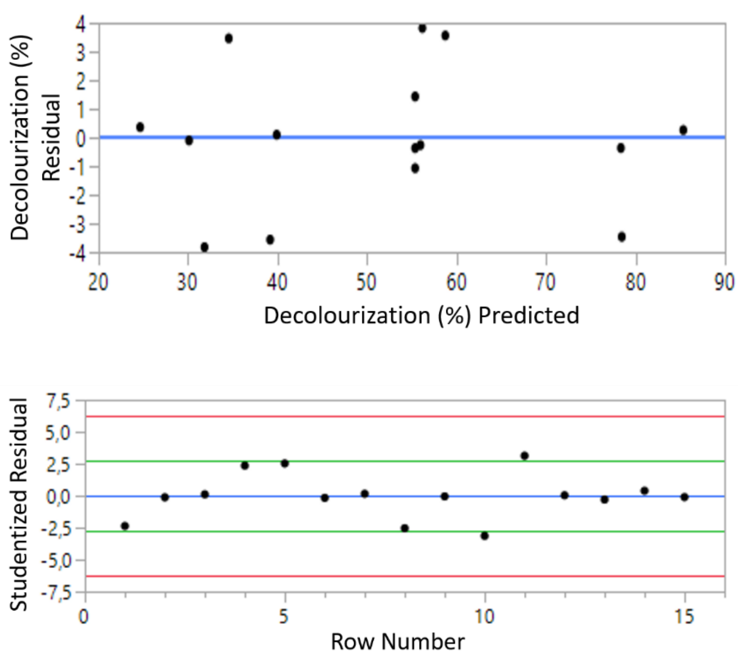

Fig. 4 Deviation diagram of standardized residuals relative to the zero line + residuals (all interactions included)

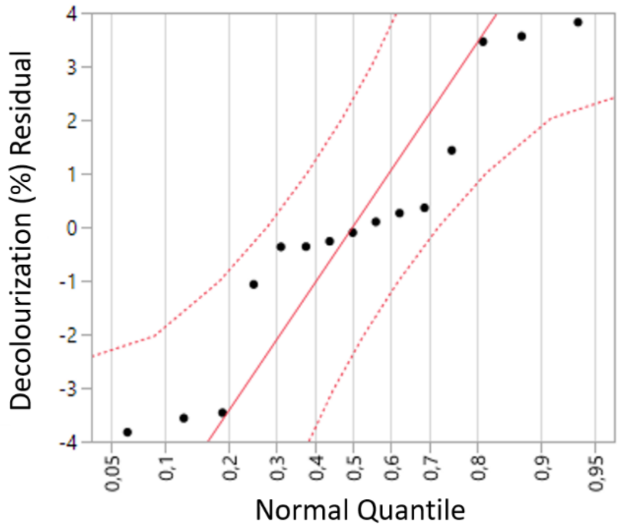

Fig. 5 Normal distribution diagram (all interactions included)

Based on the approximated parameter values and standard error, factors with statistical significance were singled out and shown in Table 4 ("bold" values), which mostly contribute to the efficiency of dye removal in the photocatalytic process. It is noticed that the statistically significant parameters are the concentration of the dye and the mass of the catalyst, with a greater positive impact on the process of removing the dye is achieved by the concentration of the dye. Within the photocatalytic process, a statistically significant two-factor interaction was found, precisely between the dye concentration and the mass of the catalyst, which is shown in the response surface diagram (Figure 6).

Table 4 Estimated regression coefficients (all interactions included)

Parameter	**Estimated value**	**Standard error**	***t* value**	**Probability> |t|**
Intercept	55.366667	2.343348	23.63	**<0.001***
Dye (mg/l)(20, 180)	-3.6375	1.435001	-2.53	0.0522
pH(3.10)	-18.325	1.435001	-12.77	**<0.001***
Catalyst (g/l)(0.02, .0.4)	8.5375	1.435001	5.95	**0.0019***
Dye (mg/l)*pH	-7.075	2.029399	-3.49	**0.0175***
Dye (mg/l)*Catalyst (g/l)	-4.5	2.029399	-2.22	0.0774
pH*Catalyst (g/l)	-1.275	2.029399	-0.63	0.5574
Dye (mg/l)*Dye (mg/l)	-1.258333	2.112265	-0.60	0.5773
pH*pH	9.4666667	2.112265	4.48	**0.0065***
Catalyst (g/l)*Catalyst (g/l)	-14.60833	2.112265	-6.92	**0.0010***

From the response surface diagram, it can be seen that at a constantly high dose of catalyst (250 mg/l) the decrease in dye concentration has a pronounced effect on increasing the removal efficiency, with the effect being most pronounced at minimum dye concentration (50 mg/l).

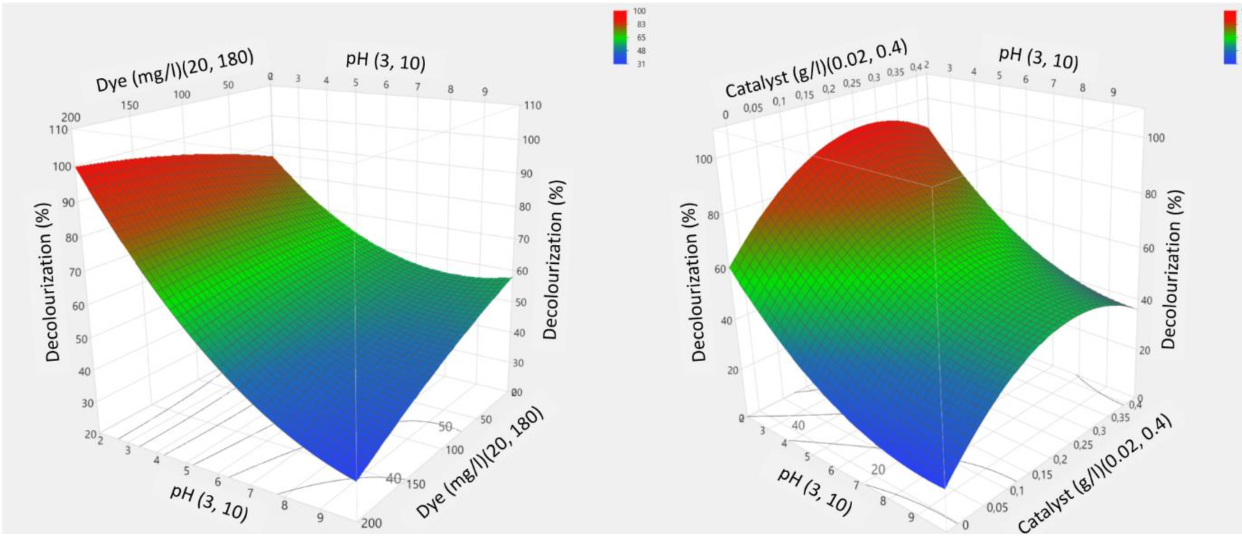

Fig. 6 Diagram of the response surface of statistically significant interactions: catalyst mass and pH value

The optimization diagram shown in Figure 7 evaluates the best dye removal capability under optimal process conditions of the applied photocatalytic process. In this case, the statistical software proposes a decolourization efficiency of the synthetic dye solution of 89.33% at the lowest concentration of dye, but at the highest mass of catalyst at the longest reaction time. From the optimization diagram, it can be seen that the concentration of dye do not greatly affect the efficiency of the applied photocatalytic process in comparison to pH value and consequently catalysis concertation.

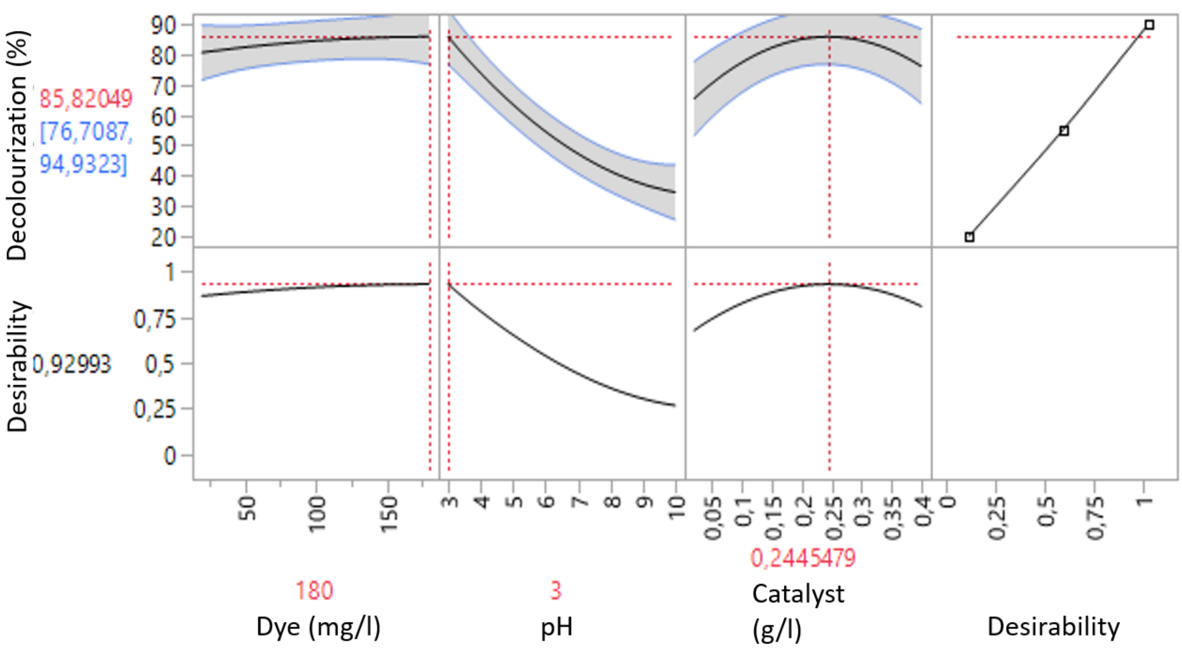

Fig. 7 Photocatalytic process optimization diagram

4. Conclusion

The possibility of decolourization of Reactive Red 120 dye using photocatalytic process was investigated in this paper. ZnO/Zeolite nanocomposite was used as a catalyst. The dye concentration, pH value and catalyst dose were varied to provide optimal decolourization conditions. Box - Behnken statistical analysis of the obtained results included the examination of the influence of the main process factors and their two - factor interactions (precisely between the dye concentration and the mass of the catalyst). The concentration of the dye has a greater positive effect on the dye removal process. The results indicate that at a constantly high dose of catalyst (250 mg/l), the reduction of the dye concentration has a pronounced effect on increasing the removal efficiency. The effect is most pronounced at the minimum dye concentration (50 mg/l). The highest decolourization efficiency (85.6%) was observed at pH 3, after 30 minutes. pH is a very important parameter, because it affects the amount of formed •OH radicals. Above a certain concentration of OH^- - ions in the solution, unfavourable electric forces are created, ie. there is a rejection between the negatively charged surface of the catalyst and the OH^- ion. Therefore, the success rate of dye degradation decreases at higher pH values. Based on this, it was confirmed that individual parameters to some extent contribute to the efficiency of the photocatalytic process. At the lowest concentration of dye, and at the highest mass of catalyst (at the longest reaction time), statistical software suggests a decolourization efficiency of synthetic dye solution of ~89%. According to the obtained experimental data, it can be concluded that this type of catalyst has a great potential in photocatalytic reactions in order to decompose complex organic molecules.

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