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Photocatalytic degradation of magenta effluent from the printing industry with composite catalyst

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Abstract Water pollution is one of the most current problems related to human life and survival. The high degree of pollution of the human environment is contributed, among other things, by the discharge of industrial wastewater into rivers, among which wastewater from the graphic industry is of great importance. With conventional wastewater treatments, such as secondary biodegradation, many pollutants cannot be completely removed. Synthetic dyes can be a potential hazard for living organisms. Also, heavy metals are present in some types of printing inks. On the other hand, with advanced technologies, it is possible to obtain high quality water. Photocatalytic degradation is a promising and widely used method when it comes to the treatment of wastewater and air contaminated with both organic and inorganic pollutants. Photocatalytic processes have many advantages when it comes to removing pollutants from water in low concentrations. The aim of this paper is to investigate the possibility of applying the process of photocatalytic degradation, using titanium (IV) oxide modified with magnetite nanoparticles, in the treatment of magenta effluent originating from the graphic industry. In order to optimize the entire process, a new statistical method of definitive screening design (DSD) was used, where the influence of individual process parameters.

Keywords: photocatalytic processes, graphic dyes, degradation, new catalysts, heterogeneous catalysis

1. Introduction

The environmental aspect in the printing industry is often viewed differently from local, national and international standards and legislation. There is a very different and large number of printing materials, but also chemicals that are used during the printing process and therefore it is very important to assess their impact on the environment. Impact assessment depends on the utilization of input material, including printing plates, printing media, graphic inks, solvents, binders, and additives. In addition to the textile industry, the printing industry is one of the largest consumers of synthetic dyes. This fact indicates a significant burden on the environment due to the release of a significant amount of colored effluents into water bodies. It is estimated that about 15% of synthetic inks are lost during the printing process and as non-biodegradable substances are released into natural watercourses in the form of wastewater (Karimifard and Moghaddam, 2018; Katheresan et al., 2018; Gvoić, 2019). Colored wastewater is characterized by being rich in high molecular weight aromatic compounds, which make it difficult to apply conventional biological treatments in order to remove them (Xu et al., 2018; Collivignarelli et al., 2019). Dyes also affect aesthetic properties, affect the absorption and solubility of atmospheric gases in water. They also interfere with the growth of aquatic species, as they have the ability to absorb and reflect sunlight and limit the oxygenation of water surfaces, while preventing photosynthesis and reducing the biological activity of aquatic organisms. During the degradation of dyes and intermediates, by-products with pronounced carcinogenic potential and mutagenic activity are formed, with acute and chronic effects on living organisms depending on their concentration and length of exposure (Natarajan et al., 2018). The ideal method for solving the problem of treatment of colored wastewater should provide efficient removal of a large amount of dye in a short period of time, without creating secondary pollution, where the treated wastewater could be used again (Gvoić, 2019). Great importance and efficiency in the treatment of colored effluents has been established during the application of conventional and advanced chemical processes, including advanced oxidation processes (AOPs). The diversity of AOPs in terms of different ways of producing hydroxyl radicals (HO •) allows researchers to select the appropriate process to suit the specific needs of the experiment. There is a growing interest in the application of UV light to reduce environmental pollution, and especially in reducing the impact of potentially carcinogenic and toxic effects of pollutants on water. As a result of this increased interest, numerous scientific studies investigate and apply UV radiation, as a method for the degradation of different classes of organic and inorganic compounds in the environment (Jovanović, 2014). In order for a photocatalytic system to be applied on an industrial scale, it is necessary to thoroughly study it, from testing in laboratory conditions to testing for the so-called. pilot plants and finally in real conditions. Research on the basis of solar energy and is widely used for solar detoxification, when it comes to the decomposition of harmful toxic compounds in water using photocatalysis using solar photons is starting point to extrapolate this treatment on a large-scale (Malato et al., 2002).

2. Experimental work

A parabolic concentrating reactor was used to create the experiment in order to make better use of solar radiation and improve the photocatalytic performance of the process (Figure 1). The experiment was performed on the campus of the University of Novi Sad on the open roof of the UNSPMF (Latitude: 45 ° 14′44.19 ″ N; Longitude: 19 ° 51′11.29 ″ E) during the summer period of the year, in July, under clear sky conditions. , with constant solar radiation of 950 W/m^2 for summer. The intensity of solar radiation was maintained by the constant rotation of the reactor along its axis and the east-south orientation. The maximum time of exposure to solar radiation was 60 minutes, after which the absorbance of the graphic dye were measured at the established wavelength.

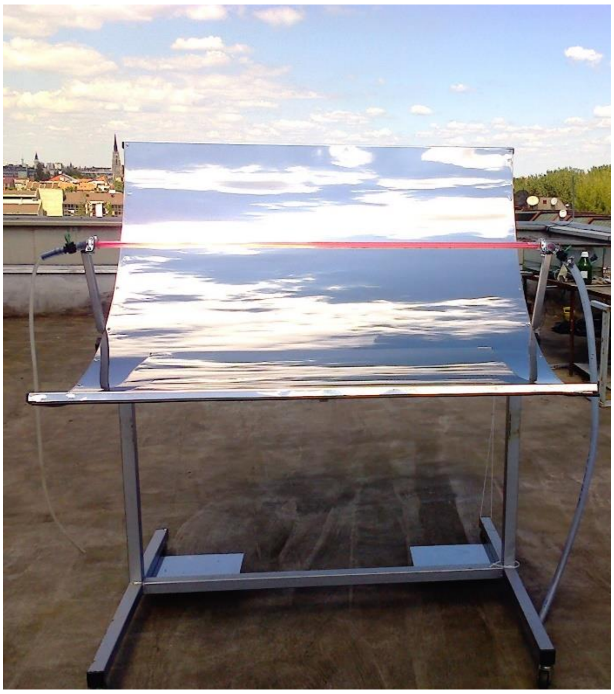


Figure 1. Solar parabolic concentrating reactor used in the experiment

Deionized water and chemicals of purity *pro analisy* were used for the preparation of all working solutions of the desired concentrations, and the analyses of the tested samples were performed directly, without prior treatment. The experiments were performed on samples of aqueous solutions of synthetic Magenta graphic dye originating from the graphic industry, which was produced by the Flint group.

Synthesis of composite catalyst (TiO_2-Mag) was produced by modification of TiO_2 with magnetite nanoparticles. In this experiment, the influence of the following process conditions was investigated: dye concentration, TiO_2-Mag concentration and pH value. The DSD statistical method was used both for the design of the experiment and for the processing of the obtained results. The basic scheme of the DSD experiment with four numerical factors consists of 13 experiments, which were done in duplicate with the addition of two more central points, which gives a total of 28 experiments.

3. Results and discussion

Based on the results, it is concluded that the range of decolourization efficiency is 30.2 - 95.6%. Based on this, it was determined that the efficiency of decolourization, ie the minimum and maximum values are influenced by different set process conditions. In order to select the regression model that can most closely approximate the obtained results, the JMP stepwise regression analysis is performed. In this way, a large number of regression models with different numbers of parameters are created, but it is important to take into account the main factors and their two-factor interactions. The final values of the model take into account the lowest values of AIC (*Akaike Information Criterion*), BIC (*Bayesian Information Criterion*) and RMSE (*Root Mean Square Error*), but the simplicity of the model is also important.

A summary of the descriptive factors of the adopted regression model, 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 selected are determined, part od results is presented in table 1.

Table 1. Chosen regression model

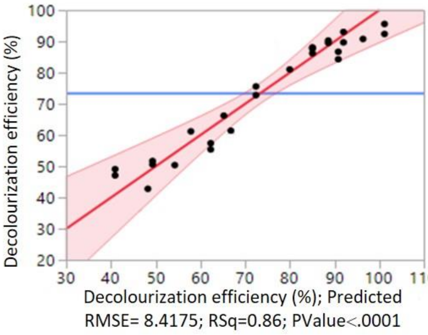
Descriptive factor	Value
R^2	0,862
R^2 adj	0,814
AIC	217,337
BIC	219,327
RMSE	8,417

The coefficient of determination (R^2) and the adjusted coefficient of determination (R^2adj) show high values, which represents 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^2adj represent the percentage of data closest to the best fit line, and indicate the fact that 86% of the variance for Magenta dye removal efficiency is explained by an independent variable, while the remaining 14% of the total variance is not covered by the model.

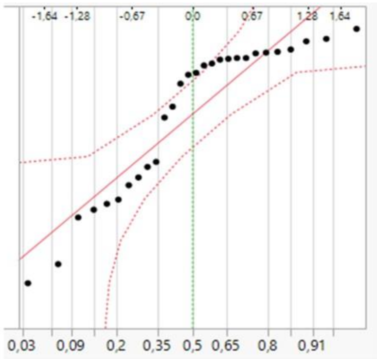
By applying and analyzing diagnostic diagrams, we can determine the adequacy of the selected model (Figure 2).

The diagrams included are: the diagram of the normal distribution, the diagram of the dependence of the real in relation to the predicted values of the decolourization of the Magenta dye and the diagram of the deviation of the standardized residuals in relation to the zero line. Adequate approximation is confirmed by the diagnostic graph of the dependence of the real, ie. experimental values in relation to the predicted values of decolourization efficiency, which are in good correlation (shown in Figure 2a). It can be seen from Figure 2b that the residues generally follow the right of normal distribution and are within the confidence interval, with a pair of scatterings outside the interval. From the deviation diagram of the standardized residuals in relation to the zero line (Figure 2c), there is no tendency for the values to scatter, but the points are randomized in space, which means that the regression model describes the examined problem well.

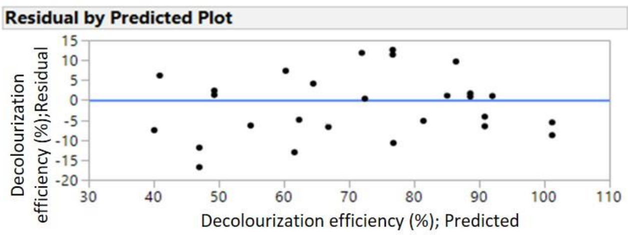
Based on the obtained results, it is concluded that in the case of photocatalytic degradation, all process parameters (dye concentration, catalyst concentration and pH value) are important, and two two - factor interactions have been established: dye concentration and pH; dye concentration and catalyst concentration. The results indicate the fact that the catalyst concentration, as well as the two two-factor interactions have a positive impact on the photocatalytic degradation process, while other variables have a negative impact.



a)



b)



c)

Figure 2. Diagnostic diagrams: a) Diagram of the dependence of the actual in relation to the predicted values of the discoloration efficiency of the dye removal; b) Normal distribution diagram; c) Diagram of deviation of standardized residues in relation to the zero line

If the dye concentration is at least (20 mg/l), the efficiency of the process will increase sharply with decreasing pH value. pH therefore largely controls the process. Also, the concentrations of dye and catalyst represent a significant two-factor interaction. If the dye concentration is the highest (180 mg/l), the efficiency of the degradation process will increase when the catalyst concentration increases only to the value of 0.6 mg/l, which is also established in the optimization diagram. A further increase in the catalyst concentration causes a decrease in the efficiency of the photocatalytic degradation process. The same effect of catalyst concentrations is achieved on the efficiency of the photocatalytic degradation process even at the lowest concentrations of Magenta dye (20 mg/l), but its influence in that case is much weaker. It was found that decreasing the pH value increases the decolourization efficiency, while at more neutral and basic values the decolourization efficiency decreases. The removal efficiency at a neutral pH of 6.5 reaches up to 85.07%. Acidic pH values, in this case pH 3, have negative effects on the environment, as well as the release of acidic treated effluents into the recipient. High consumption of acidifying chemicals are necessary in this case, as well as neutralization of the effluent before its release into the recipient. Therefore, the potential effect of pH change to more neutral values was examined. The convenience of JMP 13 software is reflected in the fact that it offers the researcher the opportunity to vary the optimal values and thus gain insight into changing the efficiency of the monitored process, in order to improve the operational conditions of the process itself.

The statistical model showed high dye removal of 85.07% under the following optimal conditions: dye concentration of 100 mg/l, pH value 6.5, TiO_2-Mag concentration 0.6 mg/l.

4. Conclusion

In this paper, the possibility of application of photocatalytic degradation process was investigated, using TiO_2 modified and coupled with magnetite nanoparticles on magenta effluent originating from the graphic industry. Catalyst doses, dye concentrations and pH values were varied to ensure the best possible decolourization efficiency. The obtained results show that the range of decolourization efficiency is 30.2 - 95.6% after 60 min of sun exposure. Based on this, it was determined that the efficiency of decolourization, ie the minimum and maximum values are influenced by different set process conditions. Descriptive factors point to the fact that 86% of the variance for Magenta dye removal efficiency was explained by an independent variable, while the remaining 14% of the total variance was not covered by the model. ANOVA test results indicating the significance of the regression model since the value of the parameter F <0.0001. Within the obtained results, it is concluded that in the case of photocatalytic degradation, all process parameters (dye concentration, catalyst concentration and pH value) are important, and two two-factor interactions have been established: dye concentration and pH; color concentration and catalyst concentration. It was found that decreasing the pH value increases the decolourization efficiency, while at more neutral and basic values the decolourization efficiency decreases. However, the statistical model presented in the paper has a high removal efficiency (85.07%) of the magenta dye even at pH 6.5.

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