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Fenton-like oxidation of flexographic water-based Key (Black) dye: a Definitive Screening Design optimization

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Introduction

More than 80% of the global demand for synthetic dyes is directed to azo dyes production, which are mostly used for dyeing of paper, leather textiles and plastics. These dyes represent heterocyclic systems with chromophore azo group (-N=N-) bond to the sp^2 carbon atoms of the aromatic rings. They are soluble in water, showing high stability at different pH values, high temperatures and brightness.

Wastewater generated after the printing process are characterized with high pH value, temperature and conductivity, high content of suspended solids and total organic carbon (TOC), high values of chemical oxygen demand (COD), but low values of biological oxygen demand (BOD), where low BOD/COD ratio implies to high content of non-biodegradable organic matter.

The application of nano zero valent iron (nZVI) particles in Fenton-like process for degradation of wide range of organic substances has achieved certain advantages over conventional methods and solved their practical disadvantages, such as application of iron in high concentrations, sludge generation in a form of metal hydroxide after treatment, work in a narrow pH range, as well as the regeneration of the catalyst and the impossibility of its reuse.

Problem Description

Process optimization is crucial to enhance the efficiency of applied treatment. This paper aims to investigate and examine the impact of Fenton-like process conditions (dye concentration, nanoparticles dosage, pH and H_2O_2 concentration) for Black printing dye degradation, by using a novel statistical approach - Definitive Screening Design (DSD).

Materials and Methods

Degradation of Black water-soluble flexographic printing dye (Flint group, CAS number: 1064-48-8; color index: PK7; molecular weight: 616.49 $gmol^{-1}$; absorption wavelength: 613 nm), is studied.

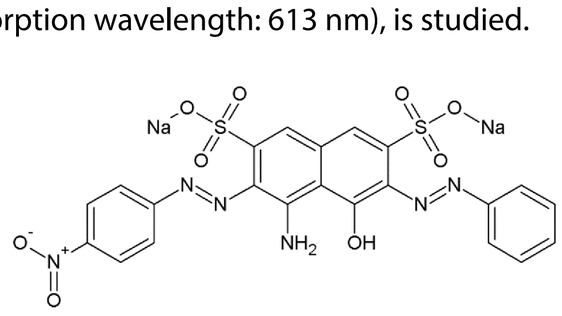

Figure 1

Chemical structure of Black printing dye

Sample of wastewater was obtained from one flexographic printing facility in Novi Sad. Aqueous dye solution was prepared by dissolving appropriate amounts of Black dye with deionized water to the desired concentration.
nZVI particles, as Fenton catalyst, were synthesized according to the previous report through the ''green'' synthesis method.

The degradation process of Black dye was carried out in a 500 mL glass beaker containing 250 mL dye solution. Various concentrations of nZVI and H_2O_2 were mixed with the solution, whereby pH value was adjusted using 0.1 M ccH_2SO_4 and NaOH. All reaction systems were mixed on a JAR apparatus (FC6S Velp Scientific, Italy) at 120 rpm and constant temperature of 23 °C. The residual dye concentration was established immediately by measuring the absorbance of the aqueous solutions at 613 nm with UV/VIS spectrophotometer (UV-1800 PG Instruments Ltd T80+ UV/VIS, Japan).

The DSD platform was utilized to evaluate the main and interaction effects of the Fenton-like process parameters on the decolorization efficiency. The experimental design was built around four factors, each having three levels representing the low (-), central (0), and high (+), with the addition of two central points. The factors and corresponding operating conditions are: dye concentration (20 mgL^{-1}, 100 mgL^{-1} and 180 mgL^{-1}), nZVI dosage (0.75 mgL^{-1}, 30 mgL^{-1} and 60 mgL^{-1}), H_2O_2 concentration (1 mM, 5 mM and 10 mM) and pH value (2, 6 and 10). A randomized experimental sequence was followed and the obtained values for the decolorization efficiency (%) were obtained.

Results

Using the fitted full quadratic model, a response surface regression analysis for decolorization efficiency was performed. Black dye decolorization efficiency yield was 0.43 - 88.86%.

The adopted regression model explains approximately 84 per cent of variance in the observed experiments. Although the correlation factor (R^2 = 0.834) was characterized with low level, the result of ANOVA test indicates that regression model is highly significant (F <0.0001), while the validity of selected model is confirmed based on the "lack of fit" test (F> 0.05).

It is concluded that dye concentration and pH value achieve the greatest impact on the Fenton process efficiency. Although both statistically significant, dye and H_2O_2 concentration are a part of a statistically significant interaction. Its interaction plot shows that maximum decolorization efficiency is obtained for H_2O_2 concentration at lowest level (1mM), and dye concentration at highest level (180mgL^{-1}).

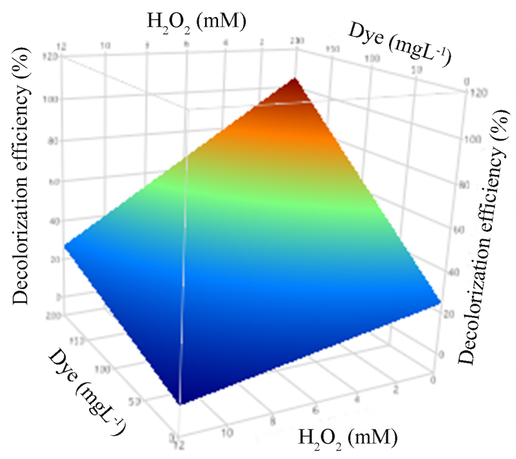

Figure 2

Surface plot showing the interaction effects between dye and H_2O_2 concentration

Discussion / Conclusion

Within the nZVI/H_2O_2 Fenton treatment, statistical software proposes a maximum decolorization efficiency of 78.89% within the following optimum process conditions: dye concentration of 180 mgL^{-1}, nZVI dosage of 0.75 mgL^{-1}, H_2O_2 concentration of 1 mM and pH value 2.

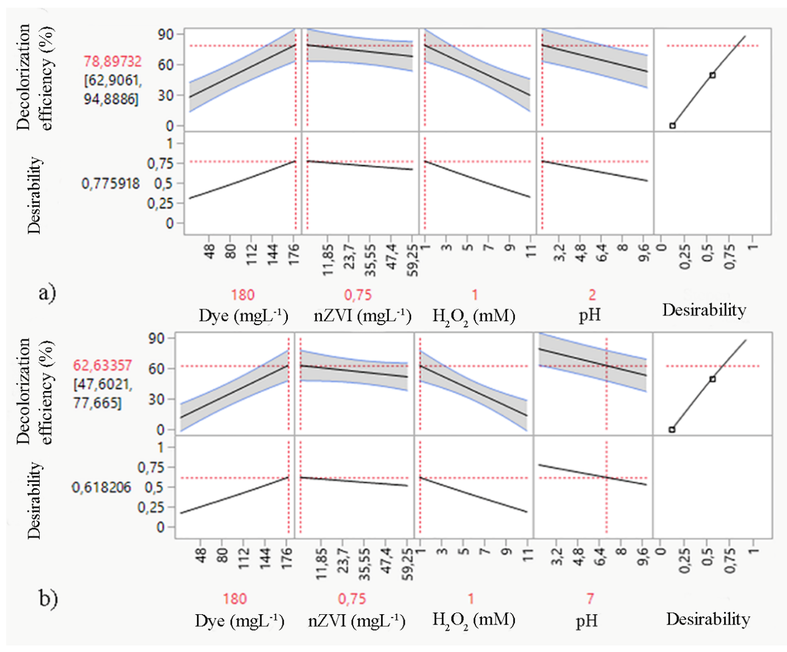

Figure 3

Optimization plot in: a) acidic and b) neutral medium

However, the pH value 2 is unfavorable from the environmental aspect: experiment requires the consumption of large amounts of chemicals in order to acidify the treated medium and subsequent neutralization of the effluent before its release into the recipient is required. When the pH values increase to 5, 6 and 7, the efficiency of Fenton process decreased from 79% to 69.14%, 65.89% and 62.63%, respectively. In this way, process can be optimized to pH 7, but a limitation in a sludge formation in neutral environment is noticeable.

The obtained results implied that Fenton-like process can be used for printing dye removal from synthetic solutions. However, this study can be extended by considering real printing effluent treatment under obtained optimal process conditions, as well as by additional treatment for sludge formation.

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