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Application of advanced oxidation process for the removal of synthetic water-based printing dye and microplastics from aqueous solution

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Introduction

Printing inks and varnishes are industrial mixtures. In the manufacture process of certain printing dyes, polymers as resins and waxes are an essential ingredient, used in order to provide superior adhesion of dyes to non-porous surfaces. These polymers may fall under the proposed definition of microplastics (MPs): solid non-biodegradable polymeric particle with physical dimensions between 1 µm - 5 mm originating from anthropogenic sources.
Additionally, MPs and dyes can be found in wastewater after the printing process on the polymer packaging material, or screens that are usually made of polyethylene or polypropylene, mainly in flexo and screen-printing process. In that way, MPs can act as a carrier of synthetic dyes, heavy metals and other toxic contaminants.

Problem Description

The aim of this study is directed on examination of advanced oxidation treatment based on the Fenton-like process to remove synthetic water-based Cyan dye in the presence of MPs, polyethylene.

Materials and Methods

Water-based printing dye, Cyan, was produced from Flint group and obtained from one printing facility in Novi Sad, Serbia.

Granulated polyethylene (PEg) standard microplastic particles (Sigma Aldrich) were added to synthetic dye solution in order to investigate Fenton-like process efficiency for the removal of printing dye in the presence of MPs.

Table 1

Physico-chemical characteristics of PEg

Characteristic	Value
Particle size (mm)	3.0
Density (gcm^{-3})	0.918
Cristallinity (%)	44.0
Melting Temperature ($^{\circ}C$)	114
Glass Transition Temperature ($^{\circ}C$)	-120

''Green'' synthesis method of nZVI particles was conducted by using green-tea leaves combined with iron chloride.

The lab scale of Fenton-like process was performed by a series of 15 experiments on a JAR test apparatus. The initial, as well as residual dye concentrations in the reaction mixture were determined by measuring the absorbance of the aqueous solutions at 636 nm by using UV/VIS spectrophotometer. The decolorization efficiency was calculated according to equation (1):

$$E\ (\%) = (A_0 - A_t)/A_0 * 100 \qquad (1)$$

where: A_0 is the initial dye absorbance of Cyan dye aqueous solution; A_t is absorbance of Cyan dye aqueous solution after Fenton-like process.

Results and Discussion

Fenton process resulted with the efficiency in range 0.15 - 91.67% for 15 experimental runs. Maximum and minimum decolorization efficiencies during Fenton process are achieved under different sets of process conditions, which confirms the assumption that dye removal process mostly depends on the applied experimental conditions.

The adopted regression model explains approximately 99.9% of variance in the observed Fenton efficiency values. The value of adjusted R^2 is 99.8%, which reveals good relationship between the expected values and the actual values. Compared to mean of response (29.885), root mean square error (1.361) is small, indicating good fit and accuracy of model prediction. Results of ANOVA test confirmed the significance of the adopted regression model (the value of the parameter F <0.0001).

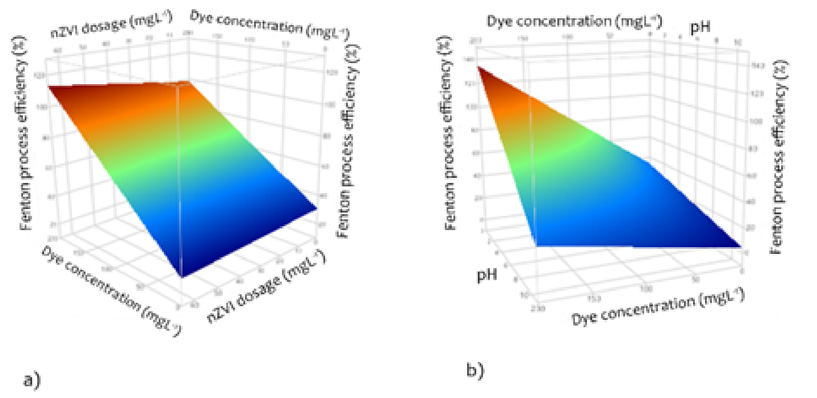

Figure 1

Surface response plots illustrating two significant interactions between: a) dye concentration and nZVI dosage; b) dye concentration and pH; c) PEg concentration and H_2O_2 concentration; d) pH and H_2O_2 concentration

According to optimization results, maximum Fenton process efficiency of 91.8% is obtained for the following settings: 155 mgL^{-1} of Cyan dye concentration, 55 mgL^{-1} of nZVI dosage, 2.35 gL^{-1} of PEg concentration, 2 mM of H_2O_2 concentration and pH 2.5. This confirms that the process efficiency increases with H_2O_2 and pH decreasing.

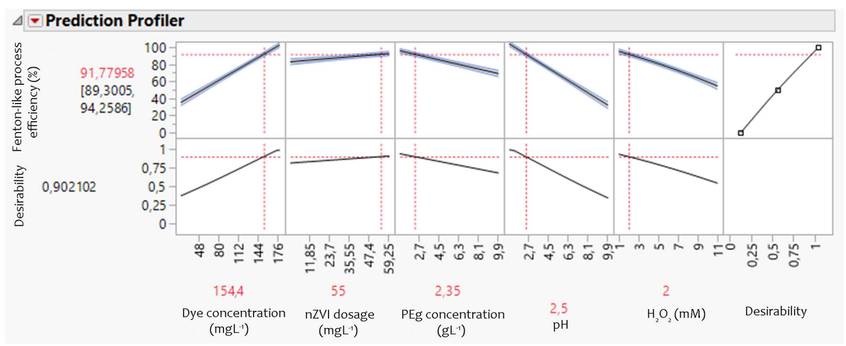

Figure 2

Optimization diagram for Fenton-like process

Statistical analysis revealed that all main process parameters are statistically significant and contribute to the decolorization efficiency. Furthermore, all single terms are a part of four significant two-way interactions, whereby dye concentration, pH and H_2O_2 concentrations are involved in two significant interactions.

From the surface plot diagram, it follows that maximal Fenton process efficiency is reached when nZVI dosage is kept at its high level (60 mgL^{-1}), while dye concentration increases from 20 to 180 mgL^{-1}. However, maintained at low level (1 mM), H_2O_2 concentration exhibits the most pronounced influence on the impact of PEg concentration on dye removal. The phenomenon can be ascribed to the fact that dye removal can be achieved with both advanced oxidation process and adsorption process of dye on MPs surface.

Conclusion

The obtained results indicated that possible adsorption dye mechanism with the simultaneous Fenton process is conduction. Nevertheless, further investigation should be directed towards the evaluation efficiency of various treatments for the synthetic dye removal in the presence of microplastic in wastewater treatments, while focusing on possible influence of microplastic on desorption of synthetic dyes into the aquatic environment and assessment of effluent toxicity before and after treatment.

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