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Factorial experimental design for the optimization of catalytic degradation of malachite green dye in aqueous solution by Fenton process

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A B S T R A C T

This work focuses on the optimization of the catalytic degradation of malachite green dye (MG) by Fenton process "Fe^{2+}/H_2O_2". A 2^4 full factorial experimental design was used to evaluate the effects of four factors considered in the optimization of the oxidative process: concentration of MG (X_1), concentration of Fe^{2+} (X_2), concentration of H_2O_2 (X_3) and temperature (X_4). Individual and interaction effects of the factors that influenced the percentage of dye degradation were tested. The effect of interactions between the four parameters shows that there is a dependency between concentration of MG and concentration of Fe^{2+}; concentration of Fe^{2+} and concentration of H_2O_2, expressed by the great values of the coefficient of interaction. The analysis of variance proved that, the concentration of MG, the concentration of Fe^{2+} and the concentration of H_2O_2 have an influence on the catalytic degradation while it is not the case for the temperature. In the optimization, the great dependence between observed and predicted degradation efficiency, the correlation coefficient for the model (R^2=0.986) and the important value of F-ratio proved the validity of the model. The optimum degradation efficiency of malachite green was 93.83%, when the operational parameters were malachite green concentration of 10 mg/L, Fe^{2+} concentration of 10 mM, H_2O_2 concentration of 25.6 mM and temperature of 40 °C.

1. Introduction

Dye wastewater is one of the major industrial water pollution sources in developing countries. Industries such as textiles, leather, paper-making, plastics, food, rubber and cosmetics use different types of dyestuffs which also appear in the effluents discharged from some of these industries. Synthetic dyes are toxic as well as noxious, hence they must be removed immediately from aquatic sources, and otherwise they will lead to severe detrimental effect on the individual health and on the sustaining diversified flora as well as aquatic fauna. For example, malachite green (MG) is the most commonly used dye for cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite green has properties that make it difficult to remove from aqueous solutions. It belongs to the same group of triphenylmethane dyes. A lot of studies

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have reported its teratogenic [1], carcinogenic [2] and reproductive abnormalities [3] spanning its effect from various fish to mammals [4].

Dyes in wastewater can be treated by different processes like: adsorption [5–10], membranes processes [11–14], coagulation/flocculation [15–17], combined coagulation/flocculation and adsorption on activated carbon [18], biological processes [19,20], etc. Most of these methods are non-destructive and/or they generate secondary pollution, because the dyes are transferred to another phase and this phase has to be regenerated.

It was necessary to develop novel and cost-effective technologies to treat the dye wastewater. Recently, advanced oxidation technologies have been accepted as efficient ways for the degradation of toxic and refractory organics [21–29]. Advanced oxidation processes, in which oxygen-based radicals ($^{\circ}OH$, HO_2°, and $O_2^{-\circ}$) are generated in situ from water and O_2, have been applied to dye degradation. These species take part in different reactions to degrade dye molecules completely. The processes are cleaner because dyes totally decompose to low-molecular-weight compounds, CO_2 and H_2O, and no significant or solid secondary pollution is generated. Especially, Fenton processes have been proved as one of the best methods for the control of organic pollution, in which cheap and environmentally friendly reagents are employed [30].

Fenton's reaction is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in an acidic medium, which was firstly discovered by Fenton in the 1890s [31]. In the last decades, Fenton's reaction has been introduced into wastewater treatment processes, and it has been well proven that a variety of refractory organics could be effectively degraded through Fenton's reaction without producing any toxic substances in water environment [32,33].

The generation of hydroxyl radicals in Fenton process is described in the following equations [34]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\circ}OH + OH^{-}$$

$${}^{\circ}OH + \text{Pollutants} \rightarrow \text{Degradation by products}$$

Several parameters influence the Fenton process, in particular the pH of solution, the concentration of ferrous ions, the concentration of hydrogen peroxide, the stirring speed, the initial concentration of the element to deteriorate, the volume of the solution, temperature, and contact time. Studying of the effect of each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time.

Factorial design is employed to achieve the best overall optimization of a process [35,36]. The design determines the effect of each factor on the response as well as how the effect of each factor varies with the change in level of the other factors [37]. Interaction effects of different factors could be attained using design of experiments only [35,36]. This technique was used to reduce the number of experiments, time, overall process cost and to obtain better response. The advantages of factorial designs over one-factor-at-a time experiments are that they are more efficient and they allow interactions to be detected [38]. The studies using the experimental designs showed the relevance of this methodology [39,40].

In our work, the optimization of the catalytic degradation of malachite green in aqueous solution by fenton process, using a 2^4 factorial experimental design was performed. Four factors were chosen to build the full factorial design with two levels. The effects of factors and their interaction and compatibility of the chosen model with the response have been studied.

2. Materials and methods

2.1. Reagents

In all experiments, we used analytical grade chemicals. The malachite green oxalate form: $C_{23}H_{25}N_2$, C_2HO_4, 0.5[UNI002] CH_2O_4, of molecular weigh 463.5 g/mol, was supplied by Sigma-Aldrich (United Kingdom). Ferrous sulfate $FeSO_4 \cdot 7H_2O$, the sulfuric acid H_2SO_4 (95–97%) and sodium hydroxide NaOH were purchased from Sigma-Aldrich (Germany). The hydrogen peroxide H_2O_2 (30%) was obtained from Soparma (Morocco).

2.2. Experimental procedures

A stock solution of 20 mg/L was prepared by dissolving required mass of MG dye in deionized water and the other solutions were prepared by dilution. The degradation tests were performed in a beaker containing 50 mL of malachite green solution at designed concentration. The pH of the solution was adjusted to 3 by addition of H_2SO_4 (1 M). Thereafter, the required mass of ferrous sulfate was added. The Fenton reaction was initiated by adding the required volume of hydrogen peroxide (H_2O_2). The mixture was kept at a constant stirring of 300 rpm at the temperature of the experiment.

2.3. Analysis

Concentration of MG was determined by measuring absorbance at 618 nm using a TOMOS V-1100 spectrophotometer.