



Experimental design approach applied to the elimination of crystal violet in water by electrocoagulation with Fe or Al electrodes

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ABSTRACT

An experimental design methodology was applied to evaluate the decolourization of crystal violet (CV) dye by electrocoagulation using iron or aluminium electrodes. The effects and interactions of four parameters, initial pH (3–9), current density (6–28 A m⁻²), substrate concentration (50–200 mg L⁻¹) and supporting electrolyte concentration (284–1420 mg L⁻¹ of Na₂SO₄), were optimized and evaluated. Although the results using iron anodes were better than for aluminium, the effects and interactions of the studied parameters were quite similar. With a confidence level of 95%, initial pH and supporting electrolyte concentration showed limited effects on the removal rate of CV, whereas current density, pollutant concentration and the interaction of both were significant. Reduced models taking into account significant variables and interactions between variables have shown good correlations with the experimental results. Under optimal conditions, almost complete removal of CV and chemical oxygen demand were obtained after electrocoagulation for 5 and 30 min, using iron and aluminium electrodes, respectively. These results indicate that electrocoagulation with iron anodes is a rapid, economical and effective alternative to the complete removal of CV in waters. Evolutions of pH and residual iron or aluminium concentrations in solution are also discussed.

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1. Introduction

Crystal violet (CV) belongs to the triarylmethane dye family and is largely used in the paper, leather, cosmetic, and food industries. The textile industry consumes large quantities of these dyes for nylon, wool, cotton, and silk, as well as for colouring oil, fats, waxes, varnish, and plastics [1]. Furthermore, triphenylmethane dyes are applied as staining agents in bacteriological and histopathological applications. These compounds in wastewater cause colouration and also represent a serious risk to aquatic life. In addition, their presence in drinking water constitutes a potential human health hazard.

Biological processes are the most economical option for eliminating organic pollutants. However, due to the toxicity of the dye, the application of such substances is restricted. Physicochemical methods based on the production and use of hydroxyl radicals called advanced oxidation processes (AOPs) (e.g. H₂O₂ + UV,

UV + O₃, H₂O₂ + O₃, TiO₂ photocatalysis, Fenton's reagent, photo-Fenton), have been successfully tested for the elimination of dye compounds [2,3]. However, these methods often lead to secondary products that are not significantly eliminated by the same technique and can be more hazardous than the original compound [4–6]. Additionally, due to the hydroxyl radical scavenger effect, these processes have limited applications in waters containing large quantities of inorganic ions.

Electrocoagulation (EC), using iron or aluminium electrodes, has been effectively tested in the treatment of a variety of dye effluents [7–9]. This technique is very attractive from an economical point of view since the equipment is easy to install and operate, it reduces the production of sludge, it does not use chemical products as coagulant agents, the process is easy to control and the reaction time is short.

Two mechanisms have been proposed for iron electrocoagulation which can be summarised as follows [7,8]:

Mechanism 1

Anode:



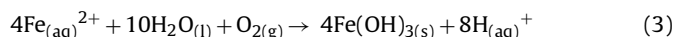
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E-mail address: rtorres@matematicas.udea.edu.co (R.A. Torres-Palma).

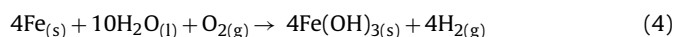
Cathode:



Bulk solution:



Overall:

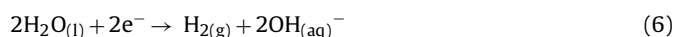


Mechanism 2

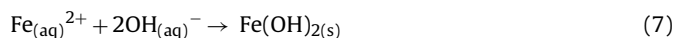
Anode:



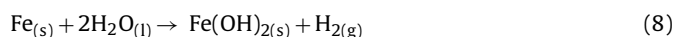
Cathode:



Bulk solution:



Overall:

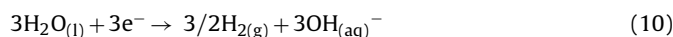


When aluminium electrodes are used, the most commonly accepted mechanism can be summarised by the following reactions [9]:

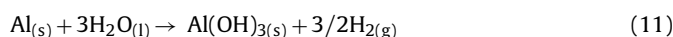
Anode:



Cathode:



Overall:



Both iron and aluminium hydroxides, generated during electro-coagulation with iron or aluminium electrodes, respectively, can remove dye molecules by sedimentation or H_2 flotation prior to surface complexation or electrostatic attraction of the formed particles [7].

When compared with traditional flocculation and coagulation processes, electrocoagulation has, in theory, the advantage of removing small colloidal particles, since they have a higher probability of being coagulated due to the electric field that sets them in motion. Furthermore, excessive amounts of coagulants can be avoided, due to their in situ generation by electro-oxidation of a sacrificial anode.

In the present work, we have studied the influence of important electrocoagulation parameters (initial pH, current density, substrate concentration and supporting electrolyte concentration) using two types of sacrificial anodes, iron and aluminium electrodes, on the elimination of a triarylmethane dye model, CV, using an experimental design methodology. This methodology provides a systematic way of working that allows conclusions to be drawn about the variables (or combinations of variables) that are most influential in the response factor while carrying out the minimum number of experiments [10].

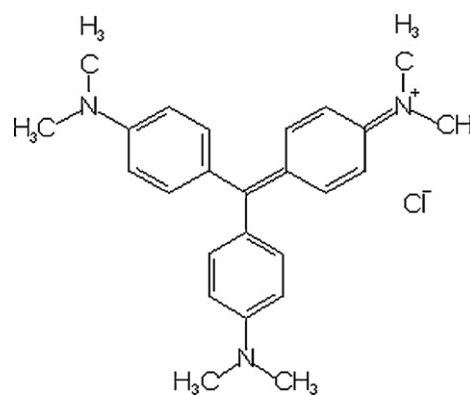


Fig. 1. Chemical structure of crystal violet.

2. Experimental

2.1. Reagents

Crystal violet (Fig. 1) was purchased from Aldrich. Anhydrous sodium sulphate, sulphuric acid and sodium hydroxide were provided by Merck. Distilled water was used throughout for the preparation of aqueous solutions.

2.2. Electrochemical cell

The experimental set-up is shown in Fig. 2. All experiments were performed, under galvanic conditions and magnetic stirring, in a 1000 mL acrylic cell containing the dye dissolved in distilled water (500 mL). Seven monopolar electrodes, four cathodes and three anodes, each one of 0.012 m², were interspersed in the cell. The anodic electrodes consisted of iron or aluminium plates, while the cathodic electrodes were stainless steel plates. The spacing between electrodes was 1.1 cm. The electrodes were connected to a digital dc power supply (Thurlby Thandar Instruments).

Even though NaCl is the most common supporting electrolyte used for electrocoagulation process, its use remains controversial due to the possible formation of organic chlorine by-products. In a recent paper [11], it was shown that Na₂SO₄ is the best supporting electrolyte for the electrocoagulation process, from an economical, effective and environmental point of view. Therefore, Na₂SO₄ was selected as the support electrolyte in this work.

The electrolytic medium was made basic or acidic as required by the addition of aqueous NaOH or H₂SO₄, respectively; and once the current density was chosen, the coagulation was started and samples were taken at different time intervals. The samples were allowed to settle for 15 min in a vessel before analysis after which the solution was filtered and the filtrate was analyzed. The solution in the electrolytic cell was sampled periodically for UV, pH, atomic absorption and chemical oxygen demand (COD) analysis.

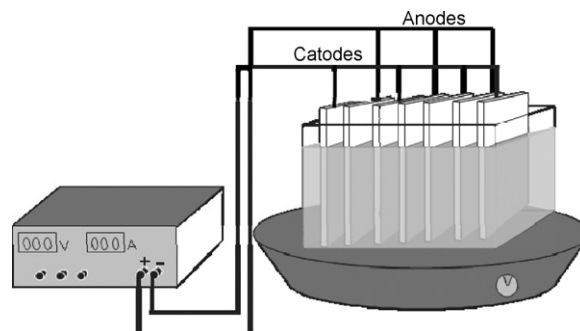


Fig. 2. Electrochemical reactor.

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