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Industrial wastewater treated by galvanic, galvanic Fenton, and hydrogen peroxide systems

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ABSTRACT

Industrial wastewater containing effluents from 190 factories located at an industrial park in Toluca State, Mexico, was subjected to galvanic (GT), galvanic Fenton (GF), and hydrogen peroxide treatments to remove organic matter. The galvanic system uses iron-copper electrodes to produce Fe^{2+} in situ. For the GF system, hydrogen peroxide was applied to produce hydroxyl radicals. The GF system does not require energy, unlike the analogous electro-Fenton system, and, in fact, it is possible to generate an electric current (~220 mV) from the chemical reactions. A synergistic effect was observed with GF treatment at pH 2.8 and a H_2O_2/Fe^{2+} ratio of 19:1 (i.e. 7840 mg H_2O_2/L and 408 mg Fe^{2+}/L), leading to high removal percentages for color (76%), soluble chemical oxygen demand (71%), and total organic carbon (79%), while degradations of 43% and 48% were achieved for biochemical oxygen demand and nitrates, respectively.

Fluorescence and IR spectroscopy analyses of raw and treated wastewater samples were performed with the aim of establishing the anthropic origin of the dissolved organic matter. Fluorescence spectroscopy showed that GF treatment eliminated the anthropogenic organic matter associated with aromatic groups and proteins, enhanced effluent biodegradability, did not increase toxicity, and reduced the sub-lethal effects observed for lettuce radicles. Most importantly, the removal efficiencies of GF treatment were comparable with those of analogous electrochemical advanced oxidation processes based on Fenton reactions.

1. Introduction

Two million tons of wastewater are discharged into the world's waterways daily [1]. This wastewater has a complex composition, comprising mainly organic matter, organic refractory compounds, inorganic ions (such as nitrates, sulfates, and phosphates), total dissolved solids, suspended material, dyes, detergents, fats and oils, and recently emergent compounds such as pharmaceuticals, personal care products, and hormones [2]. All these materials have environmental and human health effects, ranging from eutrophication and generation of anaerobic conditions in water bodies to carcinogenic, mutagenic, and teratogenic effects in humans [3–5].

It is estimated that the Upper Course of the Lerma River (UCLR), a drainage basin that is associated with an area of 2118 km^2 located in the State of Mexico, receives 536 × 10^6 m^3 of municipal and industrial wastewater per year, both treated and untreated, from approximately 20 municipalities and the hundreds of industries located in the industrial parks in Toluca city. Consequently, the river carries an organic load of 350,946 tons, 33% of which comes from urban discharge and 67% of which originates from industrial discharge [6]. Approximately 190 factories located at the industrial park in Toluca State, Mexico send the wastewater they generate during industrial production for centralized treatment before it is discharged into the environment. The influent is typically treated by primary sedimentation, biological treatment, and secondary sedimentation. However, the soluble chemical oxygen demand (COD) at the end of the treatment train is around 1500 mg/L, with a biodegradability index (BI), defined as the biochemical oxygen demand (BOD)/COD ratio by Metcalf and Eddy, of

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around 0.2 [4]. This is a matter of concern because wastewater with a BI index lower than 0.5 is considered poorly biodegradable [7]. In addition, this wastewater has a persistent brown color, caused mainly by the presence of humic acids and melanoidines, and exhibits high salinity, which translates into high electrical conductivity. The treated wastewater also contains dissolved solids that are inorganic and may constitute the majority of the pollutants in the wastewater (80%). The fixed solids in the wastewater correspond to cations and anions such as Na^+, K^+, Cl^-, SO_4^{2-}, and PO_4^{3-}, and the wastewater is also excessively alkaline owing to the presence of HCO_3^-. The biodegradability index is low because of the large quantity of inert COD.

Established technologies such as biological treatments are no longer able to remove persistent compounds [8]. Furthermore, environmental regulations and their enforcement have become more stringent, so there is growing interest in the development of new treatment methods.

A combination of advanced oxidation processes (AOPs) and advanced electrochemical systems has been developed for the removal of persistent organic pollutants and represent an attractive alternative to conventional methods [9–15]. These techniques involve the use and generation of strong oxidant species, O_3, H_2O_2, and hydroxyl radicals (·OH) [10,12,14], a highly reactive species that acts as a higher oxidant to destroy refractory compounds and has an electrochemical oxidation potential (EOP) of 2.80 V. Its attack mode is non-selective, it can operate at normal temperature and pressure, and it can oxidize almost all materials in wastewater [4].

Consequently, electrochemical AOPs have been successfully employed for the treatment of leachates [16,17], municipal wastewater [18], and dyes [19,20]. A more recent classification of these techniques includes electrocoagulation, which uses sacrificial iron or aluminum anodes to induce coagulation or flotation of pollutants; anodic oxidation and electroperoxidation for in situ and bulk pollutant oxidation by $\cdot OH_{(physisorbed)}$, H_2O_2, and O_3 oxidants; and electro-Fenton treatment and peroxicoagulation, which exploits the Fenton reaction (Reaction (1)) between H_2O_2 produced at the cathode and Fe^{2+} added or produced at the anode to oxidize and coagulate pollutants [21]. However, although renewable energy sources can be incorporated into these systems [22], all the methods mentioned above require external energy and expensive electrode materials such as boron-doped diamond, Pt, and IrO_2, making these treatments an expensive option.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\circ} \quad (1)$$

Given the current global energy crisis, galvanic systems such as those used in cathodic and anodic protection (employed to prevent the corrosion of metals) that do not require external energy to produce metal ions have been developed as an alternative method to treat wastewater. The principles of these systems may be explained by considering the corrosion of a typical metal (M) in an acidic environment. The electrochemical reactions that occur are basically the dissolution of the metal and the evolution of hydrogen gas:

$$M \rightarrow M^{n+} + ne^- \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \quad (3)$$

The active metal serves as a sacrificial anode in the electrochemical couple as it is consumed. Oxidation and dissolution of the sacrificial metal is faster in a galvanic couple than they would be for an individual metal. Likewise, if the M^{n+} species needs to be controlled, the cathodic/anodic area can be optimized [23]. Consequently, in previous studies, galvanic reactors have been investigated for the treatment of industrial wastewater containing hexavalent chromium. In these studies, the ratio of anode/cathode areas and pH were optimized, leading to excellent results, i.e., the removal of 100, 92, 50, and 38% Cr(VI), chlorides, nitrates, and sulfates, respectively, in batch mode [24].

Accordingly, the aim of this study was to propose and evaluate an industrial wastewater treatment method involving the application of a galvanic system and a novel galvanic Fenton (GF) system to remove the organic matter from industrial effluent. Iron-copper electrodes were proposed as the anode/cathode in both systems. These electrodes produce Fe^{2+} ions that, in the galvanic system, induce coagulation of organic matter and, in the GF system, oxidize organic matter through the Fenton reaction that occurs upon the addition of hydrogen peroxide. It is important to mention that neither the galvanic nor the GF systems require energy, unlike the analogous electro-Fenton system, peroxicoagulation, and electroperoxidation. Thus, the system is inexpensive, sustainable, self-contained, and portable for operation in remote locations.

2. Materials and methods

2.1. Sampling and characterization of wastewater

A combined sample was obtained from six simple samples of wastewater taken before the primary clarifiers in an industrial wastewater treatment plant that receives the effluent from 190 factories in different sectors, including chemical, food, and pharmaceutical manufacturers, slaughterhouses, municipal waste sources, and tanneries. Three-hour periods were allowed to elapse between the taking of each simple sample over the course of a 16-h operation in order to obtain a representative sample of the influent. The sample was collected in a plastic container and was stored at 4 °C prior to physicochemical characterization and further treatments.

Raw and treated wastewater samples were characterized physicochemically to compare results and evaluate the removal efficiencies. The parameters, determined according to standard methods [25], were color, total organic carbon (TOC), total inorganic carbon (TIC), total carbon (TC), pH, temperature, turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), acidity, alkalinity, total suspended solids (TSS), total dissolved salts (TDS), electrolytic conductivity (EC), total phosphorous (P_T), sulfates (SO_4^{2-}), hardness, chlorides (Cl^-), and metals (calcium, magnesium, sodium, potassium, iron, and copper). The standard methods used to determine these parameters were HACH TNT-40 and TNT-21 for total nitrogen (N_T), HACH TNT-831 for ammoniacal nitrogen (N-NH_3), HACH TNT-835 for nitrates (N-NO_3^-), HACH TNT-839 for nitrites (N-NO_2^-), and HANNA H13844 for residual H_2O_2. Additionally, fluorescence spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), and acute toxicity analysis were performed.

2.2. Galvanic treatment (GT)

The galvanic system was designed for use in a 1-L glass cell considering the following criteria: a) a monopolar system comprising parallel carbon steel (SAE 1010) electrodes as sacrificial iron anodes and electrolytic copper as cathodes was used (the electrodes were conditioned previously by sanding and polishing with alumina, followed by washing with distilled water and immediate drying); b) an inter-electrode gap of 2 mm; c) an electrode area/liquid volume ratio suggested by Holt [26] of 124–500 cm^2/cm^3; and d) an optimum copper-iron area ratio of 3.5:1, as reported by Lugo et al. [23], to maintain the iron corrosion rate. Fig. 1 shows the experimental set-up.

A 0.5 L sample of the selected industrial wastewater was added to a batch system so that it entirely covered the electrodes. The treatment was carried out over 4 h. The operational pH values evaluated were 2.8, 4.0, and 5.0. In the course of the treatment time, aliquots were taken for monitor-control parameters such as COD, TOC, color, and turbidity. Finally, the whole procedure was performed in triplicate.

2.3. GF treatment

For the GF treatment, galvanic design, volume, time, and pH values were investigated. To promote the generation of ·OH radicals and