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Evaluating removal of metribuzin pesticide from contaminated groundwater using an electrochemical reactor combined with ultraviolet oxidation

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ABSTRACT

The main purpose of this study was to evaluate the removal of the pesticide metribuzin from contaminated groundwater by means of an electrochemical reactor equipped with iron cylindrical concentric bipolar electrodes. The optimization of the experimental parameters such as current density, pH, initial concentration of metribuzin and salt concentration, for pesticide removal was first assessed. The elimination of the pollutant was found to be up to 89%. When this electrochemical process was combined with an ultraviolet oxidation process, the contaminant removal rate reached 95%. However, the results also suggested that the addition of hydrogen peroxide may reduce the process performance possibly due to increased turbidity.

1. Introduction

Pesticide (i.e. insecticides, herbicides and fungicides) contamination of groundwater is a major health concern. These contaminants, for example, have been detected in the milk from lactating women [1,2]. The herbicide metribuzin has been used to control grasses as well as broadleaved weeds in soya beans, potatoes, tomatoes, sugar cane, alfalfa and asparagusone [3,4]. In Algeria, approximately 95,000 ha of potatoes are grown annually, with metribuzin being applied to three quarters of the land mainly during pre-emergence to control grasses and weeds [3]. Reports suggest that leaching of metribuzin to lower soil profiles is the main factor responsible for the loss in its activity [5,6].

Metribuzin, which is a colorless crystal with a slight sulphur odour and is highly water soluble (1.05 g/L), is considered as a general use pesticide which belongs to the group of triazinone herbicides. Its adsorption in low-organic sandy soils is rather weak; sorption coefficients varying from 0.56 in a very sandy loam to 31.7 in a soil containing 60% organic matter [7]. The pesticide is considered to be of short to moderate persistence in soils. The half-lives measured have been specified between 5 and 50 days [8]. Furthermore, the inhalation and/or ingestion of this contaminant may induce a nervous breakdown in humans. The maximum allowable concentration limit in drinking water is 0.08 mg/L (WSSA, 1983).

The removal of pollutants from effluents or contaminated water by electrocoagulation (EC) has become an attractive method [9–13]. The EC process consists of creating metallic hydroxides flocs within wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions may be summarized as follows. Compression of the diffuse double layer occurs around the charged species by the interactions of ions generated by oxidation of the sacrificial anode. This is followed by charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process. Finally floc is formed as a result of the coagulation and this creates a sludge blanket that entraps and bridges colloidal particles that are still remaining in the aqueous medium [14]. In addition, water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and float the pollutants to the surface through buoyancy [15,16].

In an electrocoagulation reactor consisting of one anode and one cathode, when a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals.

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The reactions with metal M as anode may be summarized as follows:
At the anode:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad (1)$$

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \quad (2)$$

At the cathode:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \quad (3)$$

$$2H_2O_{(l)} + 2e^- \rightarrow 2H_{2(g)} + 2OH^- \quad (4)$$

If iron or aluminum electrodes are used, the generated Fe^{3+} or Al^{3+} ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. These compounds have a strong affinity for dispersed particles as well as for counter ions thus causing coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials [17]. The electrocoagulation technique can be used to effectively treat a variety of wastewaters including from restaurants [18], textile mills [19], and electroplating industry [20]. It has also proven effective for defluoridation of drinking water [21–25].

It is generally believed that a typical E-Fenton reaction should involve three key reactions: the generation of hydroxyl radicals ($^{\bullet}OH$) between H_2O_2 and Fe^{2+} (Reaction 5), and by photocatalytic effect of UV irradiation (Reaction 14), the degradation of organic substance by the $^{\bullet}OH$ (Reaction 15), and (16).

The metribuzin degradation depends upon H_2O_2, pH and the presence of UV lamp. Hence the following mechanisms of electrochemical oxidation can be proposed:In anodic reaction

$$Fe(s) \rightarrow Fe(aq)^{2+} + 2e^- \quad (5)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (6)$$

At cathodic reaction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (7)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (8)$$

This shows hydrogen peroxide to be the product of a two electron transfer to oxygen. However, if oxygen is reduced by a four-electron process, water is formed as the end product:

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \quad (9)$$

Hydrogen peroxide can reduce further to water

$$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (10)$$

In alkaline media, the reaction stoichiometry is given by

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^- \quad (11)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (12)$$

The per hydroxyl ion (HO_2^-), is formed by hydrogen peroxide dissociation in base

$$H_2O_2 \rightarrow H^+ + HO^{2-} \quad (13)$$

In presence of UV lamp

$$H_2O_2 + \lambda h \rightarrow 2OH^{\bullet} \quad (14)$$

$$^{\bullet}OH + \text{metribuzin} \rightarrow \text{metribuzin intermediate} \quad (15)$$

$$^{\bullet}OH + \text{metribuzin intermediate} \rightarrow CO_2 + H_2O + \text{mineralization product} \quad (16)$$

The main purpose of the current work was to evaluate the removal of pesticide from contaminated groundwater using an electrochemical reactor equipped with cylindrical concentric iron electrodes and combined with an ultraviolet oxidation technique. Metribuzin was used as the model contaminant. The pesticide removal process was optimized by taking into account current density, pH, salt concentration, and pollutant concentration.

2. Materials and methods

2.1. Materials

Metribuzin is a complex molecular with formula $C_4H_{14}N_7OS$ and systematic name 4-amino-6-tert-buthyl-3-méthylthio1,2,4-triazine-5 (4 H)-one. The main physicochemical characteristics of this pesticide are given in Table 1. A synthetic metribuzin solution was prepared with deionized water. The metribuzin concentration of the solutions studied was in the range of 50–300 mg/L. The values used in our study were similar to those measured in discharges from metribuzin manufacturers. The metribuzin concentration in the contaminated water solution was determined with a spectrophotometer (SHIMADZU, 1240CE) at a wave length $\lambda = 293$ nm. The peroxide solution used was 50% in mass. The advantage of working with this high concentration is that it adds very little volume (in the order of a microliter) to the reactor containing the metribuzin solution. The peroxide concentration employed varied between 5×10^{-4} and 0.1 M. The effect of supporting electrolyte (S) on metribuzin removal was studied using NaCl with a concentration in the range of 0.01 to 1 g/L.

2.2. Equipment

The electrochemical reactor (Fig. 1) was equipped with cylindrical coaxial electrodes. The internal electrodes were iron metal and the external electrode used as the cathode was stainless steel. The cathode had a diameter of 85 mm and length of 300 mm. The smallest iron electrode diameter was used as the anode. Two sacrificial cylindrical electrodes were placed between the two parallel electrodes without any electrical connection when an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared with the parallel side beside it. The sacrificial electrodes are known as bipolar electrodes. This electrode is commonly called the bipolar electrode. Three intern electrodes have diameters of about 55, 65, and 75 mm and height of about 275 mm. The photocatalytic electrochemical reactor was equipped with a mercury lamp (Kadatyn, France) with an output power of 14 W, which mainly emits irradiation at 253.7 nm and can be considered monochromatic. The lamp was inserted in the central compartment near the anode.

Table 1
Physicochemical characteristics of metribuzin [3].

Molecular weight	M = 214.3
Water solubility at T = 20 °C	1.2 g/L
Vapour pressure	$1 \cdot 310^{-3}$ Pa
Octanol–water partitioning coefficient	1.70
Fusion temperature	125 °C
Density d^{25}	1.28 mg/mL