



An in situ electrosynthesis of metal hydroxides and their application for adsorption of 4-chloro-2-methylphenoxyacetic acid (MCPA) from aqueous solution



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ABSTRACT

This research article deals with an in situ electrosynthesis of metal hydroxides by anodic dissolution of different sacrificial anodes and their application for the adsorption of 4-chloro-2-methylphenoxyacetic acid (MCPA) from aqueous solution. Materials like iron, magnesium, zinc and aluminum are used as sacrificial anodes. The optimization of different experimental parameters like initial concentration, current density, pH, temperature, inter electrode distance etc., on the removal efficiency of MCPA was carried out. The maximum removal efficiency of 83.72% was achieved with magnesium as sacrificial anode at a current density of 0.10 A dm^{-2} and pH of 7.0. The adsorption of MCPA preferably followed the Langmuir adsorption isotherm. The adsorption kinetic studies showed that the adsorption of MCPA was best described using the second-order kinetic model. Thermodynamic parameters indicate that the adsorption of MCPA on magnesium hydroxides was feasible, spontaneous and endothermic. Results from the pilot plant study confirm the laboratory scale study. FTIR analysis confirmed that MCPA was adsorbed on to the magnesium hydroxide.

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Introduction

Industrial, agricultural and commercial augmentation in many countries around the world in the recent decades has been accompanied by rapid generation of municipal and industrial wastewater, which creates the most serious environmental problems to humans and animals [1]. Among the emerging organic contaminants that have been detected in wastewater, ground water and surface water include pesticides, herbicides, dyes, pharmaceuticals and personal care products etc. These types of contaminants are daily released into many types of wastewaters and enter into natural water channels to be accumulated in the aquatic environment [2–7]. These contaminants cannot be significantly reduced in conventional wastewater treatment plants because the vast majority of these compounds are persistent organic pollutants (POPs), owing to their high stability to sunlight and resistance to microbial attack and temperature. Their presence in water causes toxicity towards human and animals. In addition to

acute toxicity from high exposures there is concern of possible carcinogenicity as well as other long-term problems such as contributing to Parkinson's disease. Most of the organic compounds cause a range of health effects ranging from skin rashes to death. Hence, it is necessary to remove these organic pollutants from water to prevent the hazardous health effects to human beings. Research on water treatment is experiencing a new and definitive awakening, and current interest is focusing on the development of simple, safe, effective, and economical technologies for the total destruction of POPs before final disposal.

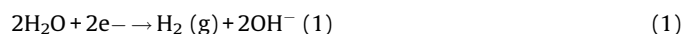
Among the persistent organic pollutants (POPs), the presence of chlorinated aromatic pesticides in the environment represents a very serious problem because of their toxicity, persistence and their widespread utilization. In particular, chlorophenoxy herbicides are used worldwide on a large scale for weed control on cereal crops, grasslands and lawns. The presence of chlorophenoxy acid herbicides in US, India and European ground waters and surface waters at relatively high contamination levels has been recently documented [8–10]. These compounds resist biodegradation and have potential toxicity towards humans and animals [11], being considered as moderately toxic (class II or III) by the World Health Organization. Their widespread use in industrialized and developing countries for agricultural and non-agricultural purposes generates

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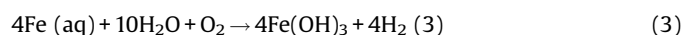
continuously reinstate, waste product and contaminated soil at hundreds of thousands of application sites. They are found as pollutants in natural waters; with contamination levels up to 10–30 $\mu\text{g L}^{-1}$ in ground and surface waters resulting millions of people are affected [12,13]. For this reason, there is great interest in the development of environmentally clean methods to destroy such compounds in aqueous medium for avoiding their dangerous accumulation in the aquatic environment.

In this scenario, the electrochemical technologies have received great attention for the prevention of pollution problems, as reported in several books and reviews [14–18]. Its main advantage is its environmental compatibility since the electron, the main reagent, is a clean reagent. Electrochemistry also offers other advantages such as versatility, high energy efficiency, amenability of automation, and safety because it operates at mild conditions. Comparing with electrochemical technologies, electro-dissolution process, where the adsorbents are generated by in situ, is an efficient and cost-effective method for removing organic pollutants [19]. Also this process is found to be more effective than advanced oxidation process (e.g., UV/TiO₂) for removal of organic compounds in terms of intermediate formation, removal efficiency, cost of the process and electrical energy consumption [20,21]. Although electro-dissolution process has been utilized for over a century, the available literature reveals little studies on the removal of herbicides by this method. The primary reactions taking place in the cell with different anode materials are as follows [19],

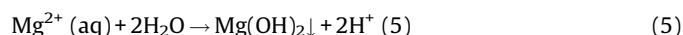
At the cathode:



At the anode, (when iron as sacrificial anode)



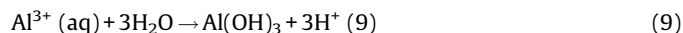
(when magnesium as sacrificial anode)



(when zinc as sacrificial anode)



(when aluminum as sacrificial anode)



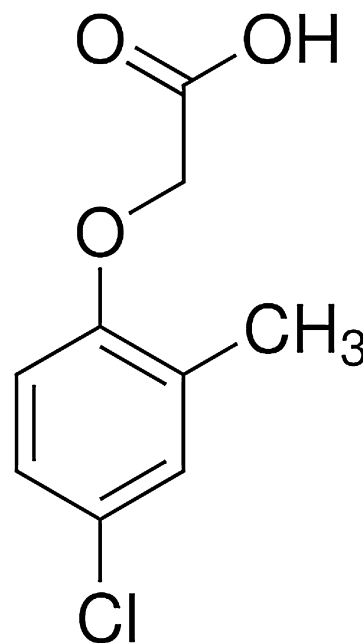
To optimize the maximum removal efficiency of MCPA, different parameters like effect of anode materials (iron, magnesium, zinc and aluminum), initial concentration, temperature, pH, current density and inter electrode distance were studied. In doing so, the equilibrium adsorption behavior is analyzed by fitting models of Langmuir, Freundlich and D–R. The adsorption kinetics was modeled by first- and second-order rate, Elovich and Weber and Morris intra-particle diffusion models. Activation energy is evaluated to study the nature of adsorption.

Materials and methods

The experiments were carried out in a monopolar batch reactor using 1.0 L Plexiglas vessel that was fitted with a polycarbonate cell cover with slots to introduce the electrodes, pH sensor, a thermometer and the electrolytes. Iron (commercial grade, India), magnesium (commercial grade, India), zinc (commercial grade, India) and aluminum (commercial grade, India) of surface area (0.02 m²) acted as the anode. The cathode was galvanized iron (commercial grade, India) sheets of the same size as the anode is placed at an inter-electrode distance of 0.003 m. The temperature of the electrolyte was controlled to the desired value with a variation of ± 2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. A regulated direct current (DC) was supplied from a rectifier (10 A, 0–25 V; Aplab model).

The required concentration of 4-chloro-2-methylphenoxyacetic acid (MCPA) (Aldrich, USA) was prepared using Milli-Q water. The chemical structure of MCPA is shown in Scheme 1. The solution of 0.90 L was used for each experiment as the electrolyte. The pH of the electrolyte was adjusted and measured by a pH meter (DKK-TOC, Japan) at the beginning and during the experiment. After adjusting the initial solution pH to the desired value (2–13), the current density was set. The pH was adjusted using either 0.1 M NaOH or 0.1 M HCl as necessary. Magnetic stirring at 250 rpm provided a homogeneous solution in the batch reactor. During the electrolysis, pH of the solution was monitored and at specified time intervals, samples were taken for analysis. Temperature studies were carried at varying temperature (303–333 K) to determine the type of reaction.

The MCPA was quantified by HPLC (Shimadzu, Japan) which consists of a pump, C18 reversed phase column and UV/vis detector. The mobile phase was a mixture of acetonitrile and water in a ratio of 50:50 and then was added 0.05% (v/v) phosphoric acid. The elution flow rate was adjusted to 1.0 mL min⁻¹ and the injection volume was 10 μL . The UV/vis detector wavelength was set at 289 nm, which is the maximum absorbance wavelength of MCPA determined by scanning its spectra from 200 to 900 nm using a spectrophotometer (Merck, Germany). The SEM of



Scheme 1. Chemical structure of 4-chloro-2-methylphenoxyacetic acid (MCPA).

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