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Electrochemically assisted coagulation for the adsorptive removal of dimethyl phthalate from aqueous solutions using iron hydroxides

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ABSTRACT

In this study, the adsorptive removal of dimethyl phthalate (DMP) from aqueous solutions by electrochemically generated iron hydroxides was investigated in batch mode. Four electrode pairs were used to characterize the performance of electro-coagulation (EC) for the DMP removal efficiency. Experimental results indicated that a Fe/Al electrode pair was the optimum choice out of four different electrode pair combinations. In addition, the effects of varying current density and solution temperature on DMP adsorption characteristics were evaluated. The findings indicated that complete DMP removal could be achieved within reasonable removal efficiency and with relatively low electrical energy consumption. The optimum current density and temperature were found to be 20 mA/cm^2 and 298 K, respectively. Thermodynamic parameters, including the Gibbs free energy, enthalpy, and entropy, indicated that the DMP adsorption of aqueous solutions on metal hydroxides was feasible, spontaneous and endothermic in the temperature range of 288–318 K. The experimental data were fitted with several adsorption isotherm models to describe the EC process. The adsorption of DMP preferably fitting the Langmuir adsorption isotherm suggests monolayer coverage of adsorbed molecules.

1. Introduction

Over the years, a variety of electrochemical technologies have been proposed in wastewater treatment for environmental remediation, and there has been an increasing interest in the use of electrochemistry for environmental applications. These methods can prevent pollution problems from industrial effluents because of their versatility and environmental suitability; their main reagent, the electron, is a clean one [1]. Electrochemical methods offer some advantages over traditional chemical treatment: less coagulant ion is required, less sludge is formed, and equipment is very compact; thus, suitable for installation where the available space is rather limited. In addition, the convenience of dosing control only by adjusting current makes automation quite easy. Electrocoagulation (EC) is an electrochemical method of treating polluted water whereby sacrificial anodes dissolve to produce active coagulant precursors into solution. The electrochemically generated metallic ions hydrolyze near the anode to form a series of metal hydroxides that act to destabilize dispersed particles present in the wastewater to be treated. The destabilized particles are responsible for the aggregation and precipitation of suspended particles and for the adsorption of dissolved pollutants. Simultaneously, electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode that can enhance the process; this effect is known as electroflotation (EF) [2]. A lot of studies have proved the viability of the EC technology, which is able to eliminate a variety of pollutants from water and wastewaters, such as potable water [3], metal laden wastewater [4], dyeing wastewater [5], chemical mechanical polishing wastewater [6], restaurant wastewater [7], and wastewater containing salicylic acid [8], cadmium [9], indium [10], nitrobenzene [11], and polyvinyl alcohol [12]. To our knowledge so far, very little work, if any, has been reported in the literature to date on the removal of DMP and the adsorption of DMP onto iron hydroxides produced during the EC process in aqueous solutions.

Many environmental hormones such as phthalic acid esters have been occurred in wastewater from the manufacturing process and drinking water from the water treatment plant [13]. Phthalic acid esters (PAEs), known as dialkylesters of 1,2-benzenedi-carboxylic acid, are a group of organic compounds that are commonly used in the industrial production. Their main applications are as plasticizers for the production of polyvinyl chloride resins, cellulose film coating and adhesives in order to improve the flexibility and softness of the plastic resin. Other applications are in cosmetics, pharmaceuticals, building materials, medical devices, food packing, insecticide carries and propellants [14]. The current global productions including

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manufacturing of household goods amount to several million tons per year, and such large utilization and production are leading to a considerable environmental migration of these compounds [15]. PAEs can enter the human food chain and be known with their hazardous impact on the environment and on humans due to their carcinogenic, toxic and endocrine disrupting effects [16]. They also have been classified as priority pollutants and endocrine-disrupting compounds by the United States Environmental Protection Agency and several other countries [17]. DMP, which is a short-chain ester with two carboxyl groups on the aromatic ring, is used in cellulose-ester-based plastics and is one of the most common phthalic acid esters. DMP has been recognized a crucial environmental pollutant and has been commonly detected in natural ecosystems because of its high mobility in the aquatic system. DMP is also an endocrine-disrupting chemical which may promote chromosome injuries in human leucocytes and interfere with the reproductive system, making it as an aqueous pollutant of concern in water and wastewater systems. These pollutants are refractory to the environmental microorganism and regarded as the conspicuous influence on the ecological environment [18].

Therefore, there is a growing interest in the development of a satisfactory treatment process for the removal of DMP in aqueous solutions. Several studies have found that some phthalates with long alkyl-chains may be refractory to biological treatment [17]. A considerable amount of scientific work has focused on chemical oxidation methods which provide the destruction of DMP, most of which has focused on photocatalytic degradation using titanium in aqueous suspension [19]. Other chemical oxidation studies related to the degradation of DMP used methods such as Fenton and Photo-Fenton processes [17], ozonation with silica zeolite and UV radiation [20], ozonation with Ru/Al_2O_3 catalyst [21], catalytic ozonation with TiO_2/Al_2O_3 [22] and UV/H_2O_2 advanced oxidation process [23]. However, little attention has been paid so far to the development of an electrocoagulation technology for the adsorptive removal of DMP using iron hydroxides.

In this study, electrochemical process parameters such as type of electrode pair, current density, and solution temperature were investigated in terms of their effects on the DMP removal. The effects of the current density and solution temperature on specific energy consumption (SEC) for DMP removal were also evaluated. In addition, the adsorption thermodynamics, and isotherms characteristics involved in the DMP removal of the aqueous solution were also carried out to lay a theoretical foundation for the adsorption of DMP from aqueous solutions onto iron hydroxides.

2. Materials and methods

2.1. Chemicals and apparatus

DMP, with a chemical formula of $C_{10}H_{10}O_4$ purchased from Ferak (Berlin, Germany), has a molecular weight of 194.19 g/mol, with purity of at least 99%. Aqueous solutions containing DMP were prepared by dissolving an appropriate quantity of DMP in deionized water for EC tests. The concentration of the supporting electrolyte was adjusted by adding of NaCl (Tedia Company, USA). All of the chemicals used were at the least reagent grade. Fig. 1 shows a schematic diagram of the experimental apparatus and electrode assembly for the EC system. The cell was a 1 L glass reactor equipped with a water jacket and a magnetic stirrer. The temperature of the cell was controlled by continuously circulating water from a temperature controlled bath (Model BL-720, Taiwan). A magnetic stirrer bar (Suntex, SH-301, Taiwan) spun at the center of the bottom of the reactor. The electrode pair was dipped into an aqueous solution of DMP at a depth of 5 cm, with the two electrodes approximately 2 cm apart. The effective area of the immersed electrode pair was 30 cm^2. The assembly was connected to a direct current power source (PSM-6003, GWINSTEK).

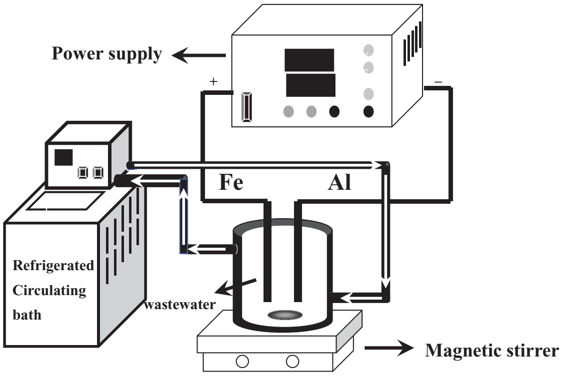

Fig. 1. Apparatus of the electrocoagulation process.

2.2. Procedure and analysis

Before each experiment, the electrodes were polished with sandpaper to remove the scale build-up and then dipped in a 3 N HCl solution at a depth of 5 cm for 10 min, and then finally cleaned with successive rinses of deionized water. During each test run, 0.5 L of aqueous solution containing DMP was placed into the reactor. The direct current power source was operated with constant current densities in 10, 20, 30, or 40 mA/cm^2. A constant temperature (288–318 K) was maintained by temperature controlled bath through the water jacket. EC test runs lasted no more than 90 min in all experiments. At the end of EC, all samples were centrifuged (Hsiangtal, Beginner's Economy Centrifuges, Taiwan) in a 15-mL centrifuge tube (set at 4000 rpm for 1 h). The DMP concentration in the aqueous solutions was determined using a HPLC (Hitachi d-2000 elite software). A calibration curve was obtained by plotting the absorbance value at 220 nm as a function of the DMP concentration. The sludge composition was confirmed with energy dispersion spectra analysis. The sample composition O, Al, Cl, and Fe are detected to be 54.17%, 5.13%, 2.48%, and 38.22%, respectively.

3. Results and discussion

3.1. Comparison of electrode pairs

In any electrochemical process, the electrode material has significant influence on the removal efficiency [24]. Hence, it is very important to select an appropriate electrode pair. Iron and aluminum usually are chosen as electrode materials because they are non-toxic. Iron and aluminum plates in four different combinations are investigated in this research to determine the optimum electrode pair. Fig. 2 indicated the effect of the electrode pair on the removal efficiency

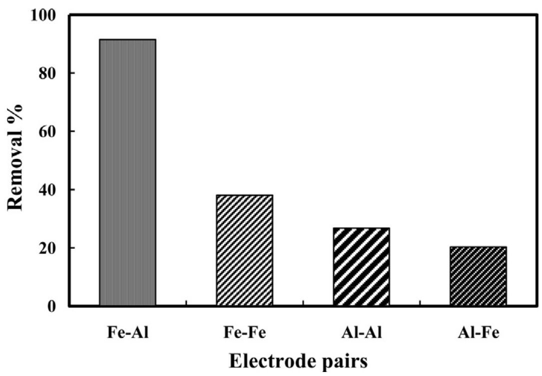

Fig. 2. Effect of different electrode pairs on the removal efficiency of DMP (C_0 = 100 mg/L, t = 60 min, current density = 20 mA/cm^2, T = 298 K).