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Effect of the continuous and pulse *in situ* iron addition onto the performance of an integrated electrochemical–ozone reactor for wastewater treatment

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HIGHLIGHTS

- Novel technology based on electrochemical–ozonation processes operated by pulses.
- We describe energy input effects (continuous and by pulses) on removing COD, color and turbidity from industrial effluents.
- Energy requirements are diminished up to half when this is pulsed without sacrificing pollutant removal efficiency.
- Sludge generation and electrodes passivation is also decreasing by pulsing operation.

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ABSTRACT

The effectiveness of electrochemical, ozone and integrated electrochemical–ozone processes on industrial wastewater treatment was evaluated. The effect of continuous and pulsing addition of energy was studied. In the electrochemical treatment under pulsing operation, the chemical oxygen demand COD removal was found to be 28% at 60 min while pulsing ozonation led to obtain 48% COD removal after 36 min. In the integrated electrochemical–ozone process with energy pulses, the COD reduction was observed to be 80% after 44 min of treatment. Initial pH was 7.5 at all experiments. Finally, the sludge produced during integrated electrochemical–ozone process with energy pulses was quantified and the morphology was evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). The amount of sludge produced and electrodes passivation after the integrated method was found to be lower than with the electrochemical method alone.

1. Introduction

Industrial effluents are difficult to satisfactorily be treated due to high variations in their compositions. In this context, there are many different techniques to improve water quality, the most common being adsorption by activated carbon, membrane filtration, ultrafiltration, coagulation–flocculation, electrocoagulation, UV light and ozone treatments [1]. In contrast, Advanced Oxidation Processes (AOPs), which involve an *in situ* generation of highly potent chemical oxidants such as hydroxyl radicals, have emerged as an important class of technologies to accelerate the non-selective oxidation. These technologies, such as Fenton oxidation, hydrogen peroxide assisted UV photochemical oxidation (UV/H_2O_2), photocatalytic oxidation (PCO), ozonation and electro oxidation with boron-doped diamond (BDD) electrodes, are widely used for the destruction of a wide range of recalcitrant organic contaminants in wastewater which cannot be biologically eliminated.

Regarding ozonation, this process implies the use of ozone which is a strong oxidant that oxidizes organic pollutants via two pathways: direct oxidation with ozone molecules and/or the generation of free-radical intermediates, such as the $^{\cdot}OH$ radical, which is a powerful, effective, and non-selective oxidizing agent [2,3]. The ozonation process has the advantage of being able to be applied when the flow rate and/or composition of the effluents are fluctuating. However, the high cost of equipment and maintenance, as well as energy required to supply the process, constitutes some of the disadvantages. Moreover, ozonation process requires the transfer of ozone molecules from gas phase to liquid phase, where the attack to the organic molecules occurs. Therefore, mass transfer limitations are also a relevant factor to be considered in the oxidation process involving ozone. In many cases, the ozone consumption rate per unit of volume can be so high that mass transfer is the limiting step, reducing the process efficiency and increasing the operating costs [4]. In addition, the ozonation performance is affected by

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the presence of organic matter, suspended solids, carbonate, bicarbonate and chlorine ions and also by pH and temperature [5]. Some studies using real industrial wastewater have pointed out that ozone by itself does not achieve high levels of pollutant removal [6]. In particular, the oxidation of wastewater from molasses fermentation with ozone results in an effective color removal but is less effective in removing organic matter [7]. Similar results were obtained when ozone was used to treat textile wastewater, since ozone treatment proves to be very effective for complete color removal but provides only partial reduction of the chemical oxygen demand (COD) [8]. Also, previous research on ozone-coupled methods indicates that the ozonation of anaerobically pretreated wastes enhances significantly the organic removal in comparison to the ozonation of unpretreated wastes, and substrate conversions in the range of 40–67% are obtained [9]. These limitations have motivated the development of complementing ozonation with other processes, i.e. electrochemical [1].

Nevertheless, it is worth mentioning that electrochemical treatments alone are interesting and promising processes to remove toxic organic compounds by applying an effective, versatile, cost-effective, ease and clean technology [10–12]. In the electrochemical processes, the oxidation occurs over anodes (graphite, TiO_2, Ti-based alloys, Ru or Ir oxides, boron-doped diamond) in the presence of an electrolyte. Pollutants can be destroyed electrochemically by a direct anodic oxidation, where pollutants are first adsorbed on the anode surface and then destroyed through the anodic electron exchange. On the other hand, if the molecules are degraded in the liquid bulk with mediation of electroactive species (such as metallic redox couples, i.e. Ag(II), Fe(III), Ce(IV), Mn(III) or strong oxidants as H_2O_2, O_3, persulfate, percarbonate, perphosphate and chlorinated species), which act as intermediaries for electrons transference between the electrode and the organic compounds, the reaction is classified as indirect [13]. The process selection depends on the nature and structure of the electrode material, experimental conditions and electrolyte composition. Usually this type of system is used to prevent electrode fouling. The efficiency of the direct oxidation depends on the electrode catalytic activity, diffusion rates of the compounds towards the active sites of the anode and the applied current, while the indirect oxidation strongly depends on the diffusion rate of secondary oxidants into the solution, temperature and pH [14,15]. Another type of electrochemical technique is electrocoagulation, in which aluminum or iron “sacrificial” electrodes are dissolved, generating *in situ* coagulant agents that destabilize colloidal pollutants and remove them from wastewater [16,17]. Electrochemical methods offer some advantages over traditional chemical treatments: less coagulant ion is required, less sludge is formed, and electrocoagulation equipment is very compact; thus its application is advised where the available space is rather limited. Furthermore, the convenience of dosing control only by adjusting current makes automation quite easy [18,19]. However, despite the proven efficiency of electrocoagulation and other electrochemical processes to treat wastewater, high energy consumption and anode passivation phenomenon have limited their further application. In this context, the advent of pulse technique has brought a significant impact on the electrochemical processes since it cannot only save energy but also shows higher activity and efficiency during the process [20–22].

In this study we propose a novel technology based on the integration of electrochemical and ozonation processes. Also, it is presented a comparison of efficiency of three wastewater treatment methods, i.e. electrochemical, ozonation and electrochemical–ozonation under two operating modes (continuous and by pulses energy input) on removing chemical oxygen demand, color and turbidity from industrial effluents.

2. Materials and methods

2.1. Wastewater samples

Wastewater samples were collected from a treatment plant of an industrial park that receives the discharge of 144 different industries (pharmaceutical, automotive, painting, textile, food and chemical). Therefore, the chemical composition of this effluent is rather complex and the presence of several compounds and functional groups are expected. Samples were collected in plastic containers and cooled down to 4 °C, then transported to laboratory for analysis and treatment.

2.2. Electrochemical reactor

A batch electrochemical reactor was constructed for the electrochemical step. The reactor cell contains an array of four paralled monopolar iron electrodes. Each electrode was 5.0 cm by 3.0 cm with a surface area of 15 cm^2. All together, the total anodic surface (A_a) was 60 cm^2. While the capacity of the reactor vessel was 1.5 L, 1.0 L was used at all experiments. A direct-current power source supplied the system with 1–4 A, corresponding to current densities of 16, 33, 50 and 60 mA cm^{-2}, in agreement with previous work [23,24]. The electrochemical iron addition was made by a continuous mode and a pulsing way. The pulsing addition was only made at a time interval of 4 min and the energy supply was interrupted for other 4 min (Fig. 1).

2.3. Ozonation reactor

The ozonation experiments were conducted in a 1.0 L glass reactor at 18 °C. Ozone was supplied by a Pacific Ozone Technology generator. The gas was fed into the reactor through a porous plate situated at the reactor bottom. The ozone concentration at the gas inlet and outlet of the reactor was measured by redirecting the flows to a series of flasks containing 0.1 M potassium iodide [25]. The mean concentration of ozone in the gas phase was 5 ± 0.5 mg L^{-1} and was measured immediately before each run. Ozonation experiments were carried out at pH 7 and samples were taken at regular intervals to measure COD, color and turbidity. The pulse addition was only made at a time interval of 4 min and the energy supply was interrupted during 4 min also.

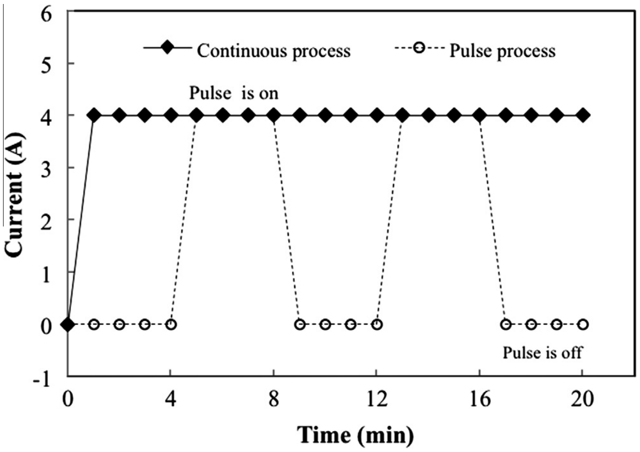

Fig. 1. Pulsed current applied mode including pulse time and relaxation time.