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Treatment of highly acidic wastewater containing high energetic compounds using dimensionally stable anode

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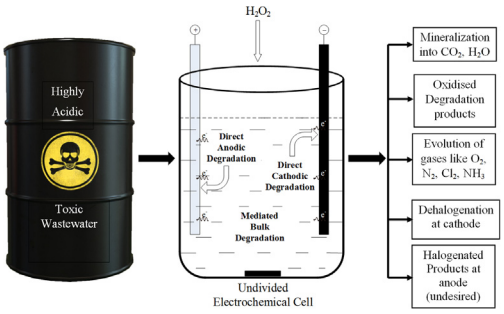
HIGHLIGHTS

- Electrochemical oxidative treatment of highly acidic wastewater by Ti/RuO_2 electrode.
- Characterization of wastewater.
- Study of effect of parameters such as initial pH, current density, H_2O_2 dose and time.
- Identification of intermediates and mineralization products by GC/MS and other techniques.
- Degradation mechanism, kinetic modeling and cost analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly acidic (pH < 2) wastewaters have toxic and carcinogenic properties and can't be treated by conventional biological treatment methods. In the work presented, investigation of the treatment of very low pH, actual wastewater containing highly energetic materials was carried out using electro-oxidation method using a dimensionally stable anode (DSA) namely ruthenium oxide coated titanium (Ti/RuO_2). Chemical oxygen demand (COD), current efficiency (CE) and specific energy consumption (SEC) were measured under various process conditions of current density (J) and time (t). Maximum COD removal efficiency of 41.83% was observed at J = 750 A/m^2, t = 150 min, and initial pH = 0.4 ± 0.1 with SEC = 1.23 kWh/kg COD. In the next phase, the addition of hydrogen peroxide (30% w/w) (H_2O_2) was done and COD degradation was evaluated by varying the dosage of H_2O_2. Maximum COD removal efficiencies of 48.83% was observed at J = 750 A/m^2, t = 150 min, pH_o = 0.3. This method produced very low or no amount of sludge and scum. The mechanistic study has been performed by carrying out scavenger study using terephthalic acid. Gas chromatography-mass spectroscopy (GC/MS), Fourier transform infrared spectroscopy and ion chromatography of the wastewater; and X-ray diffraction and Field emission scanning electron microscopy (FE/SEM) of electrodes were carried out for understanding the treatment mechanism. Operating cost analysis has been done based on the studies performed in laboratory scale EC reactor, and compared with those reported for other pollutant degradation.

1. Introduction

A number of industries such as ammunition industries/labs, pharmaceutical industries, mining sites, steel industry, electroplating and phosphorous industries discharge highly acidic effluents. This highly acidic wastewater causes severe environmental

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problems as it is highly toxic and carcinogenic. The low pH effluent engenders several problems in the effluent treatment as well as in the water body in which it is discharged. The low pH causes the heavy metal and other contaminants to dissolve, which otherwise bond with negative hydroxide ion to form dense, insoluble, metal hydroxides which are removed easily by filtering or settling. Due to this, the treatment of effluent becomes more tedious. It also affects the aquatic life adversely as such low pH doesn't allow aquatic life to sustain. Also, highly acidic medium breaks organic matter and kills any microbial growth which may help to treat the water naturally.

Many chemical industries, in particular, those manufacturing high energetic materials discharge wastewater with low pH due to the presence of high amount of nitric acid. The effluents generally have very low BOD to COD ratio which basically indicates their poor biodegradability. The wastewater can be of various varieties but some common constituents are nitro-aromatic compounds like hexamethylene, other nitrate and nitrites, waste acid like sulphuric acid, nitric acid, phosphoric Acid, etc. Other constituents may include hardness, sulphates, ammonia, fluorides, phosphates, silica, metals (Al, Fe, Mn, etc.), etc.

Conventional treatment methodology involving physio-chemical and biological pathways are generally rendered ineffective for such kind of wastewaters. Treatment methodologies reported in the literature to treat the acidic wastewater include chemical addition, advanced oxidation processes (AOP) [1], catalytic peroxidation [2], Fenton method [3], electrochemical oxidation [4,5], electro-Fenton method [6], sono-chemical [7] and photochemical processes [7]. The basic mechanism seen in these processes include degradation of pollutant by utilizing electrons as a vector. Electrochemical oxidation treatment methodology has direct or indirect treatment pathways. During direct type, the pollutant is degraded directly upon adsorption on the electrode surface, whereas, in indirect type, the oxidant (·OH, ·OOH, ·OCl, etc.) is produced in the bulk of wastewater which further degrades pollutant in the wastewater [8–10]. Electrode characteristics like electrode morphology, dimensional stability, oxygen evolution, etc. impact majorly on the efficiency of the process.

Electrodes used in electrochemical wastewater treatment are classified majorly as: sacrificial electrodes and dimensionally stable anode (DSA) electrodes. Sacrificial electrodes like aluminium or stainless steel are cheap and easily available; however, these electrodes easily get consumed in the electrochemical cell, in turn, producing sludge which act as secondary pollutant and require further handling. On the other hand, DSA type electrodes are highly stable and resistant electrodes and don't create any secondary pollutant, however, they are costlier. A number of DSA electrodes such as titanium and tantalum coated with RuO_2 [11,12], IrO_2 [12], SnO_2 [13], PbO_2, boron-doped diamond (BDD) [14], Pt/Ti [15], Ti/Pt and Ti/Pt/Ir [16], TiO_2-NTs/SnO_2-Sb [17], TiO_2-NTs/Sb–SnO_2/PbO_2 [18], RuO_2/IrO_2/TiO_2 [19], etc. have been used by various researchers for the treatment of diverse wastewaters [20]. Ti/RuO_2 is one of the highly stable electrodes which works efficiently under highly acidic conditions. It has high reusability and can be used for large number of experimental runs [21]. Being an active DSA, it provides its adsorption sites for radicals to get absorbed and degrade the pollutant over its surface area [22]. It also favours (Cl·) and oxy-chloro (O·Cl) radicals generation which also facilitates in degradation of pollutant both at anode as well as bulk of system [5,23,24].

Scavengers of HO·, for example, Cl^-, Br^-, SO_4^{2-}, carbonates, organic matter, etc. majorly affect the pollutant degradation efficiency of the overall process in more than one way [25,26]. Chen et al. [17] studied the degradation of highly acidic explosive wastewater by applying electro-catalytic technique coupled with anoxic–oxic biodegradation using TiO_2-NTs/SnO_2-Sb. Degradation of water contaminated with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) along with other nitrates using Fenton process was practiced by Tanvanit et al. [27] and Zoh and Stenstrom [28]. Rodgers and Bunce [29] also reviewed for variety of techniques been applied to degrade water contaminated with nitroaromatic explosives, for example, TNT (2,4,6-trinitrotoluene), DNB (dinitrobenzene), DNT (dinitrotoluene), TNB (1,3,5-trinitrobenzenene), picric acid (2,4,6-trinitrophenol) and tetryl (methyl-N,2,4,6-tetranitroaniline). These all works reported, prove that all these technologies are well able to reduce the strong acidic, carcinogenic and toxic behavior of such wastewaters. However, it may be noted that no studies have been reported on treatment of such high acidic and toxicity wastewater.

The present study is based on the electrochemical treatment of actual highly acidic wastewater from a nearby industry using an electro-oxidation method using a DSA electrode namely ruthenium oxide coated titanium (Ti/RuO_2). The wastewater was highly acidic with extremely high COD. The overall process was optimized over various parameters like current density (A/m^2), electrode gap and H_2O_2 dosage. Moreover, COD degradation, specific energy consumption, and operating cost were calculated for the overall treatment process. Also, the characterization of wastewater was done using various methods including gas chromatography/mass spectroscopy (GC/MS), ion chromatography (IC), and Fourier transform infrared spectroscopy (FTIR). Also, the morphology of the electrode was studied using field emission scanning electron microscope (FE-SEM) and X-ray powder diffraction (XRD).

2. Materials and methods

2.1. Materials

All chemicals used for the experiment were of analytical grade. MilliQ water was used for preparing different solutions required for the study at room temperature. Ti/RuO_2 electrodes used for electrochemical treatment were procured from Titanium Tantalum Products Limited, Gowriwakam, Chennai, India. Tributyl phosphate, used as an extractant for GC/MS study, was purchased from Hi-Media laboratories, limited. The physical and chemical characteristics of wastewater are presented in Table 1.

2.2. Experimental setup

Electrochemical treatment setup comprised of a 250 mL lab-scale glass batch reactor with circular cross section. It was mounted over by an electrode stand fitted with two Ti/RuO_2 electrodes in which one was an anode and other was a cathode. A simplified diagram of the experimental setup is shown in Fig. 1. All the batch experiments were run with the controlled action of current electrolysis process and followed by D.C. function source (4818A10) following potentiostat or galvanostat mechanism. The electrodes were of equal thickness of 1.5 mm and dimension of

Table 1
Physical and chemical properties of highly acidic wastewater.

Physical and chemical properties	
Color	0 Pt. Co. (Transparent)
pH	0.4 ± 0.1
COD	6,43,000 ± 50,000 mg/L
TDS	4209 ± 20 mg/L
Conductivity	63 ± 5 ms/cm
Nitrate	840103 ± 5000 ppm
Nitrite	563 ± 50 ppm
Phosphate	190 ± 10 ppm
Sulphate	4013 ± 100 ppm