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Research article

Combined heterogeneous Electro-Fenton and biological process for the treatment of stabilized landfill leachate

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ABSTRACT

Treatment of stabilized landfill leachate is a great challenge due to its poor biodegradability. Present study made an attempt to treat this wastewater by combining electro-Fenton (E-Fenton) and biological process. E-Fenton treatment was applied prior to biological process to enhance the biodegradability of leachate, which will be beneficial for the subsequent biological process. This study also investigates the efficiency of iron molybdophosphate (FeMoPO) nanoparticles as a heterogeneous catalyst in E-Fenton process. The effects of initial pH, catalyst dosage, applied voltage and electrode spacing on Chemical Oxygen Demand (COD) removal efficiency were analyzed to determine the optimum conditions. Heterogeneous E-Fenton process gave 82% COD removal at pH 2, catalyst dosage of 50 mg/L, voltage 5 V, electrode spacing 3 cm and electrode area 25 cm^2. Combined E-Fenton and biological treatment resulted an overall COD removal of 97%, bringing down the final COD to 192 mg/L.

1. Introduction

Sanitary landfilling is the most economic method accepted worldwide for the elimination of Municipal as well as Industrial solid waste (Zhang et al., 2012). Landfilling helps to minimize environmental impacts by allowing the waste to degrade under controlled conditions, where it's eventually transformed into relatively inert and stabilized material (Renou et al., 2008). Still generation of heavily polluted leachates constitutes a major drawback of sanitary landfill. Solid waste composition, landfill age, rainfall patterns and properties of soil comes under the major parameters influencing the characteristics of landfill leachate (Di Iaconi et al., 2006; Hermosilla et al., 2009; Park et al., 2001). Based on the “age” of landfill, leachate can be categorized as young (BOD_5/COD > 0.6), intermediate and stabilized/mature (BOD_5/COD < 0.3). High BOD_5/COD ratio and high concentration of low molecular weight organics, makes the young leachate susceptible to treatment by biological techniques. Low BOD_5/COD ratio and high concentration of high molecular weight refractory organics being the typical characteristics of mature landfill leachate, makes physicochemical techniques a better option for their treatment. Hence over the years, numerous physicochemical processes have been tried either as a pre-treatment or for full treatment of stabilized landfill leachate (Castrillón et al., 2010; Gao et al., 2015; Kurniawan et al., 2006; Renou et al., 2008).

Out of the numerous physicochemical techniques that have been studied over years in the treatment of mature landfill leachate, Advanced Oxidation Processes (AOP's) have become a popular one for the removal of refractory organics and ammonia-nitrogen from wastewaters (De Morais and Zamora, 2005; Gogate and Pandit, 2004; Primo et al., 2008). Their ability to mineralize the refractory organics and thereby enhance the biodegradability of wastewater, places the AOP's one notch above the conventional physicochemical techniques (Chidambara Raj and Quen, 2005; Pera-Titus et al., 2004; Primo et al., 2008). Being technically simple, economic and non-toxic iron and hydrogen peroxide as primary reactants; Fenton's process stand out as the most feasible AOP (De Morais and Zamora, 2005).

Conventional Fenton process which makes use of homogeneous catalyst, are faced with problems like slower ferrous ion regeneration rate and excessive iron sludge production. But in order to commercialize this technique, these drawbacks have to be overcome. This has been targeted by the heterogeneous Electrochemical Advanced Oxidation Processes (EAOP's), out of which electro-Fenton process has come out as the popular EAOP (Brillas et al., 2009; Nidheesh et al.,

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2013; Nidheesh and Gandhimathi, 2012). Applicability of heterogeneous E-Fenton process in stabilized landfill leachate treatment has not yet been studied in detail. Iron-loaded Mangosteen Shell Powder (Laiju et al., 2014) and Nanosized Zero Valent Iron particles (Shafieiyoun et al., 2012) are two of the heterogeneous catalysts that have been used in Fenton process for leachate treatment. Despite their high effectiveness, AOPs become quite expensive if applied alone (Silva et al., 2017). Greater resistance offered by the oxidation intermediates to further chemical oxidation and failure in bringing down the initial COD to meet the discharge standards, makes Fenton a non-feasible technique in some cases. On the other hand, eco-friendly biotreatment options require carefully maintained reaction conditions and could be applied only to wastewaters with pollution level that is non-toxic to microorganisms (Ganigué et al., 2012; Guo et al., 2013; Xiao et al., 2015). Considering the advantages and disadvantages of chemical oxidation and biological treatment, combining these two would be a more feasible option (Oller et al., 2011; Scott and Ollis, 1995). In the combined process, chemical oxidation as an initial step would convert the persistent organic pollutants into more biodegradable intermediates, which could be easily removed in a subsequent biological step.

In the present study, Iron molybdophosphate is being used as the heterogeneous E-Fenton catalyst. This catalyst was initially used in the Photocatalysis for the degradation of malachite green and was found to give promising results (Sharma et al., 2016). Present study also aims to combine E-Fenton process with biological processes for the successful mineralization of stabilized landfill leachate.

2. Materials and methods

2.1. Leachate

Leachate used in the present study was collected from Ariyamangalam dumping site, Trichy, Tamil Nadu, India. Spread out over 43 acres of land, this is one of the oldest dump yard in Trichy. Nearly 20 L samples were collected in 10 L plastic cans. Samples were stored at 4 °C to arrest further biodegradation. Leachate characterization was done as per standard methods (APHA, 2012).

2.2. Chemicals

Sodium molybdate (Na_2MoO_4), Orthophosphoric acid (H_3PO_4) and Ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) were used in the catalyst preparation. Other chemicals used in the E-Fenton study includes H_2SO_4 and NaOH. Apart from these, Nutrient agar and Nutrient broth were used in the preparation of inoculation medium. Sterile saline water (0.9% NaCl) was used for serial dilution while performing the biological study. All the chemicals used in the study were obtained from Merck and were of analytical grade.

2.3. Electrodes

The electrodes used in the study were TiO_2/Ti and Graphite as anode and cathode respectively. Graphite electrodes were purchased from Anabond Sainergy Fuel Cell India Private Limited, Chennai, Tamil Nadu. Dimensions of the graphite electrode were 8 cm × 7 cm x 0.5 cm. Dimensions of the TiO_2/Ti electrode were 8 cm × 7 cm x 0.4 cm. For E-Fenton process, the effective area of the electrodes was kept as 25cm^2.

2.4. Preparation and characterization of FeMoPO

Iron molybdophosphate (FeMoPO) catalyst was synthesized by co-precipitation method (Sharma et al., 2016). For the catalyst preparation 200mL of 0.1M Sodium molybdate (Na_2MoO_4) and 100 mL of 0.05M Orthophosphoric acid (H_3PO_4) were added drop wise to 100mL of 0.1M Ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), with constant stirring over a magnetic stirrer. Upon addition of Na_2MoO_4 and H_3PO_4, the clear reddish brown solution of $Fe(NO_3)_3.9H_2O$ changed to highly turbid creamish brown solution, indicating the formation of FeMoPO nanoparticles. The reaction between $Fe(NO_3)_3.9H_2O$ and Na_2MoO_4 results in the formation of FeMoPO nanoparticles, where the Fe^{3+} ions are reduced to Fe^{2+} ions by the acidic medium ensured by the addition of H_3PO_4. This mixture was then stirred and refluxed for 18 h at 80 °C over a magnetic stirrer with hot plate. The precipitates so obtained were filtered, washed and dried at 50 °C in a hot air oven. A single run yielded around 2.5 g of creamish brown FeMoPO nanoparticles.

Fourier Transform Infrared Spectroscopy (FTIR-2000, Perkin Elmer) was used to determine the surface functional groups of FeMoPO. FTIR spectra was recorded from 4000 cm^{-1} to 400 cm^{-1} using the KBr pellet method. Rigaku X-ray Diffractometer (D-Max/Ultima III) was used to obtain the X-ray diffractogram of FeMoPO samples. The prepared FeMoPO samples were exposed to X-ray with 2θ angle varying between 5º and 80º. XRD was performed with Cu Kα radiations at an applied voltage, current and scan rate of 40kV, 32mA, 40 min^{-1} respectively. To understand the surface morphology of FeMoPO samples, SEM analysis were performed in JEOL JMT-300 operated at 15 kV, which uses high energy electron beam to give microphotographs of the samples.

To investigate the stability and uniformity of the prepared FeMoPO nanoparticles, Zeta potential and particle size measurements were conducted in Malvern Zetasizer Nano ZSP. For the measurement of Zeta potential, the powder sample was dispersed in aqueous medium and loaded in the Zeta dip cell. Zetasizer makes use of the Electrophoretic Light Scattering (ELS) technique for the estimation of Zeta potential. For particle size measurement, the powder sample was dispersed in aqueous medium and loaded in Disposable sizing cuvettes of the Zetasizer, which applies Dynamic Light Scattering (DLS) technique for particle size estimation.

2.5. E-Fenton Process

In electro-Fenton process, the experiment was carried out in a batch reactor consisting of 1000mL borosil glass beaker. 750mL of leachate was taken and initial pH was adjusted to 3 using 1N H_2SO_4. Predetermined amounts of catalyst (iron molybdophosphate) were added to the sample. Inner electrode spacing was maintained as 3cm. The electrodes were connected to a DC power supply. DC voltage was maintained as 5 V. Aeration were given near cathode using fish aerator for the in-situ generation of hydrogen peroxide. Samples were withdrawn at regular time intervals (every 10min), centrifuged at 7000 rpm (inorder to separate the sludge) for 10min and the supernatant was collected for COD estimation. COD reduction was expressed as the ratio of residual COD at time t (C_t) to initial COD (C_0). Further studies were carried out by varying the initial pH, catalyst dosage, voltage and electrode spacing. Prior to use in E-Fenton process, all electrodes were thoroughly cleaned with water to remove any excess debris. The electrodes were then soaked in 1N HCl for 1 h followed by 1M NaOH for another hour. The electrodes were stored in distilled water when not in use. After each use, the electrodes were washed in 1N HCl and 1M NaOH to remove any possible contamination.

2.6. Biological study

As the E-Fenton treatment did not succeed in bringing down the COD of leachate samples to meet the discharge standards, the