Journal of Environmental Chemical Engineering 3 (2015) 2229–2235

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Treatment of pharmaceutical effluent using novel heterogeneous fly ash activated persulfate system

Senthilnathan Nachiappan[a,*], Kannappan Panchamoorthy Gopinath[b]

[a] Department of Chemical Engineering, St. Joseph's College of Engineering, Chennai, 600119, India
[b] Department of Chemical Engineering, SSN College of Engineering, Chennai, 603110, India

ARTICLE INFO

Article history:
Received 18 May 2015
Accepted 27 July 2015

Keywords:
Pharmaceutical effluent
Fly ash
Persulfate oxidation
Sulfate radical
Adsorption

ABSTRACT

In this work, a novel heterogeneous fly ash activated persulfate oxidation was proposed for the degradation of pharmaceutical effluent. The results showed that, inexpensive and difficult to degrade waste material—fly ash has the potential to degrade and mineralize the effluent effectively. In this work, two different fly ashes, one with high iron content (FA1) and another with less iron (FA2) were employed as activator. The effect of reaction time, temperature, initial pH, dose of fly ash and agitation rate on COD and TOC reduction was analyzed for both FA1 and FA2. At lower temperatures, FA1 catalyzed persulfate oxidation effectively due to the presence of high % of iron. On the other hand, at higher temperatures, both FA1 and FA2 performed in similar way as heat was acted as activator in persulfate oxidation. Maximum degradation was achieved at highly acidic conditions and the degradation decreases with increase in pH till 7.0 beyond which little increase in degradation was observed. Increase in fly ash dose enhanced the degradation. Presence of un-burnt carbon, alumina, silica and other metallic oxides on fly ash produced better adsorption. The activation energy of degradation process was found to be significantly less (23.32 kJ/mol) during the use of FA1 in comparison with FA2 (47.64 kJ/mol). The degradation process was found to follow pseudo first order kinetic model. The effluent treated using FA1 produced less toxic wastewaters than FA2. This study clearly illustrates the efficacy of fly ash on persulfate oxidative degradation of industrial effluent.

Introduction

Presence of pharmaceutically active compounds (PhACs) in water bodies is a growing concern across the world. The problem is fueled by drastic increase in demand and supply of variety of pharmaceuticals for the treatment of many newly developed diseases such as ebola, swine flu, etc. The PhACs pollute the water bodies by entering into them through different means which include discharge of industrial effluents generated from pharmaceutical production units, human excreta due to incomplete metabolism, disposal of expired medicines in dump yards, dumping the pharmaceutical wastes created during research, etc. [1]. Among these, the major contribution has been made by industrial effluents discharged from the manufacturing units as very large volume is involved and in some instances, the volume goes beyond millions of gallons/day. The problem is worsened in thickly dense countries like India, where the chance of mixing waste water with drinking water is very high. So, it is the sole responsibility of the research community to reduce the toxic level in waste water discharged from pharmaceutical production units.

Numerous technologies were employed to treat the pharmaceutical effluents to contain the toxic pollutants and many of them were succeeded in the ventures. The pharmaceutical effluents are, in many cases, highly resistant to biodegradation and cannot be treated using conventional methods [2–4]. In recent few decades, the attention of research community has been focused on advanced oxidation processes (AOPs) in which the biorefractory organics present in the waste waters were degraded using radical attack. Among the AOPs, the persulfate oxidation technology is an emerging field in which the persulfate and sulfate radicals degrade the biorefractory recalcitrant organic pollutants in effective manner. Persulfate oxidation has several advantages over conventional hydroxyl oxidation which include relatively high solubility and stability at room conditions, low cost [5] and these persulfate radicals are highly non-selective which makes them more viable for treatment of wide range of organic pollutants. Further this technology employs non-polluting reagents and does not generate any secondary pollutants as in Fenton's process.

* Corresponding author.
E-mail addresses: nachiappan2000@gmail.com (S. Nachiappan), gopinathkp@ssn.edu.in (K.P. Gopinath).

http://dx.doi.org/10.1016/j.jece.2015.07.019
2213-3437/

Nowadays solid wastes were generated in very large magnitude by manufacturing industries and houses as well. Fly ash is one of the solid wastes produced in houses as well as manufacturing industries in large level as the result of combustion of different combustible substances. Till last decade, fly ash was dumped in landfills and/or waters. In recent years, it has been used for different purposes which include concrete preparation, brick manufacture, etc. Along with these large scale applications, it has also been employed different processes such as adsorbent [6–8], catalyst support [9–11], etc. In this work, fly ash has been employed to test its ability on treating pharmaceutical effluent as source of iron for activating persulfate oxidation.

Ahmaruzzaman [12] effectively reviewed the role of fly ash in the removal of organic pollutants present in the wastewater. Nachiappan and Muthukumar [13] treated pharmaceutical effluent by using persulfate oxidation in the presence of ultrasound and hydrogen peroxide, in which no-cost waste material iron swarf was tested as source of iron for activating persulfate oxidation. Muhammad et al. [14] used coal fly ash supported Co_3O_4 catalysts for the degradation of phenol using peroxymonosulfate.

In most of the studies reported, researchers employed simulated wastewaters containing one or two pharmaceutical compounds to demonstrate the degradation efficiency of advanced oxidation processes. In this work, real undiluted pharmaceutical effluent was taken into account for degradation process. For the first time, waste combustion residue and difficult to degrade material—fly ash was tested as activating agent for persulfate oxidation of real pharmaceutical effluent. Two different samples of fly ash with differed composition were employed for exploring its potential on catalyzing persulfate oxidation. The effect of reaction time, temperature, initial pH, fly ash dose, agitation rate on degradation and mineralization of pharmaceutical effluent was investigated. The rate of degradation was determined for both FA1 and FA2 catalyzed degradation. In addition, the reusability of fly ashes and toxicity of effluent before and after treatments were also studied.

Materials and methods

Materials

Chemicals and reagents

The pharmaceutical effluent considered for degradation studies was obtained from a pharmaceutical manufacturing unit located in the outskirts of Chennai, India. The collected liquid was stored in the refrigerator facility till further use. The physico-chemical properties of effluent were listed in Table 1. The biodegradability index was calculated using Eq. (1).

$$\text{Biodegradability index} = \frac{BOD_5}{COD} \quad (1)$$

In this study, the index for the untreated effluent was found to be very low (0.14) which shows the poor biodegradability of the effluent. It might be caused due to the presence of biorefractory materials in the effluent. Hence, biological treatment is not viable to treat this effluent. So in this work, one of the least explored advanced oxidation processes called persulfate oxidation was adopted. The effluent was intentionally neither diluted nor undergone primary treatment procedures. This is to demonstrate the potential of newly developed system—persulfate oxidation activated by fly ash, on the treatment of highly concentrated and toxic effluent.

Fly ash

The dry fly ash sample 1 (hereafter represented as fly ash 1 (FA1)) was obtained from a cement industry located in Tamil Nadu, where bituminous coal was used for drying slurry in rotary dryers. The dry fly ash sample 2 (hereafter represented as fly ash 2 (FA2)) was obtained from a thermal power plant located in Tamil Nadu where the coal has been employed in boilers for steam generation. In order to make the process more cost effective, no surface activation or pretreatment was performed on the collected fly ash samples. The collected samples were screened in sieves and the particles with the size ranged between 44 and 53 μm were obtained and used in this study. The compositions of FA1 and FA2 are listed in Table 2a and the physical properties are listed in Table 2b.

Experimental

All the degradation experiments were performed in batch mode in a reactor of 1 L capacity. The experiments were conducted with 250 mL of effluent and at room conditions (30 °C). During the effect of studies on temperature, the contents were maintained at constant temperature by circulating the hot/cold water. The contents were agitated at desired speed (300 rpm unless otherwise specified) to make the system uniform as well as to prevent settling of solid particles. All the iron related experiments were conducted at initial pH of 3 unless otherwise specified.

For better understanding, initially, the Fe^{2+} activated persulfate oxidation process was performed with desired quantity of ammonium persulfate and $FeSO_4{\cdot}7H_2O$. With respect to fly ash activated persulfate oxidation processes, the desired amount of ammonium persulfate and fly ash were added to the reactor in a single dose before the experiments getting started. The blank experiments were conducted without persulfate to determine the contribution made by fly ash as adsorbent, for which, the contents were stirred at same 300 rpm.

The liquid samples were collected in regular intervals (0.5 h) and centrifuged to eliminate the solid particles. In all the iron related experiments, the pH of the sample was raised to 9.0 to prevent further reactions. Then, the sample is subjected to chemical oxygen demand (COD), biological oxygen demand (BOD_5) and total oxygen content (TOC) analyses. All the experiments unless otherwise specified were conducted for 3 h.

In this work, as real pharmaceutical effluent has been employed, it is much required to investigate the toxicity test before and after degradation. This is because, in many times, the

Table 1
Physico-chemical properties of pharmaceutical effluent.

Parameter	Value
COD (mg/L)	14,500
BOD (mg/L)	2100
TOC (mg/L)	5200
pH	5.0–5.2
Total dissolved solids (mg/L)	690
Density (kg/m^3)	965

Table 2a
Composition of FA1 and FA2.

Ingredients	FA1 (%)	FA2 (%)
SiO_2	34	40.2
Al_2O_3	22.2	18.2
Fe_2O_3	21.8	7.2
CaO	8.2	15.5
SO_3	1.2	4.2
MgO	1.3	1.9
Other ingredients	11.3	12.8