Chemical Engineering Journal 295 (2016) 20–28

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Combined biological and photocatalytic treatment of real coke oven wastewater

Naresh K. Sharma [b], Ligy Philip [a,*]

[a] Environmental and Water Resources Engineering Division, Department of Civil Engineering, IIT Madras, Chennai 600 036, India
[b] Department of Biotechnology, Kalasalingam University, Anand Nagar, Krishnankoil, Tamilnadu 626 126, India

HIGHLIGHTS

- Coke oven wastewater contains phenolics, aromatic hydrocarbons along with cyanide.
- Anaerobic–aerobic–anoxic bioreactors and photocatalysis was used for CWW treatment.
- Real CWW without pretreatment adversely affected the reactor performance.
- COD removal of 96.2% was achieved in the hybrid system with real CWW.
- The hybrid system was able to achieve discharge standards with real CWW.

ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form 22 February 2016
Accepted 7 March 2016
Available online 11 March 2016

Keywords:
Real coke oven wastewater
Photocatalysis
Aerobic
Anoxic
Anaerobic
Hybrid treatment system

ABSTRACT

Wastewater generated from coke oven industries contains highly toxic organic and inorganic compounds. In the present study, biological reactors were integrated in sequence of anaerobic–aerobic–anoxic and tested with real coke oven wastewater obtained from a Steel Plant located in India. Among several pre-treatment methods, coagulation of raw CWW was found to be effective. COD removal efficiency of 78.5% was achieved by the integrated bioreactor system after coagulation of CWW with 1000 mg/L of alum. The effluent COD, NH_4-N and TCN concentration from the integrated bioreactors was 420, 152 and 20 mg/L, respectively. It was observed that 420 mg/L of COD present in the effluent after integrated bio treatment was degraded in less than 4 h to minimum COD concentration of 94 mg/L using UV–TiO_2 photocatalysis. In absence of photocatalyst (TiO_2), there was no COD reduction from the bio treated effluent. Similarly, there was insignificant reduction in COD from the raw CWW using photocatalysis without biological treatment. Considerable COD reduction (78.5%) was observed only in the wastewater subjected to integrated biological system. The overall COD removal efficiency of the combined treatment system was found to be 96.2%, which resulted in an effluent COD concentration less than 94 mg/L.

1. Introduction

The iron and steel industry is one of the most energy intensive sectors within the Indian economy and of particular interest in the context of both local and global environmental discussions. Steel production in India has increased by a compounded annual growth rate (CAGR) of 8% over the last 10 years. In India, each ton of steel production consumes 25–60 m^3 of water on an average and 5–9 tons of coal is fed as basic raw material. It may be noted that, in developed countries, the water consumption for each ton of steel production varies from 3 to 6 m^3, i.e., 8 to 10 times less than that of the water consumption in India [1]. In an Integrated Iron and Steel Industry, wastewater generated from coke oven by-product plant is usually the most polluting one [2]. Such wastewaters contain high concentrations of toxic chemicals like phenols, cyanides and ammonia. Process wastewater is reported to contain 1000–2000 mg/L of biochemical oxygen demand (BOD_5), 1500–6000 mg/L of chemical oxygen demand (COD), 200 mg/L of total suspended solids and 150–2000 mg/L of phenols. Depending upon the quality of raw coal, carbonation temperature and methods used for byproduct recovery, wastewater contains different polycyclic aromatic hydrocarbons (PAHs) and nitrogenous heterocyclic hydrocarbons at significant concentrations (as high as 400 mg/L), along with ammonia and cyanides [2].

The physico-chemical treatment systems are uneconomical and non-sustainable for the treatment of complex coke oven wastewater (CWW) [3]. Biological treatment systems commonly employ

* Corresponding author.
E-mail address: ligy@iitm.ac.in (L. Philip).

http://dx.doi.org/10.1016/j.cej.2016.03.031
1385-8947/

activated sludge process, up-flow anaerobic sludge beds, fluidized beds, aerobic and anaerobic biofilms. Biological processes such as anoxic–oxic (A/O) or anaerobic–anoxic–oxic processes are widely applied in CWW treatment because of the high treatment efficiency and cost-effectiveness [4–6]. It has been reported that full scale applications of these biological reactors have eventually resulted in failure while treating coke oven wastewater (CWW) [4,7]. Due to the presence of refractory and toxic compounds, the growth of nitrifying bacteria and specialized microbes in the bioreactor is limited. Chemical oxygen demand (COD) could not be efficiently reduced by the conventional activated sludge process since refractory pollutants are present in CWW. In addition, due to the influence of typical nitrification inhibitors, such as phenol, thiocyanate and ammonium, the removal of NH_4^+-N is difficult. The a naerobic–anoxic–oxic process, either suspended growth or biofilm growth, has been extensively researched for CWW treatment [4,6]. In this system, anaerobic hydrolysis and acidogeneis, as a pretreatment process, converts the refractory and inhibitory compounds into readily biodegradable intermediates. This is followed by the pre-denitrification process consisting of anoxic and oxic reactor, which degrades most organics and nitrogen compounds [6,8]. Unfortunately, due to the refractory and inhibitory contaminants present in CWW, above processes are not sufficient and do not meet the discharge standards [6,9].

Advanced treatment processes such as membrane bioreactor [10], ultra violet irradiation and ozonation [11], ultrasonic irradiation and catalytic oxidation [12] and supercritical water oxidation [13] have also been effectively used as advanced treatment to remove refractory compounds in wastewater. However, these methods are either economically unfavorable or technically complicated, which makes it difficult to use them in practice. The physico-chemical treatment processes such as filtration, stripping, Fenton's reagent, carbon adsorption and membrane technology are efficient but economically not viable [14]. Coagulation, chemical precipitation and sedimentation are commonly used for treatment of industrial wastewater and are the preferred options to remove turbidity, color and suspended solids. These methods also remove COD, TOC and TN from the effluent leaving behind thick hazardous sludge which requires further treatment [3]. The efficiency of chemical oxidation reactions such as ozonation, photocatalysis and ultrasound are reported to be efficient in removing TOC, COD and TN. Among the AOPs, Fenton process has been extensively investigated in treatment of actual CWW. One of the disadvantages of this process is the large amount of Fe(II) salts added which can result in large quantities of chemical sludge which needs further attention. Regard-less of economic value, ozone, catalytic ozonation, Fenton-coagulation and supercritical water oxidation had been effectively used as advanced treatment to remove refractory compounds in wastewater. However, transformation products formed during these reactions could sometimes be even more toxic than the original pollutants [14,15] and these methods largely depend upon the feed characteristics such as turbidity, suspended and dissolved solids [15]. Increasingly, biological and physico-chemical methods are combined as pre/post treatment options for effective and economical treatment of complex industrial wastewaters. In the context of coke oven wastewater, which includes a mixture of complex pollutants, there have been reports of full scale treatment of real CWW, with different configurations of bioreactors (anaerobic, aerobic, anoxic), combined with physico-chemical pre/post treatment methods [4]. Compared to activated-sludge process, pre/post treatment using ultrasonic irradiation, catalytic oxidation and activated-sludge can significantly increase the COD degradation efficiency by 48 to 95.74% [11]. Guomin et al. [16] studied the performance of anoxic–aerobic–aerobic–aerobic–Fenton oxidation–aerobic reactors for treatment of real coke oven wastewater. Their results showed that about 80% of COD in the chemical wastewater could be removed through anoxic and aerobic degradation in the biological pretreatment section, and the residual COD in the effluent of the biological pre-treatment section belongs to refractory chemicals which cannot be removed by the normal biological process. Jin et al. [2] investigated the treatment of coking wastewater using anaerobic–anoxic–aerobic–MBR-nano filtration (NF)–reverse osmosis (RO) integrated system. The pollutant removals reached 82.5% (COD), 89.6% (BOD), 99.8% (ammonium nitrogen), 99.9% (phenol), 44.6% (total cyanide (T-CN)), and 99.7% (thiocyanide (SCN-)). However, the concentrates from the NF and RO units were polluted with toxic refractories requiring further treatment. Yuan et al. [17] used coupling of extraction replacement–biodegradation techniques for the removal of organics from coking wastewater. They showed that when n-octanol and cyclohexane, in a ratio of 1:1, were selected as the mixed extractant, nitrogen-containing heterocyclic compounds (NHCs), such as pyridines and quinolines, were effectively removed at the expense of solvent costs.

A few recent studies have shown that the aerobic degradation of anaerobic effluent was faster (high degradation rates) compared to anoxic degradation rate of anaerobic effluent and also concluded that the effluent pollutant concentration was very less in aerobic–anoxic cycle than in anoxic–aerobic cycle [18,19]. These studies emphasized the importance of anaerobic–aerobic–anoxic configuration for CWW treatment. Nevertheless, the literature is devoid of studies in treatment of coke oven wastewater with anae robic–aerobic–anoxic configuration of bioreactors. The hydroxyl radical generated using H_2O_2 and UV radiations offers great potential for increasing the biodegradability of various recalcitrant and toxic organics present in wastewater. Among different AOPs available for producing hydroxyl radicals, TiO_2/UV light process and H_2O_2/UV light process have been successfully applied for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, coloring dyes and pharmaceuticals [20]. Application of AOPs, especially TiO_2/UV light process, for CWW has been rarely reported so far. Thus, the use of AOP for coke oven wastewater post treatment is a potential research area and the effect of TiO_2/UV light process for coke oven wastewater treatment needs to be studied. It has been shown that effective and economic treatment of CWW depends upon the combination of physico-chemical and biological methods. Much of the current research is limited to the investigations on the removal of one or two combinations of CWW pollutants using synthetic wastewater to understand the substrate impact and removal mechanisms. It is necessary to demonstrate the effectiveness of bacterial consortium acclimated to CWW pollutants under different redox conditions in treatment of real CWW. Also, to meet the regulatory effluent discharge limits, there is a need to investigate the effect of photocatalysis for biologically pre-treated effluents.

Present study evaluated the performance of a combination of biological systems followed by photo catalysis for the treatment of real coke oven wastewater. Various pre-treatment options to enhance the efficiency of biological treatment system was also studied.

2. Materials and methods

2.1. Chemical and reagents

All the chemicals used in the study were of analytical grade (>98% purity) purchased from Rankem, SDFCL, Avra, Loba Chemie, India and Alfa Aesar, UK. The glassware used in these studies was supplied by Borosil, India. High density polypropylene plastic storage bottles were obtained from Tarzon, India. Prior to experiments, all the glass and plastic wares were soaked in 10% nitric acid for