Separation and Purification Technology 69 (2009) 109–117

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM

P.A. Soloman [a], C. Ahmed Basha [b,*], M. Velan [a], N. Balasubramanian [a], P. Marimuthu [c]

[a] Department of Chemical Engineering, A.C. Tech Campus, Anna University-Chennai, Chennai 600025, India
[b] Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India
[c] Seshasayee Paper and Boards Limited, Erode 638007, Tamilnadu, India

ARTICLE INFO

Article history:
Received 5 December 2008
Received in revised form 5 May 2009
Accepted 6 July 2009

Keywords:
Electrochemical pre-treatment
Pulp and paper wastewater
Biodegradability
COD removal
Response surface methodology

ABSTRACT

Biological treatment of pulp and paper industry wastewater is made effective by giving a simple electrochemical pre-treatment. Biodegradability index is found to be improved from 0.11 to 0.46 by a short (6.9 min) treatment in mild conditions (current density: 112.9 A m^{-2}, pH 7.3). The optimal operating point for maximum biodegradability has been found out using response surface methodology (RSM). It is also noticed that there exists an optimal operating point for maximum biodegradability. The specific energy consumption and current efficiency figures at the optimal condition are also promising. Moreover there is considerable reduction in the pollutant load (COD removal: 55% and color removal: 87%). Performance of the process at this operating point has been validated by running biological treatment. Considerable reduction in the requirement of biological reactor volume can be expected by giving such a simple electrochemical pre-treatment.

1. Introduction

The pulp and paper industry is one of the oldest and core industrial sector in India. It is a highly capital, energy, and water intensive industry. It is also a highly polluting process and requires substantial investments in pollution control equipments. India produces 6 million tonnes of paper per year though 311 mills by consuming around 900 million m^3 of water and discharging 700 million m^3 of wastewater. Out of these about 270 small paper mills (capacity ≤ 10 000 tonnes per annum (TPA), having a total installed capacity of 1.47 MTPA) do not have chemical recovery units [1]. India's current average fresh specific water consumption for large-scale wood based pulp and paper mill, of about 150 m^3 per tonne of product is far above the global best specific water consumption of 28.66 m^3 per tonne. This large gap is primarily attributed to the use of obsolete technology/equipments and poor water management practices. The large water requirements and consumption by the Indian pulp and paper industries has led to, water fast becoming a scarce commodity and lowering of the ground water table and thus increased pumping costs and more importantly water shortages in many regions.

The most significant sources of pollution among various process stages in pulp and paper industry are wood preparation, pulping, pulp washing, bleaching and paper machine and coating operations. Common pollutants include suspended solids, oxygen demanding wastes, color, basicity, heavy metals, alkali and alkaline earth metals, phenols, chloro-organics, cyanide, sulphides and other soluble substances [2]. The resultant effects on the environment are slime growth, thermal impacts, scum formation, color problems and loss of aesthetic beauty. They also increase the amount of toxic substances in water, causing death to the zooplankton and fish, as well as profoundly affecting the terrestrial ecosystem [3].

Conventionally pulp and paper industries in India employ biological method of wastewater treatment. Even though the preliminary and primary step of the process improves the biodegradability index (BI), it seldom crosses 0.3. Thus the biological step is slow and demands larger reactor volume. Morais and Zamora [34] reported that samples with biodegradability index (defined as the ratio of BOD to COD) smaller than 0.3 are not appropriate for biological degradation. According to Chamarro et al. [35] for complete biodegradation, the effluent must present a biodegradability index of at least 0.4. Other treatment alternatives such as adsorption [4], wet oxidation [5], ozone treatment [6], fractional precipitation [7], ultra filtration [8], combined biological and membrane based treatment [9] etc. are still questionable on their technical and economic feasibility in large-scale operation.

Over the past two decades there has been increasing interest in the use of electrochemical techniques such as electro-coagulation, electro-flotation and electro-oxidation for the treatment of organic effluents. Technical feasibility of the treatment for various

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227713.
E-mail addresses: cab_50@yahoo.co.in, basha@cecri.res.in (C. Ahmed Basha).

1383-5866/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2009.07.002

industrial effluents such as electroplating wastewater [10]; potable water [11]; oil mill wastewater [12]; urban wastewater [13]; heavy metal laden wastewater [14]; nitrite effluent [15]; defluoridation [16]; arsenic removal [17]; textile dyes [18]; landfill leachate [19]; restaurant wastewater [20]; laundry wastewater [21]; surfactants [22]; agro industry wastewater [23], etc. have been established.

Electrochemical coagulation of pulp and paper effluent has been reported by five researchers [1,24–27]. All the researchers supported the technical feasibility of the process. From the literature and experiments it can be concluded that complete mineralization of large quantity of such a heavily loaded effluent will not be economically viable. Thus it has been thought of invoking for the possible distribution of treatment loads by integrating various techniques.

During the pulping process complete removal of the lignin available in wood/bagasse is not usually tried in the digester because of economic reasons. Such a trial will affect the productivity due to loss of wood fibers with the digestion chemicals. A higher load of lignin removal in the bleaching step increases the consumption of bleaching agents and resultant pollution. Thus, in practice, the proportion of lignin removal among the digestion and bleaching steps has been optimized. The bleaching effluent is so dilute in organic matter that the heat and chemical recovery is not economical. Therefore any level of process intensification is not going to avoid the presence of lignin and hemi-celluloses in the wastewater. It has to be treated and removed.

Tamilnadu Newsprint and Papers Limited (TNPL Ltd.), is one of the large-scale paper industry in south India located in Karur, Tamilnadu state. In the Kraft pulping process, lion share of the lignin and hemi-cellulose, removed from the wood and bagasse are separated in the washing section as black liquor. It is disposed by burning, recovering its heat value and chemical value in the recovery section of the plant. The major portion of the remaining lignin is coming out through the *Decker filtrate*, a rotary drum filtration arrangement. This stream, even though less in quantity (4000 $m^3\ day^{-1}$) contributes much towards the lignin part and color of the total wastewater stream (56,000 $m^3\ day^{-1}$).

TNPL Ltd. is treating highly loaded wastewater stream (mainly from bagasse wash, COD: 4500 $mg\ L^{-1}$) and moderately loaded stream (remaining combined stream, COD: 1500 $mg\ L^{-1}$) in different routes. The fuel value of the highly loaded stream is withdrawn in two up-flow anaerobic sludge blankets (UASBs) and mixed with primary clarified moderately loaded stream for aerobic treatment. The overall performance of the system treating 56,000 m^3 every day is good. BOD of the treated effluent is 1, 2 or seldom 3 $mg\ L^{-1}$, but COD 150–250 $mg\ L^{-1}$ with light brown in color. The result shows that any type of improvement (via. residence time or adding more units) on the biological treatment step on the existing process is not going to make any improvement in the final effluent composition. The high COD in this stream is because of the dissolved lignin part in the effluent.

It is attempted in the present investigation to study the enhancement of biodegradability of the *Decker filtrate* stream by electrochemical treatment. The electro-treated filtrate is further treated biologically in order to study the advantage of pre-treatment. The mechanism of electro-coagulation and the effect of individual parameters on the efficiency of electro-coagulation have been critically examined.

2. Mechanism of electro-coagulation

The coagulants and strong oxidizing agents generated in situ during the electro-coagulation process play roles in removing the organic part of the waste. The proportion or predominance of these electro-coagulation and electro-oxidation mechanisms is decided by the electrolytic conditions. The coagulants remove the dissolved organic part by precipitation and suspended fines by adsorption. Electrolytic condition, especially pH, is influencing the predominance of these mechanisms. In general suspended fines, especially of cellulose, in the pulp and paper wastewater is the main reason for a low BI. It has been noticed from the Pourbaix diagram of iron hydroxides that at a pH of 7.3, the solubility is minimum, a condition in which adsorption may predominate causing more suspended fine removal. The current efficiencies based on amount of anode dissolved, in the order of 144% shows the involvement of non-electrochemical mechanisms of electrode dissolution such as chemical dissolution [28].

Electro-coagulation involves many chemical and physical phenomena, which can be summarized in three successive stages as the formation of coagulants in situ, by electrolytic oxidation of the sacrificial electrode, destabilization of the contaminants, particulate suspension (and breaking of emulsions) and aggregation of the destabilized phases to form flocs.

Electro-coagulation has been successfully employed in industrial effluents for removal of organic contaminants. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions. Iron upon oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)_n$, where $n = 2$ or 3. When a potential is applied from an external power source, the sacrificial anode undergoes oxidation. Mechanisms [29–31] that were proposed for the production of $Fe(OH)_n$ are

Anode

$$Fe \rightarrow Fe^{3+} + 3e^- \quad E^0 = -0.04 \tag{1}$$

$$Fe \rightarrow Fe^{2+} + 2e^- \quad E^0 = -0.44 \tag{2}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad E^0 = -0.77\,V \tag{3}$$

Bulk

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \quad pH > 7 \tag{4}$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 4H_2O \quad pH > 7 \tag{5}$$

Cathode

$$2H_2O^+ + 2e^- \rightarrow H_2 + 2H_2O \quad pH > 7 \tag{6}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad pH > 7 \tag{7}$$

In turn the ionic species of bulk may react to form $Fe(OH)_2$ according to the reaction:

$$Fe^{2+}(aq) + 2OH^- \rightarrow Fe(OH)_2(s) \tag{8}$$

The electrolytic gases generated at the cathode helps to float the flocculated particles. The metal hydroxide flocs can take part in removing the organic matter present in the solution by precipitation and/or adsorption mechanism. Other iron hydroxides can also be formed. The monomeric forms of metal hydroxides can get polymerized giving various forms of ferric hydroxo complexes namely, $Fe(H_2O)_6{}^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2{}^{4+}$, $Fe_2(H_2O)_6(OH)_2{}^{4+}$, $Fe(OH)_4{}^-$, etc. The $Fe(OH)_n$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [32]. In surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:

$$L{-}H(aq)(OH)OFe(s) \rightarrow L{\cdot}OFe(s) + H_2O(l) \tag{9}$$