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ORIGINAL ARTICLE

Combined treatment of retting flax wastewater using Fenton oxidation and granular activated carbon

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Abstract The process of retting flax produces a huge amount of wastewater which is characterized with bad unpleasant smell and high concentration of organic materials. Treatment of such waste had always been difficult because of the presence of refractory organic pollutants such as lignin. In this study, treatment of retting wastewater was carried out using combined system of Fenton oxidation process followed by adsorption on granular activated carbon (GAC). The effects of operating condition on Fenton oxidation process such as hydrogen peroxide and iron concentration were investigated. In addition, kinetic study of the adsorption process was elaborated. The obtained results indicated that degradation of organic matters follows a pseudo-first order reaction with regression coefficient of 0.98. The kinetic model suggested that the rate of reaction was highly affected by the concentration of hydrogen peroxide. Moreover, the results indicated that the treatment module was very efficient in removing the organic and inorganic pollutants. The average percentage removal of chemical oxygen demand (COD), total suspended solid (TSS), oil, and grease was 98.60%, 86.60%, and 94.22% with residual values of 44, 20, and 5 mg/L, respectively. The treated effluent was complying with the National Regulatory Standards for wastewater discharge into surface water or reuse in the retting process.

1. Introduction

Flax (*Linum usitatissimum* L.) is the main source of high quality bast fibers of which linen is produced. Egypt is considered one of the oldest countries in farming and manufacturing flax. The history goes back to the Ancient Egyptian.

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Flax can be used in many industrial sectors like textile, linseed oil, flax seed oil, pulp and paper production and composite materials (Van Dam et al., 1994). However, the conventional growing of flax pollutes water via a process called "retting". Retting is an enzymatic process of rotting away the inner layer of flax from the stalk. The traditional way of water retting is done in manmade water pools, rivers or ponds. During this natural degumming process, butyric acid, methane and hydrogen sulfide are created with a strong rotten smell. If the water is released into nature without treatment, it causes water pollution. Treatment of such wastewater has always been a difficult process because of the refractory organic compounds such as lignin. There are many studies regarding the treatment of flax retting wastewater such as the use of up flow anaerobic sludge blanket (UASB) conducted with membrane bioreactor (MBR) (Liu Shi-qing et al., 2009). Also, Yan (2011) studied the treatment of retting flax wastewater using air flotation/fly/soil-percolation process. It was found that, the maximum removal rate of COD and lignin removal was 95–98% and 80–89% (Zhao and Fan, 2008). They also suggest the application of pretreatment of the flax producing wastewater by hydrolytic acidification process prior to further treatment. Furthermore, electro catalysis-oxidative degradation of pretreated fiber flax wastewater was studied by using three-dimension electrodes which were made of $Ce/RuO_2/SnO_2$-Sb_2O_3/Ti anode.

Recently, the development of novel treatment methods such as advanced oxidation processes (AOPs) has been considered for the oxidation of hardly degraded organic pollutants. Among various AOPs, the Fenton oxidation process (H_2O_2/Fe^{2+}) is one of the most effective decontamination method of organic pollutant. The Fenton oxidation process has been found to be effective for treating various industrial wastewaters (Mantzavinos and Psillakis, 2004). It has the advantage of coagulation and catalytic oxidation, as well as being able to generate oxygen in water. Fenton and photo-Fenton processes have proven to yield very good results either for complete mineralization or destruction of organic compounds (Comninellis et al., 2008). However, there are no previous studies investigating the effects of treating flax wastewater treatment using Fenton oxidation process. Therefore, the aim of this study was to treat a real retting flax wastewater in an attempt to reduce the organic load to a level that complies with the National regulatory standards for wastewater discharge into the surface water or reuse in retting flax process.

2. Materials and methods

2.1. Sources of wastewater

Wastewater produced from a retting flax industry provided material of this study. The company produces 5000 tons/year fibers. The flax retting process was carried out in 32 open ponds and another 32 closed basins. Duration of retting process was ten days in summer and fifteen days in winter. The wastewater from retting flax was discharged into a nearby agricultural drain without any treatment. The wastewater produced was highly contaminated with organic matters as well as suspended solids.

2.2. Collection of samples and analysis

Due to great variation in the quantity and quality of wastewater produced from the retting process, a continuous monitoring program was carried out for almost four months. Composite samples from the end-of-pipe of the flax retting basins were collected and analyzed according to standard method, (APHA, 2005).

2.3. Treatability studies

The retting flax wastewater was treated via Fenton's oxidation followed by adsorption on granular activated carbon (GAC). Equalization was required prior to the oxidation process. Fig. 1 illustrates a schematic diagram of the treatment module. All chemicals used for Fenton oxidation process were of reagent grade purchased from Merck Chemical Company.

2.3.1. Fenton reaction

Fenton reaction essentially depends on three factors: temperature, hydrogen peroxide concentration and Fe^{2+} concentration. Fenton process was carried out at room temperature in order to determine the optimal operating conditions of Fenton reagent (H_2O_2/Fe^{2+}). The pH values of wastewater were adjusted in the range of 3–3.5 with the addition of 1 M H_2SO_4 or 1 M NaOH before chemical oxidation process. $FeSO_4{\cdot}7H_2O$ was added to obtain the desired Fe^{2+} concentration. Finally, H_2O_2 (35% (w/v)) was carefully added to start the Fenton reaction. The aqueous solution of Fenton reagent and wastewater was magnetically stirred during the reaction period. Predetermined amounts of H_2O_2 (35%) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) were added to wastewater. After Fenton oxidation process, pH of treated wastewater was adjusted to pH 7 by the addition of 10% lime ($Ca(OH)_2$). Lime was added under continuous stirring at a speed of 200 rpm, for duration of 2 min, followed by slow mixing at a speed of 20 rpm, for duration of 20 min, and finally settling for 60 min. The performance of raw wastewater and treated effluent was evaluated in terms of COD removal.

2.3.2. Post treatment using granular activated carbon

The effluent after Fenton treatment was post treated using GAC. Each batch adsorption study was carried out at room temperature (25 ± 0.1 °C). The effects of pH, adsorbent dosage and contact time were studied, using a mechanical shaker at 200 rpm. All samples were filtered through a filter paper (Whatman, No. 42) and the COD was determined in the filtrate. All experiments were carried out in triplicate and the means of the quantitative results were used for further calculations. For the calculation of mean value, the percent relative standard deviation for results was calculated and if the value of standard deviation for any sample was greater than 5%, data were excluded.