



Treatment of cyanide containing wastewater using cavitation based approach



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ABSTRACT

Industrial wastewater streams containing high concentrations of biorefractory materials like cyanides should ideally be treated at source. In the present work, degradation of potassium ferrocyanide ($K_4Fe(CN)_6$) as a model pollutant has been investigated using cavitation reactors with possible intensification studies using different approaches. Effect of different operating parameters such as initial concentration, temperature and pH on the extent of degradation using acoustic cavitation has been investigated. For the case of hydrodynamic cavitation, flow characteristics of cavitation device (venturi) have been established initially followed by the effect of inlet pressure and pH on the extent of degradation. Under the optimized set of operating parameters, the addition of hydrogen peroxide (ratio of $K_4Fe(CN)_6:H_2O_2$ varied from 1:1 to 1:30 mol basis) as process intensifying approach has been investigated. The present work has conclusively established that under the set of optimized operating parameters, cavitation can be effectively used for degradation of potassium ferrocyanide. The comparative study of hydrodynamic cavitation and acoustic cavitation suggested that hydrodynamic cavitation is more energy efficient and gives higher degradation as compared to acoustic cavitation for equivalent power/energy dissipation. The present work is the first one to report comparison of cavitation based treatment schemes for degradation of cyanide containing wastewaters.

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1. Introduction

Millions of tones of organic compounds are manufactured globally each year and the trend is ever increasing though the fact to worry is that significant quantities of several organic compounds also appear as pollutants in the discharge streams of chemical processing industries. Most of the toxic compounds, particularly biorefractory ones, are the substances that pose significant environmental concern. Cyanide is a commonly found biorefractory contaminant in wastewaters from various industries including metal cleaning, plating, electroplating, metal processing, etc. The effects of different forms of cyanides on the microorganisms may not be completely known, particularly the long-term exposures at very low levels. The industrial effluents generally contain between 0.01 and 10 mg/L of total cyanide. However, some cyanide wastes from individual operations at electroplating and metal finishing plants can be stored for periods of years, after which the effluent may contain from 1% to 3% (10,000–30,000 mg/L) of total cyanide [1]. Removal of biorefractory pollutants from industrial effluents is an important practical problem.

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Existing waste water treatment methods like adsorption on activated carbon, extraction, and chemical oxidation suffer from limitations such as limited applicability and low efficiency. Conventional approaches may be problematic and unsustainable due to high treatment time, formation of mutagenic compounds and potential production of various secondary wastes which need further treatments [2]. The advantages and disadvantages of various cyanide treatment technologies commonly adopted in the current practice are reported by Dash et al. [1]. Research into new or more efficient waste water treatment technologies is required to degrade the complex refractory molecules into simpler molecules like mineral salts, CO_2 and water which is vital to improve the deteriorating water quality [3]. In recent years, advanced oxidation processes (AOP's) have been widely developed as promising methods for the treatment of water and wastewater containing toxic and recalcitrant organic pollutants. Compared with other processes, AOP's offers several advantages such as high efficiency, easy operation, less production of residuals and toxic intermediates in the treatment. AOP's involve generation and subsequent attack of highly reactive free radicals such as $OH\cdot$, $O\cdot$ and $HOO\cdot$ in solutions which are capable of degrading biorefractory or hazardous organic compounds [4]. Cavitation also generates similar conditions of formation of reactive free radicals and can be considered as advanced

oxidation process. In addition, cavitation also generates hot spots and intense liquid turbulence at micro scale. The two main mechanisms for the destruction of organic pollutants using cavitation are (1) thermal decomposition/pyrolysis of the volatile pollutant molecule entrapped inside the cavity and (2) reaction of OH[•] radicals with the pollutants.

Hong et al. [5] have studied the sonochemical degradation of cyanide anions in aqueous solution using 20 kHz ultrasound and reported that reaction rate constant is dependent on the operating parameters like solution volume and intensity of ultrasound. Bonyadi et al. [6] have studied the efficacy of sonochemical reactors for cyanide removal and reported that the degradation efficiency was dependent on pH, frequency, time of reaction and cyanide concentration. The aim of the current work was to investigate the effect of operating parameters for the cavitation (both ultrasound and hydrodynamic cavitation) on the extent of degradation of potassium ferrocyanide and also to perform studies using hydrogen peroxide to intensify the destructive effects so as to get maximum degradation. The work related to degradation of potassium ferrocyanide using hydrodynamic cavitation has not been reported to the best of our knowledge and this forms the novelty of the work. It is also important to note that the trends in terms of effect of operating parameters such as optimum concentration or optimum pH cannot be essentially generalized and need to be established for the specific compounds using laboratory scale studies.

2. Materials and methods

2.1. Chemicals

Potassium ferrocyanide (AR grade) and Hydrogen peroxide (30%, w/v) were obtained from S.D. Fine Chem. Pvt. Ltd, Mumbai, India. Chemicals were diluted to required concentrations using distilled water for experimental studies. H₂SO₄ and NaOH were used for adjustment of pH and were procured from S.D. Fine Chem. Pvt. Ltd, Mumbai, India. All the chemicals were used as received from the supplier.

2.2. Experimental set-up

2.2.1. Acoustic cavitation

The experimental set up based on ultrasonic irradiation consists of an ultrasonic horn (Sonics Vibracell) operating at 22 kHz frequency and rated power output of 750 W equipped with single transducer and was procured from Sonics and Materials Inc., USA. A schematic representation of the reactor assembly has been shown in Fig. 1. The actual energy dissipation into the system was

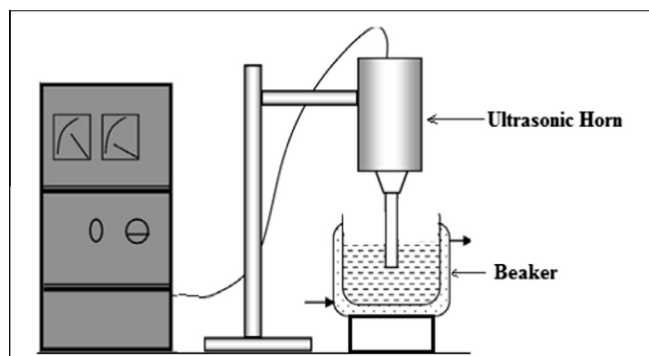


Fig. 1. Schematic of ultrasonic horn.

determined by calorimetric method using water. Calorimetric efficiency of the horn was found to be $10.2 \pm 0.5\%$. Calorimetric studies were also carried out under varying temperature conditions as used in the work and it was found that the calorimetric efficiency was marginally influenced by temperature ($\pm 2\%$). It is not expected that the calorimetric efficiency will be affected by pH and also the liquid physicochemical properties do not change much with the levels of additives used in the current work.

2.2.2. Hydrodynamic cavitation

Schematic of the experimental setup used for hydrodynamic cavitation is shown in Fig. 2(a). The set-up essentially consists of a closed loop circuit including a holding tank, a reciprocating pump of power rating 1.1 kW and a valve. The suction side of the pump is connected to the bottom of the tank. The discharge from the pump incorporates a venturi in the main line which acts as a cavitating device. A by-pass line is provided to control the liquid flow through the main line using control valves provided at appropriate places. Pressure gauges are provided to measure the inlet pressure (P_1) and the fully recovered downstream pressure (P_2) which in most of the cases was equal to 1 atm. All experiments were carried out with 5 L of solution. During the experiment, the by-pass valve was kept open till the pump reached its maximum speed and then it was completely closed. The inlet pressure (pump discharge pressure) was varied from 3 to 7 bar. Schematic of venturi which was used as a cavitating device is shown in Fig. 2(b), while Table 1 gives the geometrical details of the venturi.

2.3. Analytical technique

The concentration of potassium ferrocyanide at any instance of time was determined using SHIMADZU-1800 UV-VIS Spectrophotometer operating at a wavelength of $\lambda = 217$ nm. Kinetic analysis of the degradation process was carried out using integral method of analysis. All the experiments were repeated at least two times to check the reproducibility and average values have been reported in the figures. Error bars have also been shown to depict the variation which was within 2% of the reported average value.

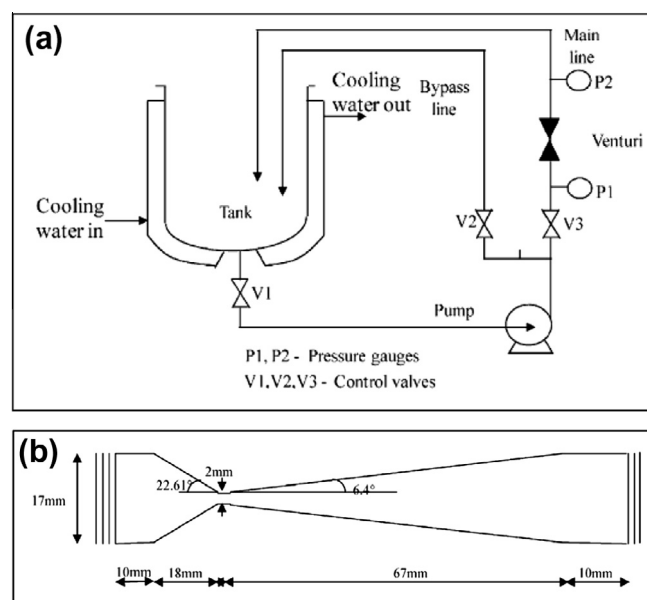


Fig. 2. (a) Hydrodynamic cavitation set-up. (b) Schematic of venturi.

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