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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 ($K_4F_e(CN)_6$) as a model pollutant has been investigated using cavitational 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 cavitating 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 $K_4F_e(CN)_6$: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.

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.

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

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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 $OH^{\cdot}$ 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. H_2SO_4 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 determined by calorimetric method using water. Calorimetric efficiency of the horn was found to be 10.2 ± 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 (±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.

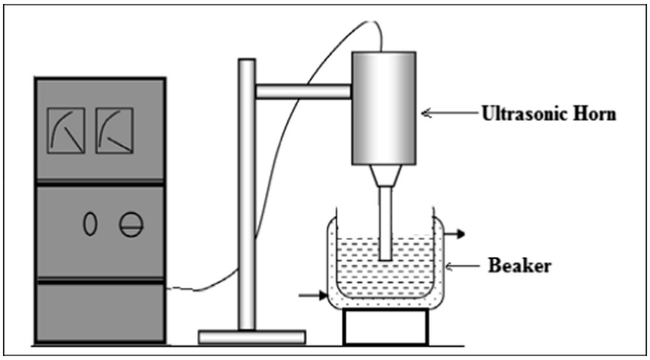

Fig. 1. Schematic of ultrasonic horn.

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.

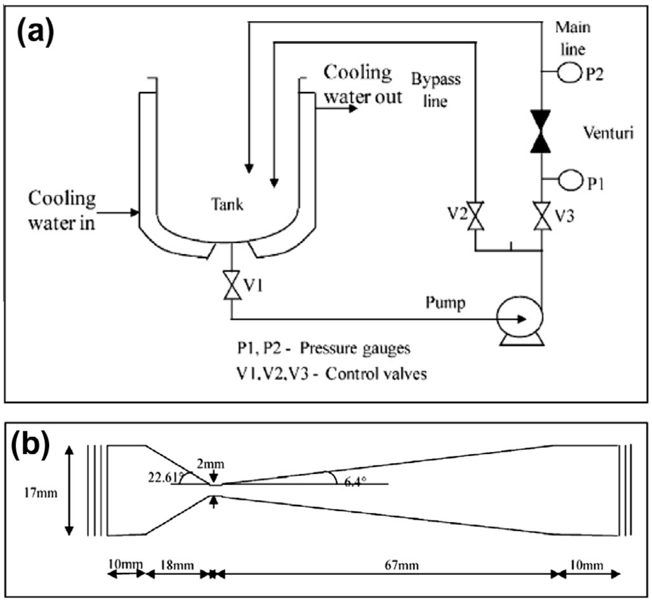

Fig. 2. (a) Hydrodynamic cavitation set-up. (b) Schematic of venturi.

3. Results and discussion

3.1. Acoustic cavitation

3.1.1. Effect of operating volume

Experiments related to operating volume were carried out at different volumes (100, 200 and 300 ml) at constant initial concentration of 100 ppm of potassium ferrocyanide at original solution pH of 7.3. Fig. 3 shows the effect of the reaction volume on the extent of degradation. It can be easily seen from the figure that the extent of degradation decreases with an increase in the reaction volume at same supplied ultrasonic power dissipation. To give a quantitative idea, in 80 min of irradiation time, the extent of degradation at 100 ml reaction volume is 13.98% (3.3×10^{-6} mol degraded) which is higher as compared to 6.78% (4.87×10^{-6} mol degraded) degradation at 300 ml of reaction volume. Table 2 gives extent of degradation at various operating volumes. The observed results may be attributed to the fact that, increase in the reaction volume decreases the power density of the system (power dissipation per unit volume) resulting in a corresponding decrease in the cavitational activity. Also, in the case of ultrasonic horn, the active cavitational volume is restricted very near to the transducer surface (there is only one transducer in the case of ultrasonic horn unlike ultrasonic bath type of systems where multiple transducers can be used; thus in the case of ultrasonic bath, the effect of reaction volume would be different though it is not within the scope of present work) resulting in nonuniform distribution of the cavitational activity. Indeed with an increase in the operating volume, the non-uniformity of the cavitational activity increases (more dead zones where the cavitational activity is minimal) resulting into detrimental effects.

Table 1
Specifications of venturi.

Outer diameter of venturi	17 mm
Venturi length	105 mm
Convergent section	18 mm
Divergent section	67 mm
Throat diameter	2 mm
Convergent angle	22.61°
Divergent angle	6.4°

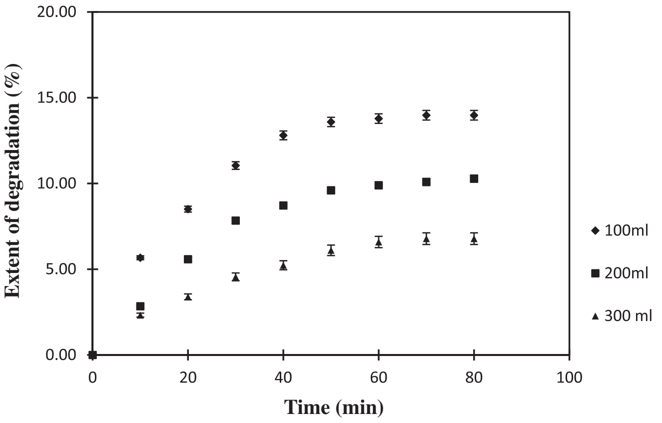

Fig. 3. Effect of operating volume on the degradation (%) in ultrasound. Conditions: initial concentration: 100 ppm, pH: 7.3 (original solution pH).

Table 2
Effect of operating volume on the extent of degradation.

Operating volume (ml)	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
100	13.98	3.3×10^{-6}
200	10.28	4.81×10^{-6}
300	6.78	4.87×10^{-6}

Similar results in terms of effect of power density (P/Vr) have been reported for degradation of a pink colored dye (Rhodamine B) by Sivakumar and Pandit [7]. Harkal et al. [8] also reported similar result for the change in viscosity at 2% polymer concentrations for ultrasonic degradation of poly (vinyl alcohol) in aqueous solution. Hence all the sets of experiment were performed at optimized volume of 100 ml.

3.1.2. Effect of initial concentration

The effect of initial concentrations (20, 50, 100 and 200 ppm) of potassium ferrocyanide on the extent of degradation has been investigated. Fig. 4(a) depicts the variation in the extent of degradation with respect to time at different concentrations. It can be seen from the figure that the extent of degradation decreases with an increase in the concentration at same supplied ultrasonic power dissipation and constant volume of solution as 100 ml. In 80 min of irradiation time, the extent of degradation at 20 ppm concentration is 20.76% (9.83×10^{-07} mol degraded), which is higher as compared to the 8.02% (3.8×10^{-06} mol degraded) degradation at 200 ppm concentration. It is interesting to note here that even though the extent of degradation is decreasing the net moles degraded increases indicating that in actual practice, it might be important to compare the benefits in terms of faster degradation obtained by dilution as against the actual moles degraded.

As mentioned by Mahamuni and Adewuyi [9], in the case of non-volatile compound, the main mechanism for the destruction of pollutant is the attack of $OH^{\cdot}$ radical on the pollutant molecules and the degradation typically follows pseudo first order kinetics.

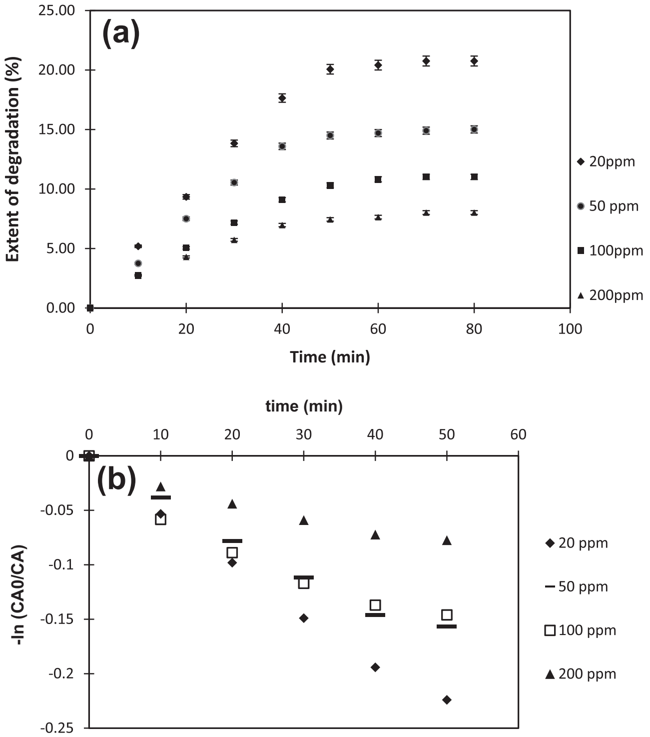

Fig. 4. (a) Effect of initial concentration on the degradation (%) in ultrasound. (b) Estimation of kinetic rate constant at different initial concentrations (Conditions: operating volume: 100 ml, pH: 7.3).

To correlate the observed data, pseudo first order kinetics was assumed and rate constants for degradation were calculated. Fig. 4(b) shows the plot of $\ln C_{A0}/C_A$ vs time (t). The plot of $\ln C_{A0}/C_A$ vs time (t) is a straight line passing through the origin, which confirms that, the degradation of potassium ferrocyanide using acoustic cavitation follows a pseudo first order reaction kinetics. It is observed from figure that the kinetic rate constant decreased from $4.71 \times 10^{-3}\ \text{min}^{-1}$ to $1.76 \times 10^{-3}\ \text{min}^{-1}$ for an increase in the concentration from 20 to 200 ppm. The maximum extent of degradation as 20.76% (9.83×10^{-07} mol degraded) was obtained at initial concentration of 20 ppm. Similar results for the dependency of degradation of p-nitrophenol on the initial concentration have been reported by Sivakumar et al. [10] over the concentration range of 10–500 ppm. Mishra and Gogate [11] have also investigated the effect of Rhodamine B concentration on the dye removal efficiency at different concentrations of 10, 25, 50 and100 ppm. It has been observed that extent of degradation decreases with an increase in the initial concentration of Rhodamine B. The maximum degradation of 28% was obtained at concentration of 10 ppm of Rhodamine B using only ultrasound.

3.1.3. Effect of pH

Solution pH plays an important role in determining the physical and chemical properties of the solution, which decides the location as well as the nature of the pollutant. The experiments related to effect of pH were carried out at different pH ranging from 2 to 10. It was observed that the degradation was enhanced at lower pH values. The maximum degradation of 43.44% (2.1×10^{-06} mol degraded) was obtained at concentration of 20 ppm potassium ferrocyanide at pH 2 and in general, extent of degradation was found to decrease with an increase in the pH as depicted in the Fig. 5. Table 3 depicts kinetic rate constants and moles of potassium ferrocyanide degraded at different operating pH. From Table 3, it is clear that the kinetic rate constant decreased from $7.63 \times 10^{-3}\ \text{min}^{-1}$ to $1.19 \times 10^{-3}\ \text{min}^{-1}$ for an increase in the pH from 2 to 10. Based on the results of experiments at various pH, further experiments were carried out at pH of 2.

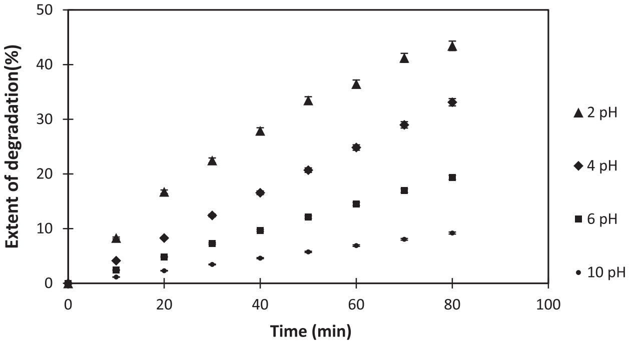

Fig. 5. Effect of pH on the degradation (%) in ultrasound. Conditions: operating volume: 100 ml, initial concentration: 20 ppm.

Table 3
Kinetic rate constants at different pH.

pH of potassium ferrocyanide solution	First order rate constant $k * 10^3$ (min^{-1})	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
2	7.63	43.44	2.1×10^{-6}
4	4.82	33.12	1.6×10^{-6}
6	2.63	19.36	9.2×10^{-7}
10	1.19	9.2	4.4×10^{-7}

The enhancement in the degradation rate at lower pH can be attributed to the fact that potassium ferrocyanide molecule is present in the molecular state at lower pH when the pH is less than the pKa value (9.2) of ferrocyanide and hence can easily locate or prefer to be at the gas–water interface of the collapsing cavities due to its hydrophobic nature. Thus the potassium ferrocyanide molecule is more readily subjected to the direct attack of $OH^{\cdot}$ radicals in the close vicinity of the collapsing cavity, resulting into increased degradation rate. Whereas, in the basic medium (pH > 7.0) potassium ferrocyanide molecules get partially ionized and become hydrophilic in nature, thereby remaining in the bulk liquid. Due to the recombination of $OH^{\cdot}$ radicals, only a fraction of the generated $OH^{\cdot}$ radicals diffuse into the bulk, resulting into lower concentration of $OH^{\cdot}$ radicals being used and made available for the oxidation of the potassium ferrocyanide as only about 10% of the $OH^{\cdot}$ radicals generated in the cavity can diffuse into the bulk solution. Also the quantum of free radicals generated under acidic conditions and the oxidation potential of hydroxyl radicals is higher which also contributes to the enhanced degradation. Ince and Tezcanli-Guyer [12] reported that enhancement in the degradation rates at acidic conditions is also due to the formation and accumulation of HOO radicals in the liquid bulk (upon H_2O_2 dissociation), which contributes to the oxidation.

Similar results for the dependency of degradation on the initial pH have been reported in the literature. Shriwas and Gogate [13] carried out experiments with sonication time of 60 min at different operating pH over the range of 2.5–9.3. The maximum degradation of pollutant over the range of study was observed under acidic conditions at pH 2.5. The degradation at this operating pH was 10.2% and decreased to negligible extents (1.4%) at operating pH of 7.0. The first order reaction rate constant for removal of methyl parathion was observed to be $1.75 \times 10^{-3}\ \text{min}^{-1}$ at pH of 2.5 as against $2.35 \times 10^{-4}\ \text{min}^{-1}$ at pH of 7.

3.1.4. Effect of operating temperature

The experiments related to the effect of operating temperature were carried out (volume of 100 ml, 20 ppm of potassium ferrocyanide solution and pH of 2) at different temperatures ranging from 20 to 50 °C. The constant temperature at the desired value was maintained using cooling/heating bath. Fig. 6 depicts the variation in the extent of degradation at different operating temperatures. It was observed that the extent of degradation initially increases with an increase in the temperature till an optimum value of 30 °C beyond which the extent of degradation decreases with a further increase in the temperature at same supplied ultrasonic power dissipation. It is clear from Table 4 that the rate constant decreased from $15.72 \times 10^{-3}\ \text{min}^{-1}$ to $9.61 \times 10^{-3}\ \text{min}^{-1}$ for an increase in the temperature from 30 to 50 °C. Also, the rate constant at a temperature of 20 °C was lower at $12.51 \times 10^{-3}\ \text{min}^{-1}$. The maximum degradation of 54.17% (2.56×10^{-06} mol of potassium ferrocyanide degraded) was obtained at an optimum temperature of 30 °C with initial concentration of 20 ppm potassium ferrocyanide at pH 2. The observed effects may be attributed to the counteracting effects of enhanced kinetics and lower efficacy of the collapse of the cavities. The vapor pressure of a fluid is dependent on its temperature and it increases exponentially with temperature. Thus, with an increase in the operating temperature, it is likely that vaporous cavities will be generated due to the entrapment of the vapors leading to lower cavitational activity. Also, the kinetic rate will be directly proportional to the operating temperature and hence it is likely that an optimum operating temperature might exist for the specific conditions due to the counteracting effects of enhanced kinetics and decreased cavitational effects.

Wang et al. [14] reported that three different regions are formed in the aqueous sonochemical degradation process: (1) The gas

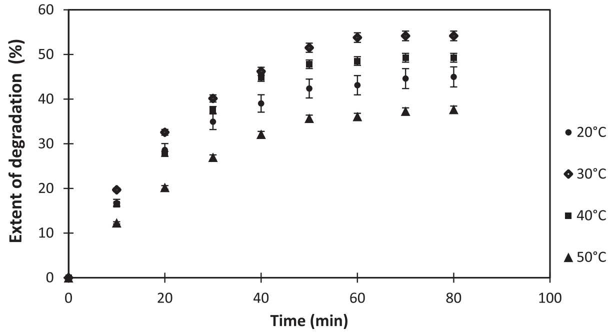

Fig. 6. Effect of temperature on the degradation (%) in ultrasound. Conditions: operating volume: 100 ml, initial concentration: 20 ppm, pH: 2.

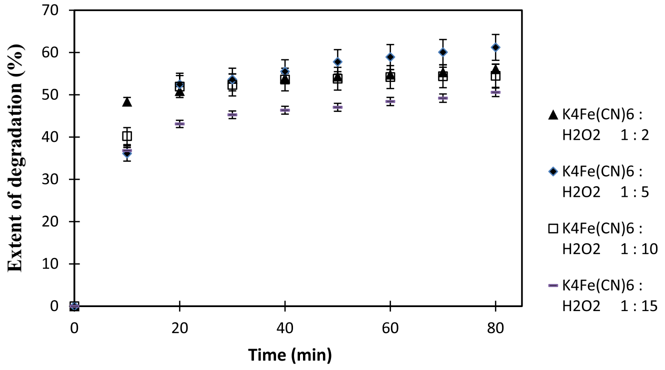

Fig. 7. Effect of H_2O_2 concentration on the degradation (%) in ultrasound. Conditions: operating volume: 100 ml, initial concentration: 20 ppm, pH: 2, temperature: 30 °C.

Table 4
Kinetic rate constant for degradation at different temperatures.

Operating temperature (°C)	First order rate constant $k * 10^3$ (min^{-1})	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
20	12.51	44.98	2.12×10^{-6}
30	15.72	54.17	2.56×10^{-6}
40	14.32	49.72	2.23×10^{-6}
50	9.61	37.7	1.78×10^{-6}

phase within the cavitation bubble where elevated temperature and high pressure are produced, (2) the interfacial zone between the bubble and the bulk solution where the temperature is lower than that inside the bubble but still high enough for a sonochemical reaction, (3) the bulk solution at ambient temperature where the reaction still takes place due to attack of hydroxyl radicals. Out of the above mentioned three regions, we prefer the interfacial zone as the region where potassium ferrocyanide is destructed. As the bulk temperature of water increased, the vapor pressure of water and volatile solutes inside the cavitation bubbles increased. The collapse of cavity is thus cushioned more than that at a lower bulk temperature, resulting in moderate conditions of cavitational intensity and a lower sonochemical degradation rate. Sehgal and Wang [15] demonstrated that the degradation of thymine using sonication increased with the temperature for experiments up to 30 °C, and then they were almost unaffected by the temperature between 30 and 52 °C.

3.1.5. Effect of hydrogen peroxide (H_2O_2)

Hydrogen peroxide is known to dissociate into hydroxyl radicals in the presence of ultrasonic irradiations and hence can be used as an intensifying agent to enhance the extent of degradation of pollutants. In the present work, approach of H_2O_2 assisted acoustic cavitation was used for the degradation of 20 ppm potassium ferrocyanide concentration with different H_2O_2 mole ratios viz. 1:2, 1:5, 1:10 and 1:15. The obtained results for the extent of degradation of potassium ferrocyanide have been given in Fig. 7. It is interesting to note that the time profile for variation in extent of degradation is different in the presence of hydrogen peroxide. The enhancement in extent and rate of degradation is due to an increase in the hydroxyl radical concentration due to sudden decomposition of hydrogen peroxide added into the system and also some inherent chemical oxidation effects from hydrogen peroxide [16]. The net result is that the initial degradation rate increases and hence a different time profile is obtained. It is also clear from Fig. 7 that the extent of degradation increases with an addition of the hydrogen peroxide till an optimum loading of 1:5 ratio of moles of potassium ferrocyanide to H_2O_2, beyond which a marginal decrease in the extent of degradation is observed at a ratio of 1:10 and then the extent of degradation decreases further at an H_2O_2 addition ratio of 1:15. Maximum degradation of 61.22% (2.9×10^{-6} mol degraded) was obtained at 1:5 ratio of moles of potassium ferrocyanide to H_2O_2. The initial rate constant (Table 5) decreased from 44.82×10^{-3} min^{-1} to 31.74×10^{-3} min^{-1} for an increase in the ratio of moles of potassium ferrocyanide to H_2O_2 from 1:5 to 1:15. The observed results can be attributed to the fact that above the optimum loading of 1:5 ratio excess hydrogen peroxide acts as a radical scavenger and hence the net extent of degradation of potassium ferrocyanide decreases. As a result, there is a critical hydrogen peroxide concentration where beneficial results have been observed for the removal of potassium ferrocyanide using hydrogen peroxide assisted acoustic cavitation. It is also observed that extent of degradation increases by 13% due to optimum H_2O_2 addition as compared to only acoustic cavitation in 80 min reaction time.

Similar trends, in terms of existence of an optimum concentration of hydrogen peroxide have been reported in the literature. Iordache et al. [17] reported that CN^- ions were found to be destroyed in the presence of ultrasound, possibly via the oxidative action of hydrogen peroxide. Time required for 74% degradation was increased from 40 min for CN^-/H_2O_2: 1/30 ratio to 115 min for CN^-/H_2O_2: 1/1 ratio. Guo et al. [18] showed that the efficiency of 2,4-dinitrophenol (DNP) degradation increased in the presence of hydrogen peroxide and increasing the concentration of hydrogen peroxide enhanced DNP degradation. It is worthy to note that further increasing the concentration of hydrogen peroxide only slightly enhanced the degradation efficiency when the concentration of hydrogen peroxide was higher than 300 mg/L. Our results also suggest that the concentration of hydrogen peroxide must be kept at optimum levels in order to achieve high decomposition efficiency. It is important to note here that the optimum loadings of hydrogen peroxide is different for each of the reported illustration confirming the requirement 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.

3.2. Hydrodynamic cavitation

3.2.1. Effect of operating pressure

To investigate the effect of inlet pressure on the degradation rate, the concentration of potassium ferrocyanide and the pH of the solution were kept constant at 20 ppm and 7.3 ± .05, respectively. The different sets of experiments were carried out at inlet pressure over the range 3–7 bars. Fig. 8 shows the effect of inlet

Table 5
Effect of hydrogen peroxide concentration.

$K_4Fe(CN)_6$:H_2O_2 (mol:mol)	Initial kinetic rate constant	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
1:2	41.72×10^{-3}	56.16	2.66×10^{-6}
1:5	44.82×10^{-3}	61.22	2.9×10^{-6}
1:10	41.23×10^{-3}	54.49	2.58×10^{-6}
1:15	31.74×10^{-3}	50.59	2.4×10^{-6}

Table 6
Kinetic rate constant at different operating pressures.

Inlet pressure (bar)	First order rate constant $k * 10^4$ (min^{-1})	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
3	7	7.22	1.7×10^{-5}
4	7.5	8.28	2×10^{-5}
5	9.1	9.51	2.3×10^{-5}
6	11.1	11.94	2.8×10^{-5}
7	8.3	8.5	2×10^{-5}

Table 7
Kinetic rate constant at different pH.

pH	First order rate constant $k * 10^3$ (min^{-1})	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
2	5.91	44.02	10.4×10^{-5}
4	3.58	31.87	7.54×10^{-5}
6	2.21	18.78	4.45×10^{-5}
10	0.70	7.51	1.78×10^{-5}

Table 8
Kinetic rate constant at different hydrogen peroxide concentration.

$K_4Fe(CN)_6$:H_2O_2 (mol:mol)	First order rate constant $k * 10^3$ (min^{-1})	Extent of degradation (%)	Potassium ferrocyanide degraded (mol)
01:01	3.9	40.17	9.51×10^{-5}
01:05	6.29	51.29	12.1×10^{-5}
01:10	4.22	41.86	9.91×10^{-5}
01:20	3.25	33.91	8.03×10^{-5}
01:30	1.97	19.43	4.6×10^{-5}

pressure on the degradation of potassium ferrocyanide. It was found that extent of degradation increases with an increase in inlet pressure reaching to a maximum at 6 bar inlet pressure and then decreases. It was also observed that the rate constant increased from 7×10^{-4} min^{-1} to 11.1×10^{-4} min^{-1} for an increase in the inlet pressure from 3 to 6 bar and then a decrease was observed as shown in Table 6. The maximum extent of degradation as 11.94% (2.8×10^{-5} mol degraded) was obtained at an inlet pressure of 6 bar. The observed results may be attributed to the fact that as the inlet pressure increases the local energy dissipation rate and the intensity of turbulence increases thereby increasing the collapse intensity. The increase in cavitational intensity results into increased degradation rate. The reduction in degradation rate beyond 6 bar inlet pressure can be attributed to the condition of choked cavitation. Saharan et al. [19] observed that initially at lower pressure the number density of cavities are low and these cavities behave as individual cavities and they collapse as soon as they come out of the venturi. No cavity cloud formation takes place till the optimum value of the inlet pressure and as the volume fraction occupied by the cavity is quite low, each cavity tends to behave individually. At the operating condition of higher inlet pressure beyond optimum, number density of cavities becomes so high that entire downstream area is filled with cavities and these cavities then start coalescing with each other and form a cavity cloud. The condition of cavity cloud formation is called choked cavitation. Conditions of choked cavitation results in cushioned collapse of cavities leading to lower cavitational intensity and hence lower extent of degradation. Similar trends regarding increase in the extent of degradation with an increase in pressure have also been reported in some of the earlier literature illustrations. Senthilkumar and Pandit [20] have shown that with an increase in the venturi inlet pressure the pressure drop across the venturi increases, resulting in an increase in the cluster collapse pressure. It has been also reported that the cluster collapse pressure or the cavitational intensity increases with an increase in the inlet pressure reaching to the maximum and then decreases. Bagal and Gogate [21] have studied the degradation of 2,4-dinitrophenol (initial concentration of 20 ppm) at different inlet pressures over the range 3–6 bar pressure and reported an increase in the extent of degradation till an optimum pressure of 4 bar pressure. It is also important to note here that the existence of optimum inlet pressure and its magnitude also depends on the design of hydrodynamic cavitation reactor as Chakinala et al. [22] have shown that degradation of real industrial effluent increases continuously with an increase in the inlet pressure over the range of pressures investigated in the work.

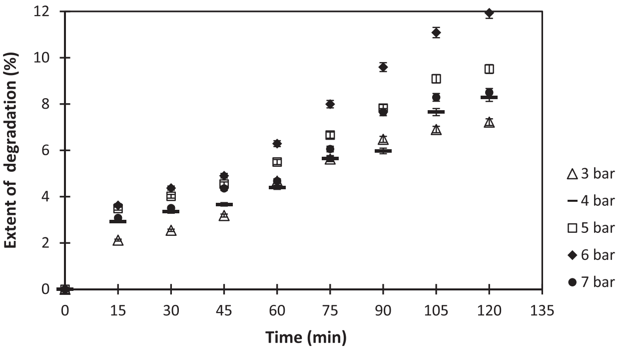

Fig. 8. Effect of operating pressure on the degradation (%) in hydrodynamic cavitation. Conditions: volume: 5 L, initial concentration: 20 ppm, pH: 7.3 (original solution pH), temperature: 30 °C.

3.2.2. Effect of pH

The effect of pH was investigated by carrying out experiments at different pH in the range of 2–10. The results indicate that the rate of degradation increases with a decrease in solution pH i.e., acidic medium is more favorable for the degradation of potassium ferrocyanide. Much lower degradation rate was observed at pH 10.0. About 44.02% (10.4×10^{-5} mol degraded) degradation was obtained in 120 min at pH 2.0 using hydrodynamic cavitation operating at 6 bar pressure. Number of moles of potassium ferrocyanide degraded and kinetic rate constants has been given in Table 7. It is observed that the rate constant increased from 0.7×10^{-3} min^{-1} to 5.91×10^{-3} min^{-1} with a decrease in the pH from 10 to 2. The discussion for the effect of pH is similar to that offered for the case of sonochemical reactors earlier. Similar illustrations can be observed in the literature where acidic conditions are found to be better for the degradation of organic pollutants using hydrodynamically generated cavitation. Pradhan and Gogate [23] have studied the removal of p-nitrophenol at three different pH values 2.0, 3.75 and 8.0 using hydrodynamic cavitation and observed that maximum removal of 63.2% was observed at pH value of 3.75. Saharan et al. [24] have also investigated the effect of pH on the decolorization of Acid Red 88 dye using hydrodynamic cavitation at different pH in the range 2–11 and reported that the rate of decolorization increases with a decrease in solution pH. A much lower decolorization rate was observed at pH 10.0 whereas about 92% decolorization was obtained at pH 2.0.

3.2.3. *Effect of hydrogen peroxide (H_2O_2)*

The effect of H_2O_2 assisted hydrodynamic cavitation was investigated for 20 ppm potassium ferrocyanide concentration with different H_2O_2 loadings as 1:1, 1:5, 1:10, 1:20 and 1:30 ratio of moles of potassium ferrocyanide to H_2O_2. Number of moles of potassium ferrocyanide degraded and kinetic rate constants are given in Table 8. It can be seen that degradation of potassium ferrocyanide was enhanced from 44.02% (10.4×10^{-5} mol degraded) to 51.29% (12.1×10^{-5} mol degraded) for operation using a combination of hydrodynamic cavitation with 1:5 ratio of moles of potassium ferrocyanide to H_2O_2 as compared to the operation using only hydrodynamic cavitation. The extent of degradation increases with an addition of the hydrogen peroxide till an optimum loading of 1:5 ratio of moles of potassium ferrocyanide to H_2O_2, beyond which a decrease in the extent of degradation is observed at higher ratios. Kinetic rate constant increased from 3.9×10^{-3} min^{-1} to 6.29×10^{-3} min^{-1} for an increase in the ratio of moles of potassium ferrocyanide to H_2O_2 from 1:1 to 1:5. The maximum extent of degradation as 51.29% (12.1×10^{-5} mol degraded) was obtained. It is also observed that the extent of degradation increases by 16.5% due to optimum H_2O_2 addition as compared to only hydrodynamic cavitation in 120 min of reaction time, which is similar to the degree of intensification obtained due to the use of ultrasonic irradiations.

Similar results were obtained by Joshi and Gogate [25] for the degradation of dichlorvos using hydrodynamic cavitation. Saharan et al. [24] also reported that the rate of decolorization increases with an increase in concentration of H_2O_2 from 0 to 4000 μM and almost 100% decolorization takes place at 4000 μM. Also, the combination of hydrodynamic cavitation and H_2O_2 gives a better result as compared to individual operation. Chakinala et al. [26] have reported that the extent of degradation increases with an increase in the hydrogen peroxide concentration over the range 500–2000 mg/L. Again it is important to note here that though the trends are similar, the exact extent of degradation and the value of optimum hydrogen peroxide loading are different for specific system under question.

4. Comparison between hydrodynamic cavitation and acoustic cavitation

To date most of the research work has been done on acoustic cavitation based degradation especially for the case of cyanide containing wastewaters and the present work was the first one to investigate the efficacy of hydrodynamic cavitation for cyanide treatment. Though, highly successful in laboratory scale operation, acoustic cavitation still has not been able to find its application on industrial scale operation due to the problems associated with the construction of high frequency or high power transducers and due to higher cost of materials and energy requirements. The advantages of a hydrodynamic cavitation reactor are that it is easy to operate and design and also the capital cost for the reactor will be lower for higher volumes of processing. Thus it becomes imperative to compare the effectiveness of hydrodynamic cavitation and acoustic cavitation. In the present work, the unified criteria of cavitational yield (net cavitational effect i.e., moles of potassium ferrocyanide degraded per unit supplied energy) has been used for the comparison. In the case of acoustic cavitation, experiments were carried out with 100 ml operating volume, fixed initial concentration of 20 ppm, at pH 2 and operating temperature of 30 °C for a fixed time of operation as 80 min. In the case of hydrodynamic cavitation, experiments were carried out with 5 L operating volume, fixed initial concentration of 20 ppm, inlet pressure of 6 bar, at pH 2 and operating temperature of 30 °C for a fixed time of operation as 2 h. It was established from the calculations (detailed calculation is given in Appendix I) that the cavitational yield in the case of hydrodynamic cavitation [1.88×10^{-10} (gmol/J)] is 27 times higher than acoustic cavitation [6.96×10^{-12} (gmol/J)]. Patil and Gogate [27] have reported that the cavitational yield for the degradation of methyl parathion in the case of hydrodynamic cavitation is 20 times higher as compared to acoustic cavitation. The basic reason for the low cavitational yield in the case of ultrasonic equipment is due to poor energy conversion efficiency and due to the fact too much intense cavitation is generated. Gogate et al. [28] have investigated the energy efficiency and cavitational yield for different reactors for the model reaction of decomposition of KI and have shown that the cavitational yield as well as the energy efficiency is much higher for the hydrodynamic cavitation reactors.

5. Conclusions

The present work involved investigations related to the application of cavitation based treatment approach for the degradation of potassium ferrocyanide. It was observed that acidic conditions, lower initial concentration and optimum temperature favored the degradation using acoustic cavitation whereas optimum inlet pressure and acidic conditions were found to give maximum degradation in hydrodynamic cavitation. The main driving mechanism for the intensification observed in the combination of acoustic/hydrodynamic cavitation with hydrogen peroxide was the enhanced formation of free radicals in the water. It was also observed that maximum benefits are obtained under optimum concentration of hydrogen peroxide. Energy consumption analysis presented in the work confirmed that moles of potassium ferrocyanide degraded per unit energy using hydrodynamic cavitation is order of magnitude higher than using acoustic cavitation. Overall, it can be said that hydrodynamic cavitation reactors offer considerable promise in treatment of cyanide containing wastewaters.

Appendix I. Sample calculation for the estimation of cavitational yield

Cavitational. yield for acoustic cavitation

Efficiency of the horn = 10.22%.
Actual power dissipated into the solution in 80 min
=input power × efficiency × time
$=750 \times .1022 \times (80 \times 60)$
=367920 J.

Cavitational yield = number of moles of potassium ferrocyanide degraded (mol)/power dissipated into the solution in 80 min(J).

Cavitational yield = $2.56 \times 10^{-6}/367920$.
Cavitational yield = 6.95803×10^{-12} (gmol/J).

Cavitational. yield for hydrodynamic cavitation

Inlet fluid pressure = 6 bar = 599800 Pa.
Downstream pressure (P_2) = 101325 Pa.
Pressure drop across the venture, ΔP = 6 bar = 599800 Pa.
Volumetric flow rate at pressure 6 bar (Q) = 461 LPH.

$$= \frac{461 \times 10^{-3}\ \mathrm{m}^3}{1 \times 3600\ \mathrm{s}}$$

$= 1.28 \times 10^{-4}\ \mathrm{m}^3/\mathrm{s}$.
Actual power dissipated into the solution in 120 min

= pressure drop across the venturi × volumetric flow rate × time

= $(599800) \times (1.28 \times 10^{-4}) \times (120 \times 60)$

= 552960 J.

Cavitational yield = number of moles of potassium ferrocyanide degraded (mol)/power dissipated into the solution in 120 min(J).

Cavitational yield = $10.4 \times 10^{-5}/552960$.

Cavitational yield = 1.88×10^{-10} (gmol/J).

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