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Dear Mr. Mihir Bhagat,

I am pleased to inform you that the submitted paper listed above, has been accepted for presentation at the Fourth International Conference on Energy, Water and Environmental Sciences, which will be held on December 15-17, 2015, in Ras Al Khaimah, United Arab Emirates. Each paper submitted to ICEWES 2015 received, at least, two reviews. In the mean time we will send you a draft copy of your paper according to the journal's format soon for you to check and approve.

On behalf of the ICEWES 2015 scientific committee, I would like to cordially invite you to attend the conference and orally present your paper in Ras Al Khaimah, UAE.

Thank you very much for your contribution to ICEWES 2015 conference.

We are looking forward to meeting you in Ras Al Khaimah.

Sincerely,

Prof. Bilal Akash
Scientific Committee Chair
Fourth International Conference on Energy, Water and Environmental Sciences
Ras Al Khaimah, United Arab Emirates



Synergistic Degradation of 4-Nitrophenol Using Hydrodynamic Cavitation in Combination with Hydrogen Peroxide

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Abstract

p-Nitrophenol (PNP), a widely utilized intermediate, is a persistent pollutant present in industrial effluent streams. The inherent toxicity of PNP necessitates its treatment before releasing it in the environment. The conventional approach pertaining to degradation of PNP is based on chemical and biological methods for decomposition. Alternatively, Hydrodynamic Cavitation (HC) is emerging as a promising technology for waste water treatment. This study investigates HC as an alternative technology to degrade PNP and subsequently enhance efficiency by varying involved parameters. The HC-H₂O₂ system is reported to exhibit synergism for pollutant oxidation, the applicability of which is also investigated for degrading PNP. A PNP solution of fixed concentration was subjected to HC using a circular Venturi. Degradation was studied by varying time, pressure, pH and H₂O₂ concentration. Decomposition of p-Nitrophenol was quantified by UV-Visible Spectroscopy at 405nm. Degradation of PNP was observed to be directly proportional to time at constant pressure and an initial increase in pressure led to higher degradation. However, on achieving a peak decomposition level, the extent of decomposition declined with further increase in pressure. Experiments done at acidic pH resulted in over two times the decomposition than those done at basic pH. The PNP-H₂O₂ system exhibited 91% more degradation than the sum of degradations affected by PNP and H₂O₂ individually. Moreover, subjecting PNP:H₂O₂ in a molar ratio of 1:5 to HC resulted in near-complete (>95%) degradation. This study proposes variations of parameters for optimum decomposition of PNP using HC and explores the HC-H₂O₂ system as a promising alternative for the degradation PNP.

Keywords: p-Nitrophenol, Hydrodynamic Cavitation, Synergism, Wastewater Treatment.

1. Introduction

p-Nitrophenol (PNP) is an important intermediate for the manufacture of dyes, pigments, pesticides (Parathion and Fluoridifen), explosives, engineering polymers and pharmaceuticals (Acetaminophen) [1],[2],[3]. Such widespread usage of PNP generates enormous quantities of PNP-laden industrial and agricultural effluents which do not degrade easily and persist in the environment for a long time [4]. Moreover, PNP is a priority pollutant as classified by the US EPA and is severely toxic having a LD50 value of 667 mg/kg (Rat, Oral) and a LC50 value of 5.8 mg/L (fish)[5]. It thus becomes imperative to treat PNP-laden effluents before discharging them in the environment.

Substantial amount of work has been conducted on PNP degradation using photocatalysts. San et al[6] have attempted degradation of PNP using a TiO₂ catalyst in presence of UV light and achieved 58.7% PNP degradation over 160 min of irradiation. Paola et al [7] have gone a step further and performed PNP degradation with a TiO₂+Mo loaded catalyst under UV light. Their experiments exhibited quantitative PNP degradation after 150 min. of treatment while using a TiO₂-HP catalyst.

Bhatti et al [3] have quantitatively degraded PNP using an activated sludge for a hydraulic retention time of 11 h when using fresh sludge. Jain et al[8] have also performed a

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biodegradation on PNP using an *Arthrobacter Sp.* strain, achieving complete degradation to give products such as 1,2,4-benzenetriol and Hydroquinone. However, all such methods require high processing times to obtain sufficient degradation.

Hydrodynamic Cavitation (HC) is an emerging technology for the effluent treatment. It utilizes the phenomena of formation, growth and implosion of bubbles to release concentrated amounts of energy [9] and generate reactive radicals such as H^\bullet and $\bullet OH$, which bring about chemical reactions [10], microbial cell disruption [11] and effluent treatment [12]. Capocelli et al [13] have studied the degradation of PNP via HC at various cavitation conditions to obtain modest yields. Though a faster technology, HC as a stand-alone process is unable to match efficiencies exhibited by conventional processes.

Hydrogen peroxide is a well-known oxidizing agent for treating persistent pollutants and microbial cells [14], [15]. It is known to synergistically enhance efficiencies of HC treatments, to great effect [16]. Pradhan et al [17] have utilized Fenton Chemistry to degrade PNP using $Fe+2/H_2O_2$ along with HC to great effect, achieving maximum PNP removal of 63.2%. The following work attempts to build upon this synergism between HC and H_2O_2 to achieve higher PNP degradation extents.

2. Materials and Methods

2.1. Materials

Laboratory grade 4-Nitrophenol was procured from Thomas Baker (Chemicals) Pvt. Ltd. and diluted using distilled water for conducting experiments. Reagent grade Sodium hydroxide pellets and Sodium thiosulfate were purchased from High Media Pvt. Ltd. Other chemicals such 98% sulfuric acid and 30% v/v Hydrogen peroxide were also obtained from Thomas Baker (Chemicals) Pvt. Ltd.

2.2. Hydrodynamic Cavitation Setup

HC was performed in a stainless steel setup as utilized by Badve et al [18], and described in Fig. 1. The setup consists of a holding tank, a 3-phase variable frequency drive (VFD)-connected positive displacement pump, a main line (connects the cavitation device) and a bypass line, all being interconnected with pipes and valves. A pipe connecting the bottom of the holding tank transfers fluid to the pump which in turn discharges fluid to a main line, via the cavitation device or to a bypass line. Both the main and bypass lines terminate in the tank. Care is taken to avoid inducing air in the fluid by ensuring discharge below the liquid level in the tank.

A circular venturi was used as the cavitation device as described by Badve et al [18], having the following dimensions:

Table 1. Dimensions of Circular Venturi Used for HC

| Dimension | Value |
|----------------------------------|---------------|
| Throat | 2 mm diameter |
| Total length | 106 mm |
| Length of convergent section | 18 mm |
| Length of divergent section | 67 mm |
| Half angle of convergent section | 22.6° |
| Half angle of divergent section | 6.5° |

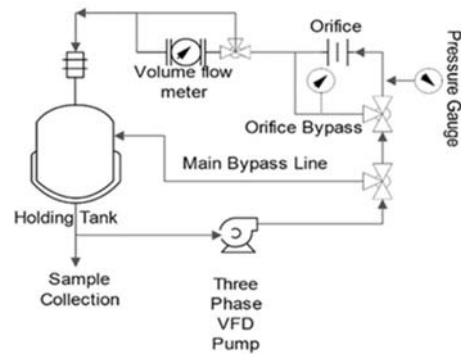


Fig. 1. HC Setup Schematic Diagram

2.3. Experimental Methods

All experiments were carried out using 5 L of a 10 ppm 4-Nitrophenol solution at 30°C. This solution was subjected to HC treatment using the venturi for parameters such as pressure, pH and H_2O_2 concentration. 50 mL samples were withdrawn at regular intervals of time for all experiments. Samples for experiments conducted in presence of H_2O_2 were quenched with $Na_2S_2O_3$ after collection to neutralize unreacted H_2O_2 . Samples were then diluted three times using distilled water and analyzed using UV-Visible spectroscopy at 405 nm at neutral pH [19]. The absorbances of samples were compared with a standard concentration-absorbance curve for 4-nitrophenol to obtain concentrations of PNP after degradation.

3. Results and Discussion

3.1. Effect of operating pressure on PNP degradation

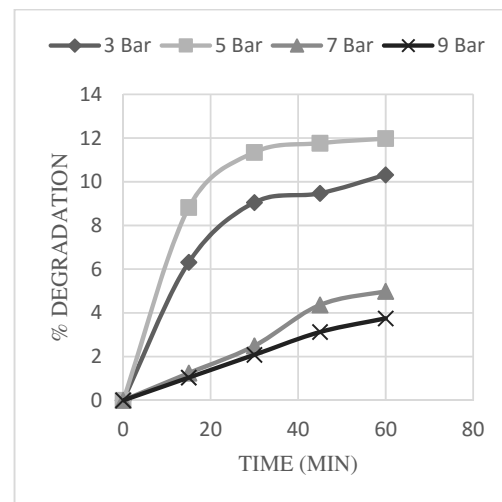


Fig. 2. Effect of Inlet Pressure on PNP Degradation

Fig. 2 describes the percentage of PNP degraded versus time, at various operating pressures. It is observed that degradation increases with pressure up to an optimum, following which it follows a decreasing pattern. It is also noted that most of possible degradation occurs within 30 minutes of treatment. Badve et al [18] have attributed this behavior to the Cavitation number, defined as:

$$C_v = \frac{(p_2 - p_v)}{(1/2)\rho v_o^2}$$

Where C_v is the cavitation number, P_v is the vapor pressure of the fluid, P_2 is the inlet pressure, ρ is the fluid density and v_o is the velocity of the liquid at the constriction. Cavitation ideally occurs for $C_v \leq 1$ [20]. Thus, as the pressure initially increased in our study, the velocity at the constriction increases, resulting in higher cavitation. However, after 5 Bar pressure, the number of cavities generated is so high that they begin coalescing, leading to lower degradation levels.

5 Bar of inlet pressure was found to display optimum PNP degradation and was fixed for subsequent experiments.

3.2. Effect of Solution pH on PNP Degradation

Fig. 3 depicts PNP degradation over time at different pH values for 5 Bar inlet pressure. It is noticed that degradation is higher at lower pH and subsequently decreases on increasing pH. Capocelli et al [13], infer that at a pH higher than its pKa of 7.15, PNP exists in its phenoxide form. This phenoxide form faces electrostatic repulsion away from cavities, resulting in lower degradation. They further report that $\bullet\text{OH}$ radicals generated as a result of HC, show reduced recombination abilities in acidic media and are thus more potent as oxidants. The degradation at pH 8 is similar to that at pH 10 which indicates that degradation could be of pH in once the phenoxide formation occurs.

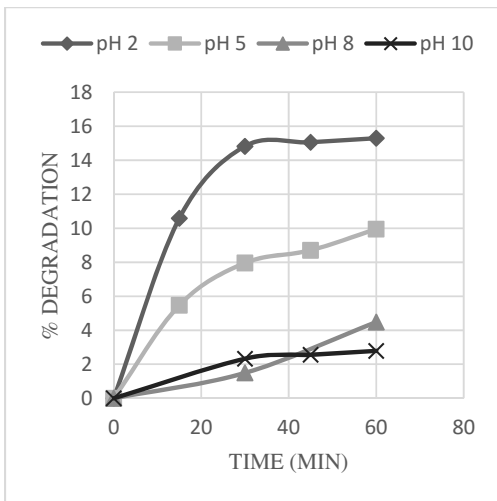


Fig. 3. Effect of Solution Ph on PNP Degradation at 5 Bar Pressure

3.3. Effect of H₂O₂ concentration on PNP degradation

H₂O₂ is a well-known reagent for treating organic contaminants such as PNP via $\bullet\text{OH}$ radical attack [18]. However, slow rates of $\bullet\text{OH}$ generation in dilute media require high concentrations of H₂O₂ to effect substantial degradation on PNP. HC is known to address this issue by enhancing $\bullet\text{OH}$ generation, as mentioned by Raut-Jadhav et al [21]. We utilized H₂O₂ in lower concentrations to generate such radicals using HC for PNP degradation. Fig. 4 describes the extent of PNP degradation using HC in presence of varying concentrations of H₂O₂, at 5 Bar pressure. A further increase in H₂O₂ concentration directly results in higher PNP degradation until a molar ratio of 1:5, at

which the optimum degradation of 95% is reported. Higher concentrations reporting no further increase in degradation suggests a saturation of $\bullet\text{OH}$ radicals.

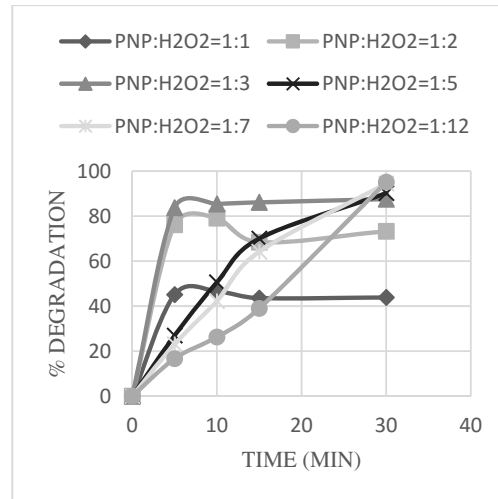


Fig. 4. Effect of PNP: H₂O₂ Molar Ratio on PNP Degradation

4. Synergism between HC and H₂O₂

In order to explore the synergism between H₂O₂ and HC for PNP degradation, three experiments were conducted as depicted in Fig. 5. The effect of H₂O₂ on PNP alone was studied by stirring a mixture of PNP and H₂O₂ in 1:1 molar ratio over 30 min. Contributions arising solely due to cavitation were analyzed by HC treatment at 5 Bar pressure to the PNP solution. Finally, the synergism between H₂O₂ and HC was studied by subjecting a mixture of PNP and H₂O₂ in 1:1 molar ratio to HC.

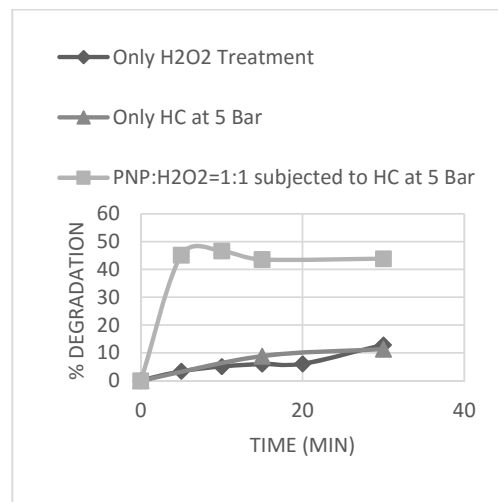


Fig. 5. Comparison of HC and H₂O₂ Effects, Individually and Synergistically

On analysis it was found that PNP degradation for the synergistic system was 44% and 11%, 12% respectively for HC and H₂O₂ being used exclusively. This represents 91% increase over the sum of degradation levels observed for individual parameters. It is also noted that all of the degradation in the synergistic system occurs within 5 min of treatment time, significantly reducing PNP effluent treatment times. A reasoning for this behavior could be derived from the fact that a

substantial amount of degradation using HC is effected by hydroxyl radicals generated during cavity implosions. Similarly, Hydrogen peroxide on being subjected to HC, rapidly undergoes homolytic cleavage produce two hydroxyl radicals. This supply of hydroxyl radicals makes good contact with PNP molecules due to efficient mixing during HC. This behavior is a likely reason for the 91% rise in efficiency of PNP by HC in presence of H₂O₂.

5. Conclusion

Hydrodynamic cavitation was utilized to study the degradation of 4-Nitrophenol. It was observed that increasing pressure increased PNP degradation upto an optimum level after which it declined. Acidic pH favored higher degradation of PNP over basic pH. However, pressure and pH variations did not sufficiently degrade PNP to acceptable levels in short times. Hydrogen peroxide, known to exhibit synergism with HC, was combined with HC to study the degradation of PNP. In this case, degradation levels were 91% more than the additive degradations exhibited by HC and H₂O₂ alone. Subjecting a mixture of 1:5 mol/mol PNP:H₂O₂ to HC effected 95% degradation over 30 min of treatment. Such results propose the HC-H₂O₂ system as an alternative to conventional treatment processes for PNP.

6. Future Scope

Further work can include identification of intermediates to propose a PNP degradation mechanism. Other parameters such as heat treatment, alternative cavity designs, other oxidizing agents (Cl₂, NaClO, O₃, etc) could be varied to enhance efficiencies, treatment times and costs. Not only does applicability of the HC-H₂O₂ synergy for degrading other such pollutants holds promise but other such oxidants to be used in conjunction with HC must be investigated upon.

Acknowledgments

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