Degradation of Prazosin by using Newer Dual Activity Hydrodynamic Cavitation Reactors

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Abstract

A study was conducted to investigate the degradation of Prazosin, an Alpha-1 Adrenergic Blocker, which is commonly used in the treatment of Hypertension. The study aimed to achieve improved efficiency using Hydrodynamic Cavitation (HC) and Process Intensification. A new cavitation technique that utilises the Dual Activity Reactor, which is a vortex flow-based cavitation device, was introduced in the study. Two different types of vortex diodes were used in a comparative investigation: a Non-Catalytic Aluminium diode and a Dual Activity Copper diode exhibiting catalytic properties. The impact of pressure on Prazosin degradation and mineralisation was studied on a pilot-plant scale with a capacity of 1 m^3/h. Process Intensification was carried out by Aeration, Hydrogen Peroxide, and pH modification. The results showed that aeration produced significant degradation (~18% degradation) using the Cu-Vortex Diode compared to the Al-Diode. The use of H_2O_2 resulted in complete (100%) degradation of the Active Pharmaceutical Ingredient (API) pollutant within just 5 minutes of treatment. Effective mineralisation of ~55% was obtained with the Cu-Diode, whereas only 34% was obtained with the Al-Diode. The development of Hydrodynamic Cavitation technology, with the incorporation of a Dual Activity Reactor-Cu Vortex Diode as a cavitation device, represents a remarkable breakthrough in the field of industrial wastewater treatment. This technology can provide an efficient and practical solution to remove various API pollutants, thereby reducing the environmental impact of industrial activities. The potential benefits of this technology for the industry are immense, opening up a world of possibilities for cleaner and more sustainable industrial practices.

1.Introduction

Hydrodynamic cavitation (HC), an advanced oxidation process, is considered to be an effective technique in various areas of water, energy, chemicals, and materials sectors. Cavitation here creates a low-pressure region within a cavitation reactor, leading to the formation of vaporous cavities; the bubbles are allowed to grow and collapse in a specified manner. These cavities undergo pressure fluctuations and collapse catastrophically, producing intense shear forces, localized high-pressure and temperature zones (T, ~10000 K and P, ~1000–5000 atm) which results in-situ generation of hydroxyl radicals[1]. Hydrodynamic cavitation reactors involve the use of specific designs of cavitating devices, which may or may not incorporate moving parts, and are used in various areas, such as biomass pretreatment[2], food and beverage processing[3], extraction of natural bioactive[4], microbial disinfection[5-7], desulfurization of fuels[8], removal of refractory pollutants like active pharmaceutical ingredients (APIs)[9,10], phenolic compounds[11], dyes[12] etc. HC offers numerous advantages over other advanced oxidation processes (AOPs) such as Fenton oxidation, photocatalysis, UV treatment, electrochemical oxidation, and ozonation, for mineralization without secondary waste generation or the use of external catalysts[13].

Various geometric configurations for hydrodynamic cavitation reactors have been reported, including linear flow devices like venturi and orifice, and non-linear flow devices like vortex diode and rotor-stator assembly. The vortex diode, employing rotational flow offers advantages such as high energy efficiency, low pressure requirements, reduced clogging, and easy scale-up[14]. The efficiency of HC processes can be intensified by adding oxidizing agents, nanoparticles, or metal/metal oxides[13], or by modifying cavitation reactors through changes in the material of construction or by coating the internal surface of the reactor with appropriate metals like copper, nickel, iron, silver[15-16]. Parsa et al. reported the catalysed HC process combined with scrap iron sheets as a catalyst for decolorization of Rhodamine B[17]. Copper oxide and peroxymonosulfate-activated copper oxide have been reported as highly promising catalysts, in the form of pellets or nanoparticles, to enhance the degradation of various organic pollutants [18-20]. Recently, dual-activity cavitation reactors combining catalytic activity with

cavitation have shown remarkably high degradation rates for API pollutants such as cephalexin, ciprofloxacin, metformin [15,16,21].

Due to the increase in emerging contaminants, particularly from pharmaceutical industries, it is crucial to develop effective methods for removing these refractory pollutants. Prazosin Hydrochloride (PRH), being an Alpha-1 Adrenergic Blocker, is widely used to treat hypertension, benign prostatic hyperplasia, and post-traumatic stress disorder. Due to its extensive use, PRH finds its way into the environment through various channels, such as the disposal of medicines through healthcare centres, industrial effluent, and human feces. Al-Qaim reported the typical concentrations of prazosin in influent sewage treatment plants (14-525 ng/L) and raw leachate (3850 ng/L)[23-24]. The rapid growth of the pharmaceutical industry, coupled with widespread medication usage, leads to elevated levels of API pollutants in industrial wastewater and in surface waters. This necessitates the development of suitable treatment technologies or modifications to ensure a sustainable and economically viable approach for treating effluents containing low to high concentrations.

Very few methods for the removal of PRH have been reported so far that include different advanced oxidation processes such as electrochemical oxidation[25-26], activated sludge process using aerobic sequencing batch reactor (SBR)[27], biodegradation[28], photocatalysis[29], stress conditions[30]. Mussa et al. reported the electrochemical oxidation of different therapeutic classes of pharmaceuticals, including PRH, using a graphite PVC composite electrode, achieving 98% degradation in 50 minutes of electrolysis [26]. Al-Qaim also reported 96% PRH degradation using an electrochemical degradation process in NaCl medium in 40 minutes[25]. Other than these methods, biodegradation of prazosin was also reported by isolating and characterising the potential microbes that help in the degradation process, resulting in 88% of the removal rate[28]. Bakshi et al. demonstrated that PRZ underwent significant degradation under hydrolytic stress[30]. Zaini et al. reported the removal of PRH using the aerobic sequencing batch reactor system and found moderate degradation efficiency of 41%[27]. Despite many reported methods achieve high removal rates (~98%), these have significant drawbacks such as high maintenance costs, high energy requirements, secondary waste generation, the formation of numerous by-products, and high treatment times. It is intuitive to develop a cost-effective and techno-economically feasible technology to degrade PRH with for industrial scale applications.

The present study demonstrates remarkably high degradation rates for prazosin by hydrodynamic cavitation. Two different vortex diodes were used: Al-vortex diode and Cu-vortex diode. The studies were carried out on a pilot plant scale with a capacity of 1 m³/h. The methodology suggests potential for redesigning reactors in the existing cavitation processes by changing the material of construction (MOC) using selected catalytic metals. It promises significant improvements in the removal efficiency and for lowering treatment costs.

2. Materials and Methods

2.1 Materials

Prazosin Hydrochloride ($C_{19}H_{21}N_5O_4.HCL$; 419.86 g/mol; CAS: 19237-84-4; Purity > 99.9%, BLD Pharma Pvt Ltd, India) in crystalline form was used to prepare synthetic wastewater. The chemical and physicochemical properties of PRH are listed in Table 1. Hydrogen Peroxide (H_2O_2; 50% w/v, AR grade, RANKEM, Mumbai) and Acetonitrile ($\geq$ 99.9% Purity, HPLC grade, Avantor Performance Materials) was used for the process intensification studies. pH modification was performed using 1N Nitric acid (70% w/v) and 1N Sodium hydroxide, both procured from Merck, India.

2.2 Experimental Methodology

The hydrodynamic cavitation pilot plant setup with a capacity of 1 m³/h was used to study the degradation of prazosin (Fig. 1). The methodology was already described in our previous research[9,15] and hence only the essential details are discussed here.

The pilot plant setup consisted of a 50 L water storage tank and a multistage centrifugal pump (Model CNP, CDLF2–26, SS316, 1.2 m³/h at 228 MWC, power rating 3 kW (4 hp), India) for pumping the wastewater. Two vortex diodes, each having an 11 mm throat diameter and a 66 mm chamber diameter, were utilized as cavitation reactors. One was a conventional aluminum vortex diode, and the other was a dual-activity catalytic reactor, a copper vortex diode, which exhibits additional catalytic activity. The pressure drop across the cavitation reactor was adjusted and measured using pressure transmitters (Honeywell ST 700, India). A flow transmitter (KRONE, H250) with a range of 150–1500 LPH and an integral analog indicator was used to measure the mainline flow rate while a thermocouple-RTD (EUREKA Eng.

Enterprises India; 0–200˚C) was used to measure the inlet temperature of the system. The temperature within system was controlled by a cooling system (JULABO, Model FL 1701, Japan). The entire setup was mounted on a stainless-steel frame with wheels.

All the experiments were performed with 20 L synthetic wastewater containing a known initial concentration of 10 mg/l prazosin. The effect of pressure drop was studied in the range of 0.5-2 bar across the vortex diode. The aeration effect on PRH degradation was studied by bubbling air into the wastewater tank using an air pump (SOBO AQUARIUM SB-9905). Additionally, the process intensification was carried out using hydrogen peroxide at different molar ratios of PRH: H_2O_2 such as 1:100 (0.081 g/L), 1:200 (0.162 g/L) and 1:500 (0.405 g/L). The effect of pH was studied by modifying the pH of the wastewater solution under acidic (pH 4) and alkaline conditions (pH 9). All the experiments were carried out for 60 minutes, with samples withdrawn at intervals of 5–10 minutes. The reproducibility of the experiments was confirmed and found to be satisfactory.

2.3 Analysis

The analysis for the removal of the model API pollutant-Prazosin was carried out using Total Organic Carbon (TOC-L-H564054; Shimadzu, Japan) and High-Performance Liquid Chromatography (HPLC, Prominence i-series LC2030c 3D plus HPLC, Shimadzu C-18 Column, 4.6×250 mm, particle size 5 μm). The mobile phase consisted of acetonitrile (75%) and 0.1% formic acid in deionized water (25%), used as the eluent for detecting Prazosin at a flow rate of 1 ml/min and a wavelength of 247 nm. The pH of the samples was measured using a Multi Para MP-5 pH meter (Spectra Lab Instruments Pvt. Ltd., India). The determination of intermediates formed during prazosin degradation was conducted through Liquid Chromatography High-Resolution Mass Spectroscopy (LC-HRMS) analysis.

3. Results and discussion

3.1 Effect of pressure drop on the degradation of PRH

Pressure drop across the cavitation reactor is a decisive parameter for the efficiency of the treatment. As in earlier findings, the cavitation inception point for vortex diode was found to be ~0.48 bar pressure drop and therefore, the pressure range for the pressure drop was selected

as 0.5–2 bar to find optimum pressure drop[8]. It may be noted that the degradation decreases or remains constant beyond the optimum point due to possible super cavitation phenomenon which eventually reduces the cavitational intensity[13].

The results from Figure 2 clearly show a significantly higher degradation of PRH at optimum pressure drop of 0.5 bar, which then decreases, indicating no requirement of high pressures beyond the pressure drop of 0.5 bar. A maximum degradation of 31% and 35% of PRH was achieved using the Al-vortex diode and Cu-vortex diode, respectively. In comparison, TOC reduction of 30% using the Cu-vortex diode was approximately twice that of the Al-vortex diode at 0.5 bar ΔP, indicating additional catalytic action of Cu metal. From Fig. 3 (a, b), the HPLC results indicate that there is no intermediate formation for only HC process. The kinetics of PRH degradation was evaluated using a pseudo-first-order reaction by equation 1, and the kinetic constant values for vortex diodes are listed in Table 2.

$$C = C_0 \, e^{-kt} \tag{1}$$

Where, C_0 and C are the PRH concentrations initial and final concentration. 't' is time in min and 'k' is the first order rate constant (min^{-1}). For the optimum pressure drop, ΔP, of 0.5 bar, the corresponding k values for the Al-vortex diode and Cu-vortex diode were $6.2 \times 10^{-3} \, min^{-1}$ and $7.2 \times 10^{-3} \, min^{-1}$, respectively.

Many researchers have investigated the effect of pressure drop on the degradation of pollutants, suggesting that significantly higher-pressure drops are required for other cavitation reactors than vortex diodes. However, the optimal pressure drop depends on the reactor configuration and the type of pollutants involved[9,31]. Raut-Jadhav reported a maximum degradation of 27.49% for the methomyl pesticide using hydrodynamic cavitation with a circular venturi having a 2 mm throat diameter, at a very high inlet pressure of 3 bar[31]. However, for the degradation of imidacloprid insecticide, a very high inlet pressure of 15 bar was required to achieve a 26.5% degradation[32]. Dixit et al. reported the superiority of the vortex diode over the orifice plate as a cavitation reactor by comparing the degradation efficiency of the naproxen compound. The orifice device required a very high pressure drop of 5 bar, more than three times than that required by the vortex diode[9].

The degradation of only 31-35% is not sufficient for industrial applications. Consequently, the improvement by catalytic devices needs further investigation through process intensification or modifications in hydrodynamic cavitation.

3.2 Effect of aeration on PRH degradation combined with HC

Introducing gases like air, oxygen, or ozone can significantly influence cavitation by affecting the number and behaviour of bubbles. Air, being cost-effective, is beneficial for process intensification. It enhances cavitation by promoting gas or vapor nuclei formation and supporting oxidation reactions through oxygen, which increases oxidizing species and, consequently, the degradation of pollutants. For evaluating synergism between the combined approach of HC and aeration, experiments were conducted at similar operating conditions, such as a constant initial concentration of 10 ppm and a pressure drop of 0.5 bar by continuously bubbling air to a recirculating tank. It was observed (Fig. 4) that the extent of degradation of PRH increases from 31% to 39% with a 26% TOC reduction, and from 35% to 46% corresponding to 35% TOC reduction through intensified process of HC and aeration using the Al-vortex diode and Cu-vortex diode, respectively. The results also indicate a higher rate of degradation due to the enhancement in the kinetic rate constant of HC + aeration compared to HC alone, confirming synergism (Table 2). The synergistic index (ξ) for the combined process of HC and aeration was calculated using equations 2 and 3 for both vortex diodes.

$$\xi_{Al-vortex\ diode} = \frac{k_{HC+aeration}}{k_{HC} + k_{aeration}} = \frac{8.3\ x\ 10^{-3}}{6.2\ x\ 10^{-3} + 0} = 1.34 \qquad (2)$$

$$\xi_{Cu-vortex\ diode} = \frac{k_{HC+aeration}}{k_{HC} + k_{aeration}} = \frac{10.3\ x\ 10^{-3}}{7.2\ x\ 10^{-3} + 0} = 1.43 \qquad (3)$$

The synergistic index values of 1.34 and 1.43, greater than 1, indicate good synergism and highlight improvement in the efficiency of the combined HC and aeration process compared to the individual processes.

Many literature studies have reported aeration as a process intensification approach in the hydrodynamic cavitation for higher efficiency in wastewater treatment applications. Bokhari et al. reported achieving 90% degradation of benzene at an inlet pressure of 3 bar within 50 minutes using a combined approach of HC and aeration[33]. Patil et al. observed a 100% improvement in the degradation of octanol solvent by employing an aeration-based process

intensification method. Nevertheless, the authors pointed out that this enhancement was not effective for degrading other chemicals like metformin, ciprofloxacin, DMF and cyclohexanol[34-36]. While aeration is expected to enhance oxidation by increasing oxidizing species, its impact on degradation rates varies with pollutant characteristics. Thus, aeration's effectiveness is pollutant-specific and minimally affected by device or process conditions. The pollutant's nature is the key factor in leveraging aeration-based intensification.

3.3 Effect of H_2O_2 addition on PRH degradation in combined with HC

Hydrogen peroxide acts as a strong oxidizing agent and the addition of H_2O_2 to hydrodynamic cavitation process increases the generation rate of hydroxyl radicals (OH•), which, if used effectively, can significantly intensify the breakdown of organic pollutants[13]. The effect of H_2O_2 at different loadings was examined, with molar ratios of PRH to H_2O_2 set at 1:100, 1:200, and 1:500. Like conventional intensification methods, the newer catalytic cavitation process can also be enhanced, offering additional benefits due to improved catalytic activity. The experiments were conducted using both Al and Cu-vortex diodes under the same conditions of a pressure drop (ΔP) of 0.5 bar and a concentration of 10 ppm. The extent of PRH degradation obtained for different molar ratios of PRH:H_2O_2 is shown in Fig. 5.

It was observed that a complete degradation of PRH with 37% TOC reduction was achieved using the Cu-vortex diode within 5 minutes by using low molar concentration of H_2O_2, 1:100 molar ratio. Whereas, with the Al-vortex diode, the extent of degradation increased from 83% to 100% within 5 minutes as the H_2O_2 loading increased from a 1:100 to 1:500 molar ratio. Fig. 3 (c, d) illustrates the HPLC analysis of PRH degradation using HC and H_2O_2, where a single peak for PRH was observed, indicating no formation of by-products during process intensification. The degradation profile shows a predominant mineralization pathway, with water and carbon dioxide as the sole products. By increasing the H_2O_2 loading to a 1:200 ratio, TOC reduction for the Cu-vortex diode increased to 55%. However, further increases in H_2O_2 loading decreased TOC reduction due to the scavenging action of residual H_2O_2. When H_2O_2 loading exceeds the optimal level, the generated hydroxyl radicals react with H_2O_2 as shown in the following reaction[37]:

$$H_2O_2 + OH \cdot \rightarrow H_2O + HO_2 \tag{4}$$

This scavenging phenomenon is also confirmed by literature reports, although different optimum values for H_2O_2 loading have been observed. Mishra et al. reported the degradation of Rhodamine B using the combined effect of HC and various H_2O_2 loadings, ranging from 10 mg/L to 200 mg/L. They found that Rhodamine B degradation improved steadily, reaching 99.9% with 200 mg/L H_2O_2, accompanied by a 55% reduction in TOC[38].

The degradation rate constants were determined to be 460.5×10^{-3} min^{-1} for the Al-Vortex diode and 921×10^{-3} min^{-1} for the Cu-Vortex diode using an optimum dose of a 1:200 molar ratio of PRH to H_2O_2. Thus, process intensification with H_2O_2 resulted in enhancements of over 70 and 127 times compared to HC alone. This indicates that the Cu-Vortex diode achieved a higher degradation rate than the Al-Vortex diode under the same conditions, further highlighting the effectiveness of the Cu-Vortex diode and the synergistic effect of hydrogen peroxide in enhancing PRH degradation. The synergistic index was again calculated as per the calculations shown in following equation 5 and 6:

$$\xi_{Al-HC+H_2O_2} = \frac{k_{Al-HC+H_2O_2}}{k_{Al-HC} + k_{H_2O_2}} = \frac{460.5 \times 10^{-3}}{6.2 \times 10^{-3} + 1.8 \times 10^{-3}} = 57.56 \tag{5}$$

$$\xi_{Cu-HC+H_2O_2} = \frac{k_{Cu-HC+H_2O_2}}{k_{Cu-HC} + k_{H_2O_2}} = \frac{921 \times 10^{-3}}{7.2 \times 10^{-3} + 1.8 \times 10^{-3}} = 102.33 \tag{6}$$

The values of the synergistic indices were observed as 57.56 and 102.33 for Al-vortex diode and Cu-vortex diode, respectively, which confirms the very good synergism of the combined approach of HC and H_2O_2. In the case of the Cu-vortex diode, an exceptionally high synergistic index was observed. This is due to the catalytic action of the modified cavitation reactor. Dixit et al. also reported the similar and high synergistic index values for dual functional cavitation reactor for the degradation of various API pollutant such as cephalexin, ciprofloxacin and metformin.[15,16,21]. Thanekar et al. reported the 53% enhancement in degradation of carbamazepine with 60% degradation using process intensification through (1:5) H_2O_2[37]. While the role of H_2O_2 has been established, the optimum loading of H_2O_2 largely depends on the nature of the pollutants in wastewater, highlighting the need for experimental investigation. Additionally, the Cu-vortex diode exhibits remarkable superiority in synergism over the Al-vortex diode due to this material change to catalytic material. It is anticipated that this innovative approach could substantially enhance the conventional cavitation processes.

3.4 Effect of pH on PRH degradation

The effect of pH on the extent of PRH degradation was investigated under varying conditions, specifically acidic (pH 4) and basic (pH 9), using the two vortex diodes as cavitating devices operated under similar optimized conditions. The pH of the medium influences the state of the pollutant molecule (molecular or ionic state), resulting in a change in the degradation pathway of pollutants. In general, the molecular form of a compound is more susceptible to degradation. Therefore, acid dissociation constant (pKa) values can indicate the influence of pH on the degradation process. The pKa values of prazosin HCl are 11.09 and 13.32, indicating that the compound predominantly exists in its molecular form at acidic pH. This suggests that prazosin HCl is more likely to degrade in acidic environments. To establish acidic and basic conditions, pH adjustments were carried out using 1 M Nitric Acid (HNO_3) solution and 1 M Sodium Hydroxide (NaOH) solution, respectively. From the experimental results, a complete degradation of PRH was observed with rate constants of $115.1 \times 10^{-3}\ min^{-1}$ for the Al-vortex diode and $921 \times 10^{-3}\ min^{-1}$ for the Cu-vortex diode under acidic condition (pH 4). The rate constants surged by over 17 times for the Al-vortex diode and 127 times for the Cu-vortex diode, demonstrating a substantial improvement in the degradation rate and highlighting the superior effectiveness of catalytic cavitation reactors compared to conventional reactors. A maximum TOC reduction of 35% was observed for the Al-vortex diode, whereas the Cu-vortex diode achieved a TOC reduction of 41% under acidic conditions (Fig. 6). The effectiveness of process intensification through pH modification was quantified by calculating the synergistic index values using equations 7 and 8 as follows:

$$\xi_{Al-pH4} = \frac{k_{Al-HC+pH4}}{k_{Al-HC} + k_{pH4}} = \frac{115.1 \times 10^{-3}}{6.2 \times 10^{-3} + 0.3 \times 10^{-3}} = 17.7 \tag{7}$$

$$\xi_{Cu-pH4} = \frac{k_{Cu-HC+pH4}}{k_{Cu-HC} + k_{pH4}} = \frac{921 \times 10^{-3}}{7.2 \times 10^{-3} + 0.3 \times 10^{-3}} = 122.8 \tag{8}$$

Significantly high values of 17.7 and 122.8 were achieved for the process intensification approach through pH modification for both vortex diodes. This confirms the excellent synergistic effect over the Al-vortex diode and surpasses individual approaches.

At basic pH, negligible degradation was observed because the PRH molecule becomes hydrophilic due to ionization. This increases the difficulty of degradation, as hydroxyl radicals

are short-lived, making it less likely for the pollutant to degrade in the bulk solution. These findings indicate that acidic conditions significantly enhance the degradation of prazosin using HC, especially with the Cu-vortex diode. The HPLC analysis showing only one prominent peak of PRH confirmed that no intermediate formation occurred during the degradation of PRH (Fig. 3(e, f)).

The enhancement in PRH degradation clearly demonstrates that pH is a critical operating parameter in the HC process for degrading API pollutants. Various studies have reported the effect of pH on the degradation of different compounds, including dyes[38], pesticides[31], and API pollutants[15,21,34,35]. Saharan et al. reported that in the HC process, the degradation mechanism includes either the thermal or pyrolytic breakdown of the pollutant trapped inside the cavity, or the reaction of hydroxyl radicals with the pollutant molecules at the gas-liquid interface and throughout the bulk solution[39]. Patil et al. reported the effect of pH on metformin degradation, achieving a significant enhancement of 3000% with 88% degradation in 180 minutes using a conventional vortex diode with process intensification through pH modification[34], whereas Dixit et al. enhanced the degradation of same compound and achieved complete degradation within 5 minutes using Cu-coated cavitation reactor, confirming the effectiveness of dual-functional cavitation reactors with process intensification through pH modification[21]. Mishra et al. found that using a combination of HC and pH modification, acidic conditions significantly enhanced the degradation of Rhodamine B, achieving 59.3% degradation at pH 2.5. Degradation was considerably lower under alkaline and neutral conditions. This is because acidic conditions favor the generation of hydroxyl radicals, reducing radical recombination and increasing their availability for pollutant oxidation[38]. Therefore, it is clear that the optimal pH condition is specific to each pollutant and must be investigated for various pollutants and operating conditions.

3.5 Per-Pass Degradation & Cavitational Yield Calculation

Conventional kinetic analysis often uses the power-law model, but the per-pass degradation model for HC offers a more detailed view of physicochemical behavior, including flow dynamics, pressure drops, performance of cavitation process, and energy dissipation. It also more accurately assesses the performance of the cavitation process by evaluating cavitational yield, offering a more realistic perspective as it considers concentration effects and pressure

drops within the cavitation device making it particularly suitable for scale-up in large-scale operations.

The per-pass degradation factor (ɸ) was calculated by equation 9^{13}:

$$Per-pass\ degradation\ factor\ (\phi) = Residence\ time\ x\ Rate\ constant \qquad (9)$$

Here, the residence time can be further defined as the volume ratio of the holding tank and the flow rate.

The per-pass degradation factor was calculated for all processes, including process intensification approaches such as aeration, optimised H_2O_2 loading and pH modifications and for both the vortex diodes. The obtained values are shown in Fig. 7 (a). The significant enhancement in the per-pass degradation factor for the Cu-vortex diode can be clearly attributed to its additional catalytic activity. Only marginal improvements were observed with the combined approach of HC and aeration, yielding per-pass degradation factor values of 0.027 for the Al-vortex diode and 0.034 for the Cu-vortex diode, compared to 0.020 and 0.023 for the HC-only process, respectively. In contrast, a significant enhancement was achieved using a process intensification approach with the addition of H_2O_2 at a 1:200 molar ratio, resulting in a 75-fold increase for the Al-vortex diode (1.53) and a 114-fold increase for the Cu-vortex diode (2.30) in the per-pass degradation factor. Similarly, combining acidic pH with HC led to an 18-fold increase for the Al-vortex diode (0.38) and a 114-fold increase for the Cu-vortex diode (2.30). The significant improvements observed with Cu-vortex diode further support the potential use of novel dual-function reactors in wastewater treatment.

Another important factor, the cavitational yield was calculated for the degradation of prazosin, for the different processes and for both the cavitation reactors. The cavitational yield (Y) was calculated using equation 10^{13},

$$Cavitational\ Yield\ (Y) = \frac{Amount\ of\ Prazosin\ degraded}{Energy\ dissipation} \qquad (10)$$

The values of cavitational yields obtained for different process alterations have been depicted in Fig. 7 (b). Very low values of cavitational yield, 0.0035 mg/J and 0.004 mg/J, were observed for the only HC process, while minimal improvements were noted with values of 0.0044 mg/J and 0.005 mg/J for the Al and Cu-vortex diodes, respectively. Higher cavitational yields of 6.8×10^{-2} mg/J and 13.6×10^{-2} mg/J were obtained using HC with (1:200) molar ratio H_2O_2, indicating an 18-fold and 33-fold enhancement for the Al and Cu-vortex diodes, respectively.

Similarly, for process intensification approach with acidic condition yield the cavitational value of 1.7×10^{-2} mg/J for Al-vortex diode and 13.6×10^{-2} mg/J for Cu-vortex diode. The results indicate that exceptionally high cavitational yields can be achieved by using a dual-function cavitation reactor with a simple change in the reactor's material, selected based on the nature of the reaction.

Per-pass degradation and cavitational yield are interrelated terms and reflect the effectiveness of the cavitation process and various process intensification. Both parameters are important for understanding the hydrodynamic cavitation, analyzing and comparing literature data, and future research on different devices. While the per-pass degradation factor is particularly useful for scaling up hydrodynamic cavitation, cavitational yield is more pertinent for assessing the energy efficiency of the process.

3.6 Cost analysis

The cost is a crucial factor for adopting any process for real life application, including new cavitation technologies. Energy required for pumping during hydrodynamic cavitation is a major cost component. Thus, the economics of cavitation processes must be thoroughly evaluated, especially in comparison to conventional methods. The treatment cost using HC process can be calculated by equation 11:

$$Cost\ of\ treatment\ per\ m^3\ of\ effluent = \frac{N_C \times \Delta P \times P_E}{36\eta} \qquad (11)$$

where, N_c is the number of passes, ΔP is the pressure drop across the cavitation reactor, P_E is the cost electricity, η is the pump efficiency (66%) for commercial usage. Electricity was assumed to cost 10 Rs/kW·h.

With a vortex diode operating at an optimal pressure drop of 0.5 bar for 60 minutes, the cost for hydrodynamic cavitation alone was 0.044 \$/m³, resulting in only a 15−30% reduction, which limits its practical use. For industrial wastewater treatment, complete degradation is desired. The cost was significantly reduced to approximately 0.0049 \$/m³, about 10 times lower, when using both vortex diodes with process intensification through the addition of H_2O_2 at a 1:200 molar ratio. Similarly, a simple acidic pH adjustment significantly reduced

the treatment cost. Cost analysis for the combined HC+ pH 4 process showed treatment costs of 0.029 \$/m³ for the Al-vortex diode and 0.0049 \$/m³ for the Cu-vortex diode. The modified hybrid approach using a dual functional vortex diode with hydrogen peroxide, or pH adjustment provides an efficient and cost-effective alternative for PRH degradation. This method offers superior cavitational yield and high efficiency. The dual-activity cavitation reactor highlights the importance of reactor design and process intensification in reducing treatment time and costs.

Conclusions

The present study demonstrated, for the first time, the effective use of hydrodynamic cavitation with vortex diode, more specifically dual activity vortex diode, as a cavitating device for degrading prazosin for exceptional enhancement in the rate of degradation and extraordinarily high cavitation efficiency. The important findings are:

1. HC alone for the degradation of PRH resulted in a limited 15-30% reduction, with a maximum TOC reduction of 35% at 0.5 bar pressure drop. Combining HC with H_2O_2 achieved complete degradation in 10 minutes for the Al-vortex diode and in 5 minutes for the Cu-vortex diode, at a (1:200) molar ratio loading.

2. The pH has significant impact and an acidic pH of 4 was found best for PRH degradation in both reactors. Complete degradation was observed within 5 minutes using the Cu-vortex diode, while the Al-vortex diode required 40 minutes.

3. Exceptionally high synergism was observed, with synergistic index values of 57.56 and 102.33 for process intensification using H_2O_2, and 17.7 and 122.8 for the combined approach of HC and acidic pH, for the Al and Cu-vortex diodes, respectively.

4. The per-pass degradation model demonstrated a remarkable improvement of approximately 114 times using the Cu-vortex diode with process intensification approaches, confirming its superiority over the conventional Al-vortex diode, which showed an 18-75 times improvement.

5. The process intensification approaches of using H_2O_2 or modifying the acidic pH highlight a 3300% enhancement for the Cu-vortex diode, compared to a 300-1800% improvement for the Al-vortex diode.

The results confirm that using a newer vortex flow-based device in hydrodynamic cavitation, combined with process intensification through H_2O_2 or acidic pH conditions, leads to significant degradation of PRH with a low treatment cost. The methodology, therefore, can provide a techno-economical alternative for the degradation of PRH and wastewater treatment.

Acknowledgement

Figures:
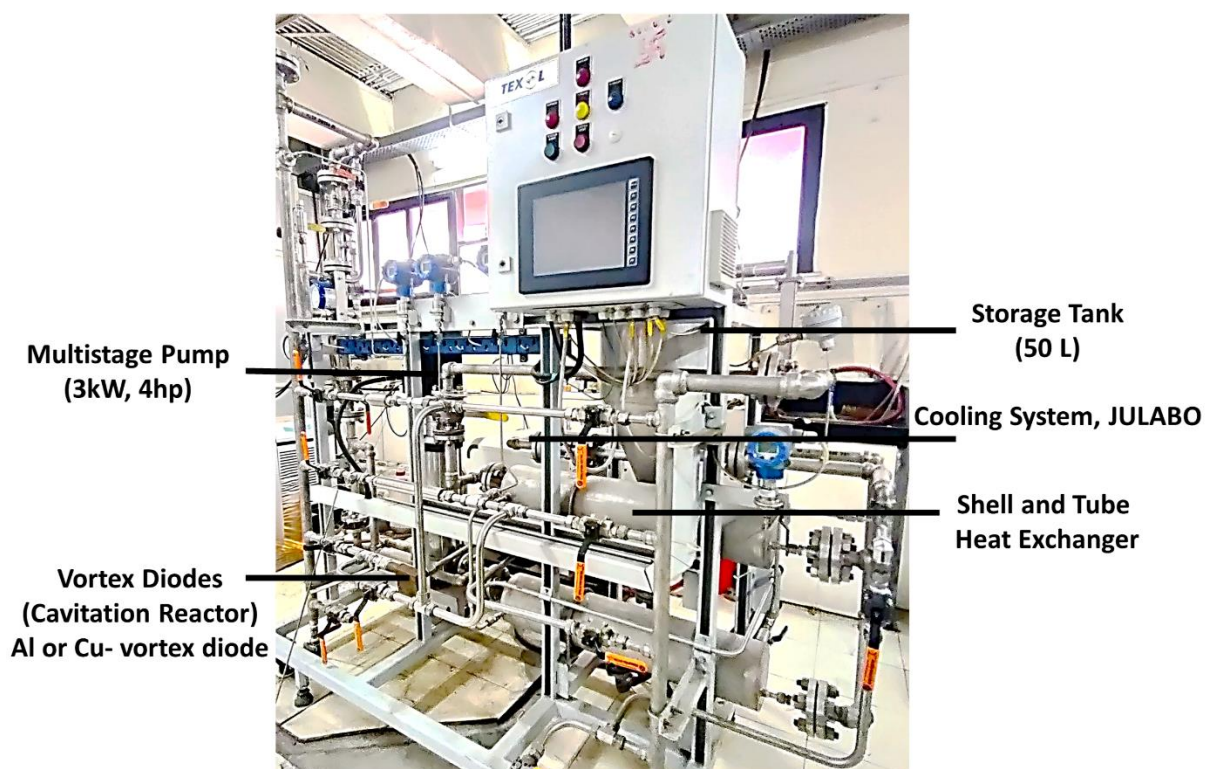
Fig. 1. The hydrodynamic cavitation experimental set-up
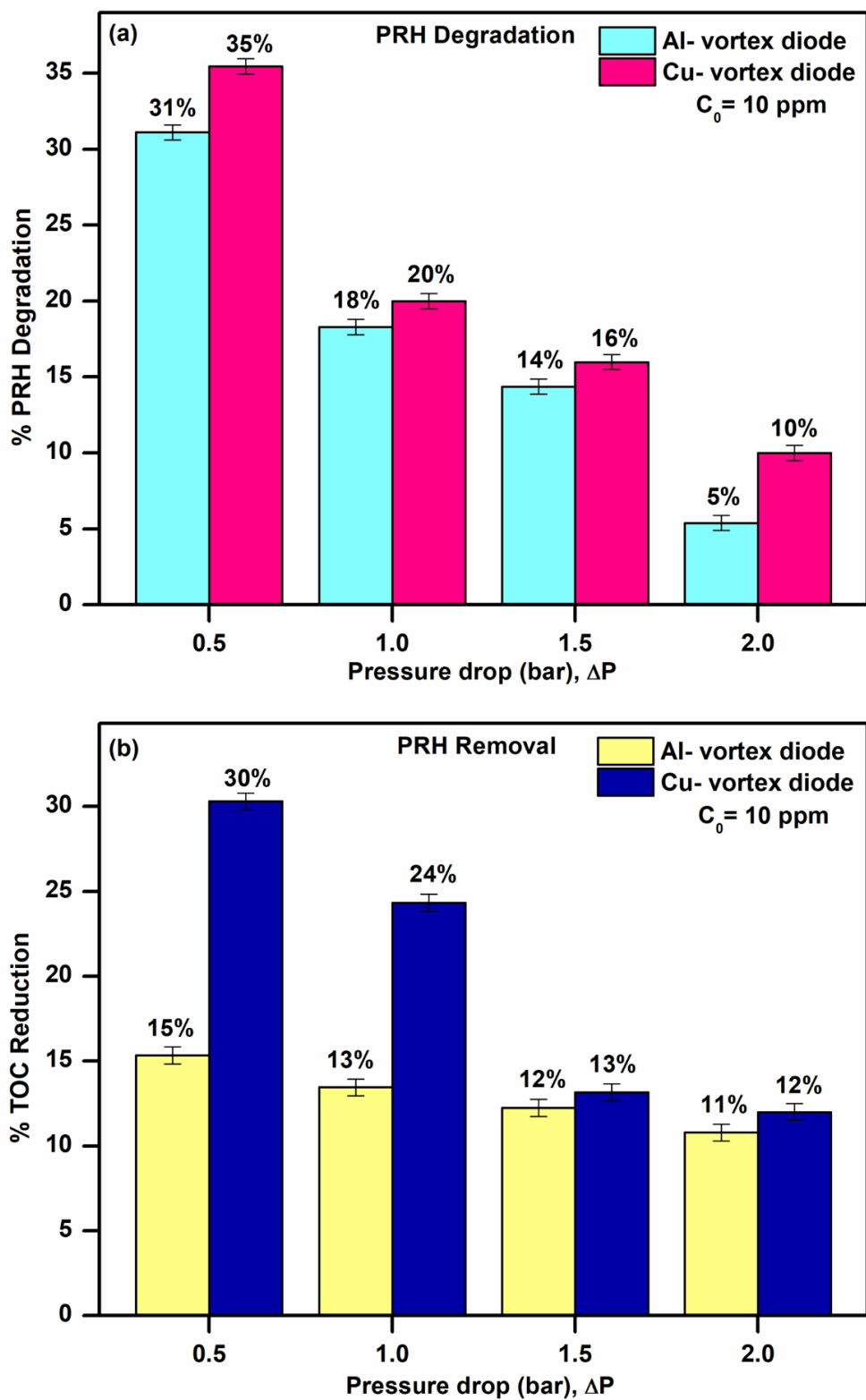
Fig. 2. Effect of pressure drop on degradation of PRH using Al and Cu-vortex diode
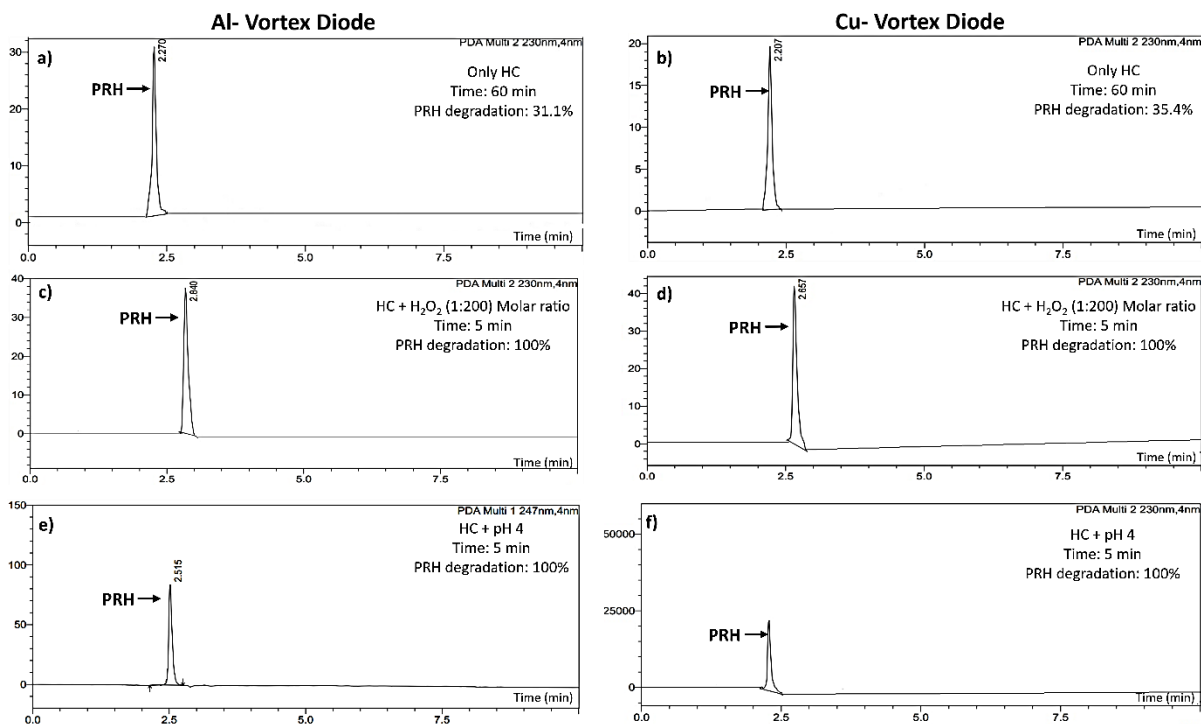
Fig. 3. HPLC analysis of different treatment approaches using both vortex diodes
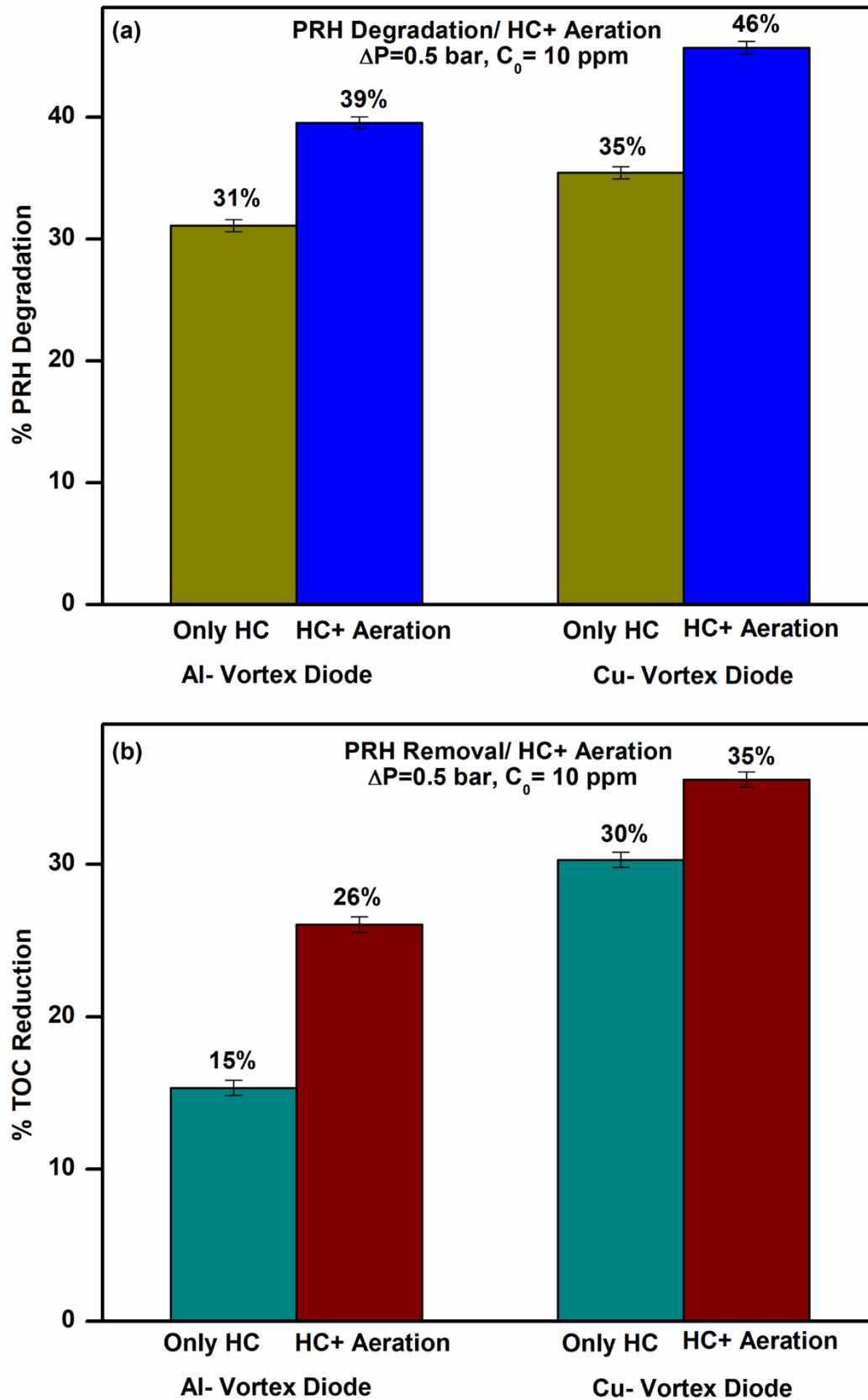
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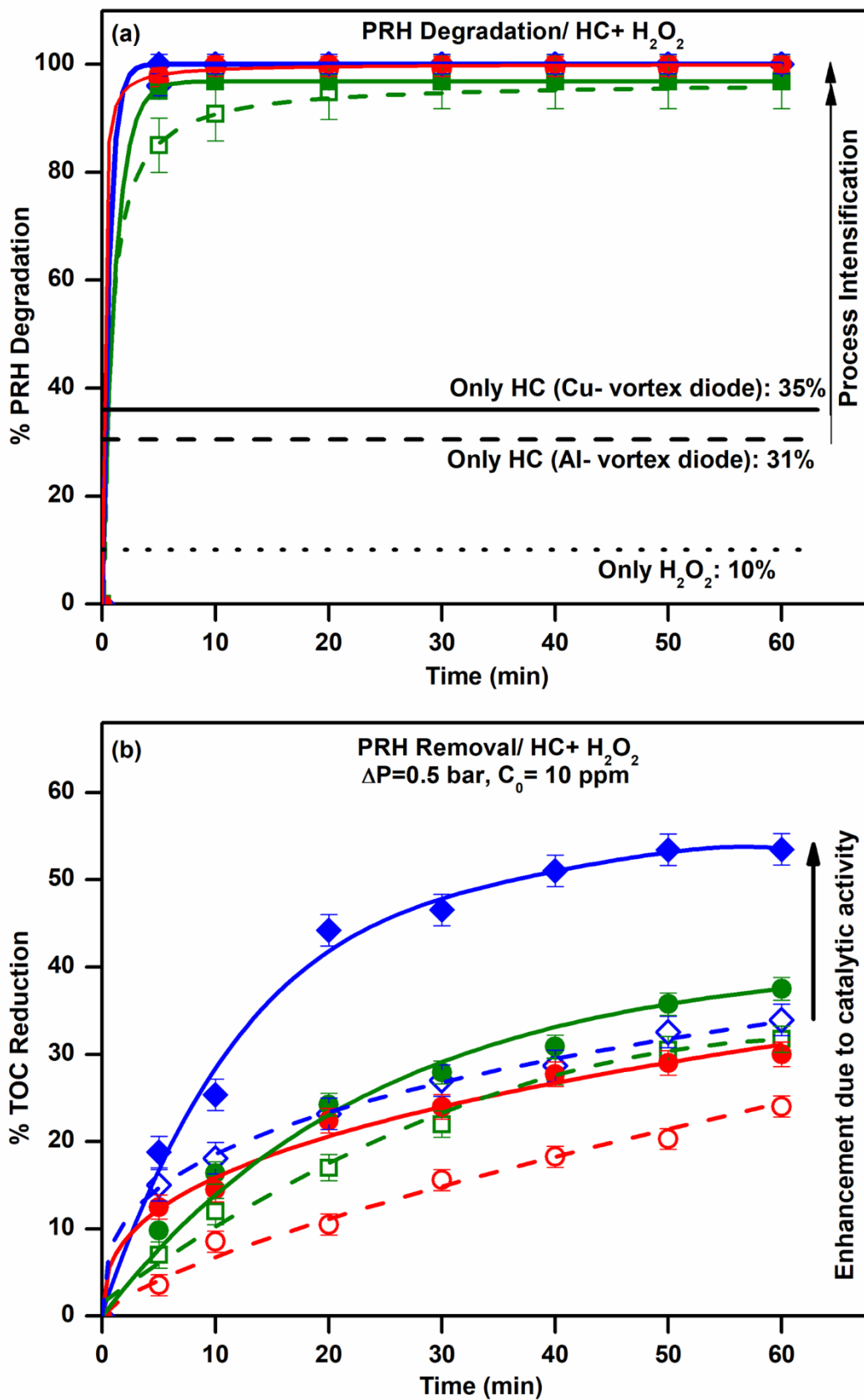Fig. 4. Effect of aeration on PRH degradation combined with HC

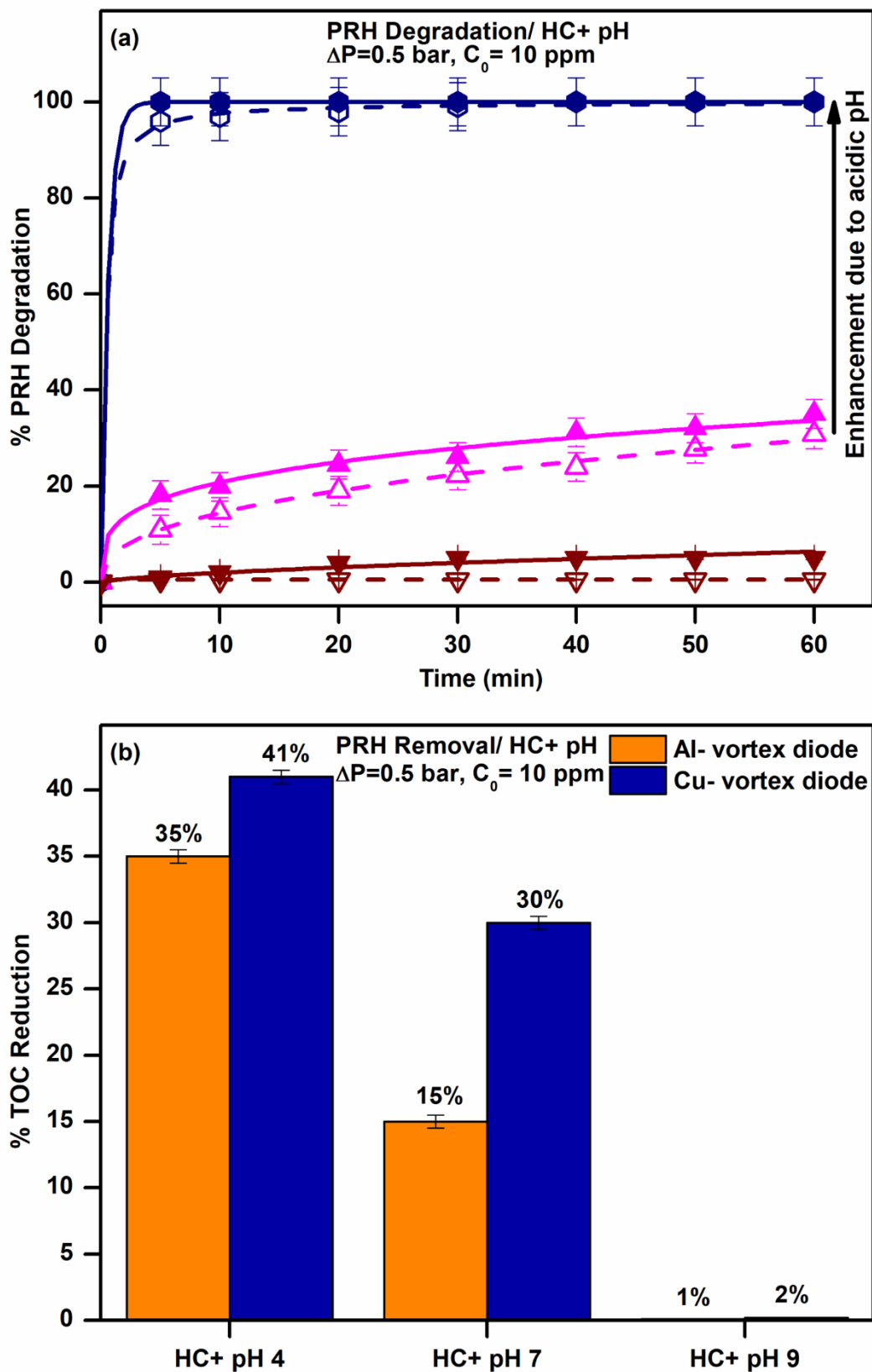**Fig. 5. Degradation of PRH using process intensification approach of H_2O_2**

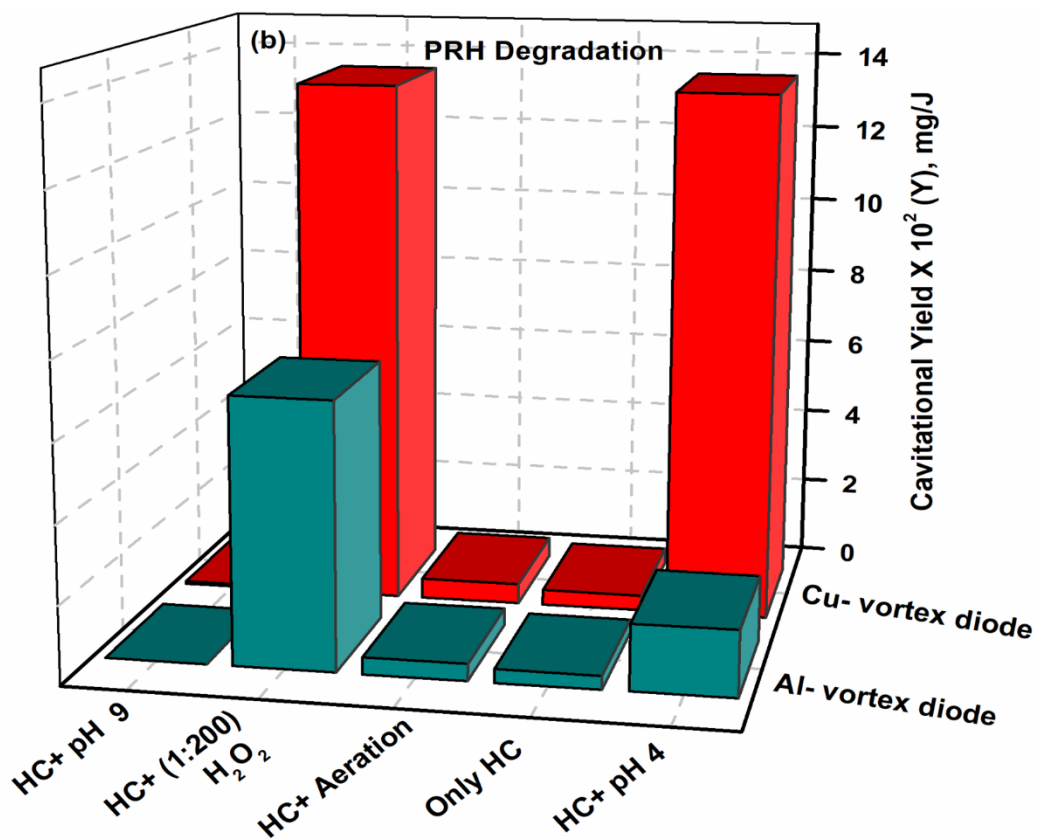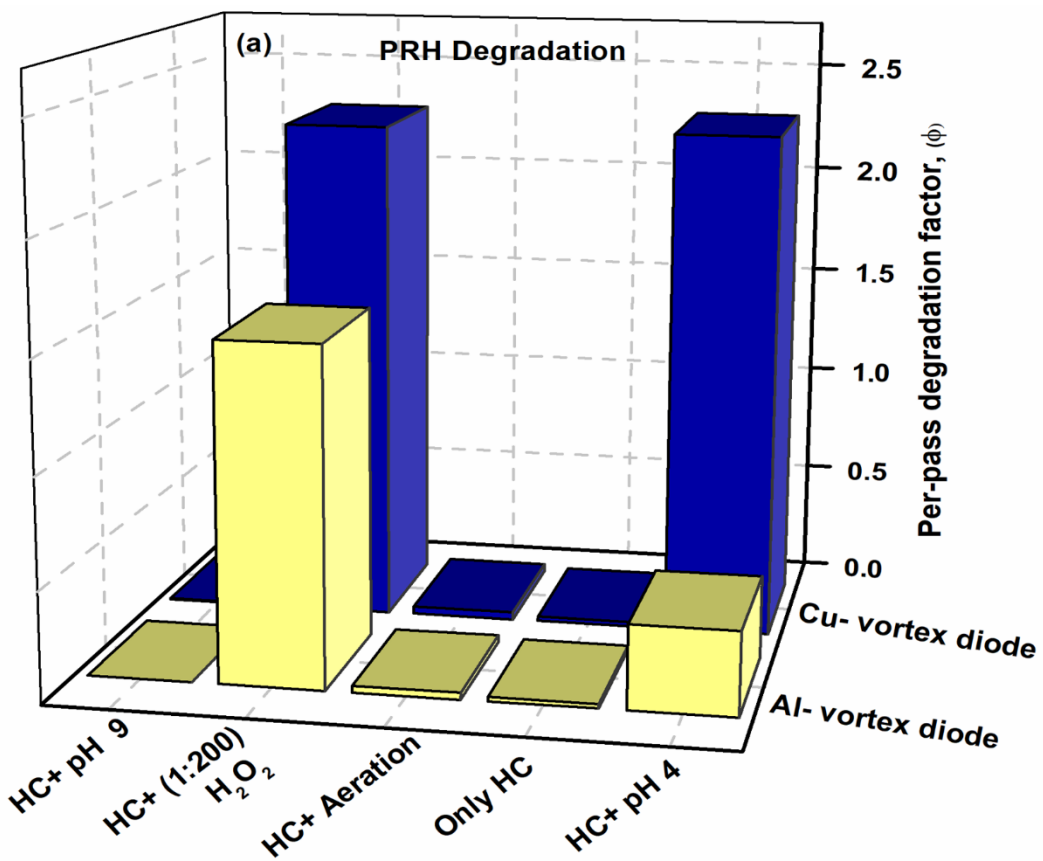Fig. 6. Degradation of MTF using combined approach of HC and pH

Fig. 7. Per-pass degradation and cavitational yield for PRH degradation

Tables:

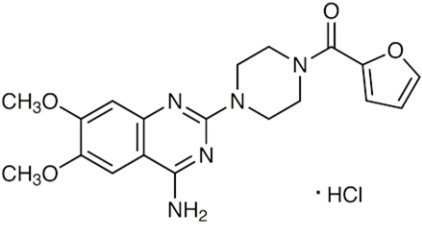**Table 1. Chemical and Physicochemical Properties of Prazosin**

Structure	Name	Prazosin HCl
	IUPAC name	1-(4-Amino-6,7-dimethoxy-2-quinazolinyl)-4-(2-furoyl) piperazine monohydrochloride
	Mol Mass (g/mol)	419.37
	pKa	6.5
	Solubility	61.9 mg/l
	Melting Point	270-280 °C
	Boiling Point	638.4 °C
	Appearance	White to Tan Powder

Table 2. PRH degradation with kinetics for different processes at 0.5 bar pressure drop

Processes	PRH Degradation (%)	TOC Reduction (%)	$k \times 10^3$
Only Aeration	0	0	0
Only H_2O_2	10	7	1.8
Only pH 4	< 2	0	0.3
Conventional Al- Vortex Diode			
Only HC	31	15	6.2
HC+ Aeration	39	26	8.2
HC + (1:100) H_2O_2	96	32	53.6
HC + (1:200) H_2O_2	100	34	460.5
HC + (1:500) H_2O_2	100	24	460.5
HC + pH 4	100	35	115.1
HC + pH 9	0.5	1	0.01
Dual activity Cu- vortex diode			
Only HC	35	30	7.2
HC+ Aeration	46	35	10.3
HC + (1:100) H_2O_2	97	37	58.4
HC + (1:200) H_2O_2	100	55	921
HC + (1:500) H_2O_2	100	30	460.5
HC + pH 4	100	41	921
HC + pH 9	5	2	0.8

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