Improving efficiency for removal of ammoniacal nitrogen from wastewaters using hydrodynamic cavitation

Pravin B. Patil\textsuperscript{a,b}, Vinay M. Bhandari\textsuperscript{a,b,*}, Vivek V. Ranade\textsuperscript{b,1}

\textsuperscript{a} Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Pune 411 008, India
\textsuperscript{b} Academy of Scientific and Innovative Research (AcSIR), CSIR-National Chemical Laboratory, Pune 411 008, India

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A B S T R A C T

The present study reports significant improvements in the removal of ammoniacal nitrogen from wastewater which is an important problem for many industries such as dyes and pigment, distilleries and fisheries. Pilot plant studies (capacity, 1 m\textsuperscript{3}/h) on synthetic wastewater using 4-amino phenol as model nitrogen containing organic compound and two real industrial effluents of high ammoniacal nitrogen content were carried out using hydrodynamic cavitation. Two reactor geometries were evaluated for increased efficiency in removal-orifice and vortex diode. Effect of initial concentration (100–500 mg/L), effect of pressure drop (0.5–5 bar) and nature of cavitating device (linear and vortex flow for cavitation) were evaluated along with effect of salt content, effect of hydrogen peroxide addition and aeration. Initial concentration was found to have significant impact on the extent of removal: ~5 g/m\textsuperscript{3} removal for initial concentration of 100 mg/L and up to 12 g/m\textsuperscript{3} removal at high concentration of 500 mg/L. Interestingly, significant improvement of the order of magnitude (up to 8 times) in removal of ammoniacal nitrogen could be obtained by sparging air or oxygen in hydrodynamic cavitation and a very high removal of above 80% could be achieved. The removal of ammoniacal nitrogen by vortex diode was also found to be effective in the industrial wastewaters and results on two different effluent samples of distillery industry indicated up to 75% removal, though with longer time of treatment compared to that of synthetic wastewater. The developed methodology of hydrodynamic cavitation technology with aeration and vortex diode as a cavitating device was found to be highly effective for improving the efficiency of the conventional cavitation methods and hence can be highly useful in industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen.

1. Introduction

A large number of chemical and allied industries generate huge amounts of wastewaters which require effluent treatment prior to discharge for meeting stringent norms on Chemical Oxygen Demand (COD), Biological oxygen demand (BOD) and Ammoniacal Nitrogen (\text{NH}_4-N). Industrial wastewater treatment is important for the sustainability of environment and ecology and at times can threaten the very existence of the industry, if the pollution norms are not complied with. The conventional wastewater treatment largely focuses on the management COD or BOD levels. In comparison, the subject of removal of ammoniacal nitrogen has received sparse attention barring standard biological methods of treatment. The nitrogen content, measured in the form of ammoniacal nitrogen, is a serious problem in many industrial wastewaters due to limitations of both biological and conventional physico-chemical methods. Ammoniacal nitrogen is a measure for the nitrogenous organic matter as ammonia, a toxic pollutant that can directly poison humans and upset the equilibrium of water ecology systems. The ammoniacal nitrogen is required to be below 30–50 mg/L \cite{1}, though the limit can vary depending on location. There are many industries such as dyes and pigment, nitrogenous fertilizers, specialty chemicals that generate wastewaters having high ammoniacal nitrogen (1500–3000 mg/L) and demand specific solutions for wastewater treatment. Similarly, industries such as fisheries generate huge volumes of wastewaters, easily treatable using conventional biological treatment methods but end up in “treated wastewater” having high ammoniacal nitrogen of the order of 400–600 mg/L that needs to be again brought down to well below 50 mg/L using cost-effective physico-chemical methods.

The ammoniacal nitrogen from effluent is conventionally removed

\* Corresponding author at: Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Pune 411 008, India.
\* E-mail address: vm.bhandari@ncl.res.in (V.M. Bhandari).
\* Present address: Bernal Institute, University of Limerick, Ireland and Queen’s University Belfast, Belfast, UK.

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using biological, physical, chemical methods or combination of these methods. Adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification/denitrification are commonly employed in this regard [2]. Physico-chemical treatment or ion exchange/adsorption are widely used for the reasons of being stable, easy to maintain and reliable. Aguilar [5] investigated physico-chemical removal of ammoniacal nitrogen by coagulation-flocculation using activated silica powdered activated carbon and precipitated calcium carbonate. The removal of ammonia was found to be rather low (3–17%). However, the removal of albuminoid nitrogen (nitrogen in the form of proteins) was appreciable (74–89%). Studies are also reported on effectiveness of variety of materials such as clay and zeolite [4–8], limestone [7]; natural and waste materials such as waste paper, refuse cement and concrete [9] for removal of ammoniacal nitrogen. Advanced oxidation processes including photocatalytic processes were also reported for model and industrial wastewater treatment [10,11]. Destructive methods such as catalyst dependent advanced oxidation processes, though can reduce ammoniacal nitrogen, have significantly high cost of operation compared to most other processes. However, for refractory pollutants, due to non-biodegradability and also because of severe limitations of conventional treatment, application of advanced oxidation methods is often required to meet the pollution control norms. The oxidation processes employ oxidizing agents such as hydroxyl radicals, ozone, hydrogen peroxide that react with the pollutant resulting into partial or total degradation through mineralization of species. Persulfates based oxidation processes are also gaining attention in recent years and have been well reviewed recently [12–15]. The severe process conditions in terms of pressure/temperature/catalyst and therefore cost intensive nature of these methods restrict their application due to economic viability. Thus, it is essential to evaluate newer methods and devices that have potential to offer techno-economically feasible option, specifically for ammonical nitrogen reduction. Hydrodynamic cavitation can offer such useful alternative in the existing treatment of industrial wastewaters for reducing the ammonical nitrogen [1,16–21]. While the use of vortex diode and hydrodynamic cavitation is reported in the literature, systematic studies to evaluate effects of various process parameters along with cost consideration are essential from practical point of view and for implementation in real life applications pertaining to the effluent treatment, which is the main objective of this study. Further, the methodology can be effectively integrated with other conventional methods of treatment.

In the present work, we report removal of ammoniacal nitrogen using hydrodynamic cavitation with 4-amino phenol as model nitrogen containing organic pollutant. Two different devices were evaluated for their efficacy in the removal of ammoniacal nitrogen- orifice, a conventional cavitation device that employ linear flow, and vortex diode employing vortex flow for cavitation. Influence of aeration and addition of hydrogen peroxide on intensifying removal of ammoniacal nitrogen was investigated. The efficacy of the developed methodology was also validated for real industrial wastewater treatment. The quantitative data on influence of initial concentration, total dissolved solids, aeration and addition of hydrogen peroxide on removal of ammoniacal nitrogen is presented together for the first time. The data is processed using the per-pass degradation (removal) factor model and dependence of per-pass removal factor on pressure drop across the cavitation device (energy dissipation rates) is presented. The data is also used to calculate cavitation yield and corresponding treatment costs. Two case studies of real life industrial effluents are also included to facilitate application of the presented results to practice. The results presented in this work will be useful for selection of cavitation device and appropriate process parameters for applying hydrodynamic cavitation for treatment of waste water containing ammoniacal nitrogen.

**2. Applications of fluidic devices without moving parts**

Cavitation fluidic devices may be broadly grouped into two types: devices with and without moving parts. The first class of devices is typically comprised of a rotating impeller and stator. These devices are rather expensive and incur higher maintenance overhead. Cavitation devices without moving parts have significantly lower costs, and are considered to be the most promising route for realizing the full potential of hydrodynamic cavitation. Cavitation devices without moving parts can be further classified into two broad types: those based on linear flow, and those based on rotational flows. In linear flow cavitation devices such as an orifice or Venturi, the working fluid is forced through a restriction, such that the flow and therefore cavitation is realized. In rotational flow devices, low-pressure cavitation region is generated around axis of rotation. In this second scenario, the cavitation zone can be sufficiently removed from solid surfaces so as to eliminate the risk of associated damage to the device [19].

Hydrodynamic cavitation demands specific designs of cavitating devices for creating low pressure regions in the flow domain, mainly by increasing the linear velocity of liquid by forcing the flow through constrictions such as orifice or venturi (conventional devices) or by increasing the rotational velocity of liquid by forcing it in the form of vortex flow through a device like vortex diode which has an outlet port from the center of vortex. The schematic of hydrodynamic cavitation process using vortex diode is shown in Fig. 1. The process integration in the form of aeration (optional) is also indicated. In the conventional devices, constrictions are designed such that velocity at the throat (smallest flow area zone) is large enough to generate cavities that subsequently collapse in a region further downstream of constriction resulting in the desired effect. In the latter case, dimensions of the cavitating device- vortex diode, and outlet port are designed such that low-pressure region are generated because of the highly swirling flow in the vortex diode chamber to generate cavities which subsequently escape the chamber via outlet port and then collapse as they enter high pressure region. The performance of cavitation depends on number density and collapse intensity of generated cavities.

**2.1. Cavitation process and hydrodynamic cavitation**

Cavitation is an advanced oxidation process that involves both physical and chemical changes. The physical process mainly involves formation, growth and collapse of micro bubbles (cavities) within a liquid. The cavities subsequently collapse (implosion) and as a consequence, very high pressure (as high as 1000 atm) and temperature (as
high as 10,000 K or more) get generated locally at the point of collapse. The extreme temperature and pressure conditions at the location of cavity collapse (implosion), generate oxidizing species such as hydroxyl radicals that can chemically oxidize and destroy refractory pollutants. Under ideal conditions, the products of oxidation of organic pollutants are water and carbon dioxide implying complete mineralization. The phenomenon can be exploited for variety of applications, especially in wastewater treatment, disinfection of water and for chemical reactions [18,22–29].

The application of hydrodynamic Cavitation using tangential flow (Vortex Diode) in wastewater treatment and other applications was reported extensively by Ranade and coworkers in recent years [18,21,28,30,31]. The design of Vortex diode is more complicated compared to conventional designs and has three essential components: an inlet tangential port to impart tangential flow, a disc-shaped chamber for generating vortex and cylindrical axial port for the exit of fluid [32]. There are several design variations that are possible which mainly include variations in diameter and height of chamber along with curved surface and providing internals. The vortex establishes a large pressure drop across the device. The flow characterization in vortex diode is well discussed in the literature and will not be repeated here [27,30,33,34]. Recently [1,20,35,36], have discussed degradation of organics such as dyes, solvents and degradation of organics from real industrial wastewater. However, no systematic studies have been reported specifically for removal of ammoniacal nitrogen using hydrodynamic cavitation. In this work, we have used vortex based cavitation device reported in the literature [18,19,30,32] for the removal of ammoniacal nitrogen, evaluated its efficacy under various process conditions and have tried to significantly enhance the removal efficiency using process intensification for overall reduction in the cost of treatment.

3. Experimental

3.1. Materials

Reagent grade 4-Aminophenol (H₂NC₆H₄OH; 99%) was obtained from Sigma Aldrich. Hydrogen peroxide (30%) was obtained from MERCK India. Sodium chloride (NaCl, greater than 99%) was obtained from Sigma-Aldrich. Air, Helium and Oxygen (all 99.99% pure) cylinders were procured from M/s Vadilal Gas, India. Single nozzle air pump (SOBO AQUARIUM SB-108, Max. 3 L/min) was also used for comparison. A synthetic wastewater solution of 4-Aminophenol was prepared using double distilled water for different known concentrations.

![Fig. 1. Schematic of hydrodynamic cavitation process using Vortex Diode.](image1.jpg)

![Fig. 2. Schematic of Hydrodynamic Cavitation Set-up.](image2.jpg)
transmitters and pressure transmitters are used to record flow and control the process (HP), 2900 RPM, discharge pressure 0-15 bar, control valves and cavitating devices in the main line. A bypass line to main flow is used to control the flow rate. Nominal Pipe diameter was 3/4 inch. Flow transmitters and pressure transmitters are used to record flow and pressure (KROHNE, H250, Honeywell ST 700). The set-up is equipped with temperature measurement (RTD make EUREKA Eng. Enterprises India; 0-200 C) and control system. Two cavitating devices were used—orifice (single hole, circular with 3 mm diameter) and a vortex diode [30] (fabricated locally; chamber diameter 66 mm, Throat diameter 11 mm, Material of construction- SS 316) operated in reverse flow mode. For the process intensification study, prior to sending the fluid to cavitation device, an arrangement was made for gas bubbling by inserting a tube in the tank and using air pump or air cylinder, oxygen cylinder or helium cylinder (typically air was bubbled using a single nozzle air pump, SOBO AQUARIUM SB-108 with maximum flow rate of 3 L/min).

The removal of ammoniacal nitrogen was investigated mainly using a synthetic wastewater system with 4-aminophenol as model nitrogen compound and for different concentrations in the range of 100–500 mg/L. In view of the inception of cavitation at <0.5 bar for vortex diode and ~1.25 bar for orifice [31], the pressure drop conditions for vortex diode were selected from 0.5 bar and above and for orifice 2 bar and above. Cavitation number for the considered operating range for orifice was less than 1 (Cavitation number of 0.75 corresponding to the flow rate of 0.41 m³/h and 0.35 corresponding to the flow rate of 0.59 m³/h, at pressure drop of 2 and 5 bar respectively). The usual definition of Cavitation number is not applicable to the vortex diode. We have ensured that both the devices are operated in cavitating regime. Experiments were conducted for 120 min and samples were withdrawn at periodic intervals and analyzed for ammoniacal nitrogen. The pH of the solution was observed to be in the range of 6.9–7.3, indicating no appreciable change.

4. Results and discussions

4.1. Effect of initial concentration and removal kinetics

The results of initial concentration effect on reduction in ammoniacal nitrogen are presented in Fig. 3 for two different reactor configurations, vortex diode and orifice. It was observed that initial concentration has significant impact on the removal. While a good removal of ammoniacal nitrogen could be obtained for Vortex diode (up to 45%) at lower concentration of 100 mg/L, it was less than 20% at high concentration of 500 mg/L. The corresponding extent of removal, for orifice was only marginally lower, however, required substantially higher pressures compared to vortex diode.

The influence of initial concentration on percentage removal of pollutant is similar to that reported in the literature [37–39]. The initial concentration of pollutant influences the vapour and dissolved gas content of the cavity during collapse, similar to that reported [40] and therefore influences overall hydroxyl radical generation rate. The overall extent of degradation depends on concentrations of generated hydroxyl radicals as well as concentration of pollutant. It should be noted that though percentage degradation decreases with increase in initial concentration, the actual amount of pollutant degraded increases with increase in initial pollutant concentration.

In order to study the kinetics of removal, a pseudo-first order kinetics was considered. The reduction in ammoniacal nitrogen could be represented as,

\[ C = C_0 e^{-kt} \] (1)

where \( C_0 \) and \( C \) indicate ammoniacal nitrogen concentration before and after the treatment, \( t \) is time (min), and \( k \) is an apparent rate constant \((\text{min}^{-1})\) of the reaction. Since removal predominantly occurs in the first 60 min, the rate data was fitted accordingly. The values of rate constants are given in Table 1. For lower concentration of 100 ppm, \( k \) value obtained in case of vortex diode was \( 7.18 \times 10^{-3} \text{ min}^{-1} \) and \( 6.61 \times 10^{-3} \text{ min}^{-1} \) for \( \Delta P \) of 0.5 and 2 bar respectively. Similarly, in case of orifice, the \( k \) value was \( 5.41 \times 10^{-3} \text{ min}^{-1} \) and \( 5.05 \times 10^{-3} \text{ min}^{-1} \) for \( \Delta P \) of 2 and 5 bar respectively. It is evident that the extent of removal was quite higher in case of vortex diode compared to orifice, especially at lower concentration of 100 ppm. At higher concentration of 200 and 500 ppm, values of apparent rate constant, \( k \), decrease for both vortex diode and orifice as compared to low-100 ppm concentration.

4.2. Effect of pressure drop

Pressure drop across the cavitating device is one of the most important parameter that not only determines the efficiency of removal but also decides the cost of operation. The results on the effect of pressure drop on percentage removal of ammoniacal nitrogen is presented in Fig. 4. It is evident that the extent of removal decreases with increase in pressure drop. For example, for vortex diode, the removal was 94% at 0.5 bar and 87% at 5 bar. Similarly, in case of orifice, the removal was 93% at 0.5 bar and 85% at 5 bar.
Pressure drop are shown in Fig. 4 for both vortex diode (0.5 and 2 bar) and orifice (2 and 5 bar) and for different initial concentrations. The results clearly reveal significantly higher rates of removal for the vortex diode compared to conventional orifice at all the concentration. Further, low pressure drop is favored in both the reactors, especially at low concentrations and the effect is also dictated by the reactor geometry (corresponding to their point of inception of cavitation). In all the cases, the performance of vortex diode was superior to conventional device-orifice for the removal of ammoniacal nitrogen; both rate as well as in terms of extent of removal. The present results highlight another important aspect concerning the pressure drop; the reduction/removal somewhat insensitive to increase in pressure drop across cavitation device up to a certain level and then decreases at very high pressure drops. This also agrees well with many reports which indicate existence of optimum pressure drop [28,41,42].

### 4.3. Effect of total dissolved solids

The hydrodynamic cavitation, by virtue of its dependence on the cavity implosion, is expected to be influenced by presence of dissolved solids; however, no systematic studies have been reported in this regard. In order to evaluate the effect, experiments were carried out using initial concentration of PAP as 100 and 500 ppm and using added initial dissolved salt concentration of 500 ppm and 2000 ppm (NaCl concentration). The results using vortex diode as a cavitating device are shown in Fig. 5. The results indicate marginal effect of TDS at low salt concentrations while the effect is more pronounced at higher values of TDS. However, within the typical prescribed limits of TDS (< 2100 ppm), effectiveness of the hydrodynamic cavitation for the removal of ammoniacal nitrogen is clearly evident.

### 4.4. Intensification by addition of H$_2$O$_2$

Conventional forms of process intensifications include addition of strong oxidizing agents such as hydrogen peroxide or ozone. Since no studies are available for removal of ammoniacal nitrogen in this regard, representative forms of process intensification have been chosen for studying their impact on removal of ammoniacal nitrogen. Fig. 6 shows some of the results with the intensification using hydrogen peroxide (30%) as additional or external- to be specific, oxidizing agent on removal of ammoniacal nitrogen (hydrogen peroxide formation is also expected in the normal course of cavitation). In the external addition, the dose of hydrogen peroxide was investigated at the level of five times than concentration of pollutant. It was observed that there is no significant improvement and at low ammoniacal concentration of 100 mg/L, vortex diode and orifice yields about 50% and ~ 40% ammoniacal nitrogen removal at ΔP of 0.5 and 2 bar respectively, while at higher concentration of 500 mg/L about ~ 30% removal in ammoniacal nitrogen was obtained. The results indicate that process intensification in the form of hydrogen peroxide does not significantly increase the removal.

The Synergistic coefficient for hydrodynamic cavitation and H$_2$O$_2$ was calculated by using formula as given below,[39]

$$\text{Synergistic coefficient } = \frac{k_{HC+H_2O_2}}{k_{HC} + k_{H_2O_2}}$$

Synergistic coefficient values less than one confirmed the above observation of no synergism for hydrodynamic cavitation with addition of H$_2$O$_2$.

### Table 1: Rate constant data for removal of NH$_4$-N with Vortex diode and Orifice.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Initial conc. (ppm)</th>
<th>% NH$_4$-N removal (120 min)</th>
<th>Apparent rate constant $k \times 10^3$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vortex diode</td>
<td>$\Delta P = 0.5$ bar</td>
<td>100  45.5</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200  26.7</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500  18.9</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>$\Delta P = 2$ bar</td>
<td>100  43.2</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200  25.7</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500  13.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Orifice</td>
<td>$\Delta P = 2$ bar</td>
<td>100  36.7</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200  21.0</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500  8.67</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>$\Delta P = 5$ bar</td>
<td>100  29.2</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200  21.9</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500  13.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of Pressure Drop for different initial concentrations (a) 100 ppm (b) 200 ppm (c) 500 ppm.
4.5. Intensification using aeration

Simple form of process intensifications such as aeration can be useful for the reason that cavities constitute vapor, air and other gases which therefore can influence the behavior in term of implosion or oxidation or both. Aeration may cause,

1. Early inception of cavitation
2. Increased number of cavities, thereby increasing probability of reaction
3. Increase number of oxidizing radicals (due to enhanced availability of oxygen)

To evaluate the effect of aeration, experiments were carried out with and without aeration (air was sparged through the effluent storage tank). Independent experiments were also carried out with bubbling of helium and pure oxygen, instead of air. Since, the extent of removal is less at high initial concentrations, a concentration of 500 ppm ammoniacal nitrogen was selected to explore the enhancement. The results of process intensification studies are shown in Fig. 7. A very high removal of ammoniacal nitrogen was obtained (4 to 10 times), by aeration that was otherwise not possible by normal cavitation. About ~ 80% removal was obtained using aeration at 500 mg/L concentration. Suryawanshi et al. [28] reported ~ 10% enhancement in COD reduction due to aeration for the removal of solvents and suggested that the nature of the pollutant species may be important in this regard. Thus, process intensification in the form of aeration was not very effective for the removal of ammoniacal nitrogen.

In view of the present results, a substantially different mechanism may be expected for the removal of ammoniacal nitrogen. The results of the experiments using oxygen and helium independently are also shown in Fig. 7. As can be expected, bubbling of oxygen produces more or less similar effect as bubbling of air. In fact, the close similarity of the two clearly indicates role of oxygen in the enhancement rather than any of the physical factors mentioned above. Bubbling of the inert gas such as helium (used only for establishing proof-of-concept and is not required in any form for real application) has not shown any positive impact on cavitation. The observations, therefore, clearly imply chemical form of the process intensification due to increased availability of oxygen as the critical component in the removal of ammoniacal nitrogen. Naturally, it is believed that the removal occurs via formation of NOx and water in the process similar to that of CO2 and water in COD reduction.

The removal mechanism is believed to include set of reactions due
to collapse of cavities [43], resulting in generation of oxidizing species followed by possible formation of intermediates such as ketone, 4-benzoquinone imine and finally product of oxidation as benzoquinone, water and NOx [44]. This implies no significant reduction in the COD as the carbon number get only partly reduced, as has been confirmed in the present study, where separate COD measurement indicated average COD reduction of only 15%. However, more detailed investigations are required to establish the exact mechanism in this regard.

4.6. Per-pass removal

Instead of using an apparent first order kinetic constant to represent removal, it may be useful to use per-pass degradation factor to describe hydrodynamic cavitation experiments presented in this work [21]. The per-pass degradation factor is defined as,

\[ \text{Per-pass degradation factor (Ø)} = k \tau \]  

(2)

where, \( \tau \) is residence time defined as a ratio of volume of holding tank and flow rate through cavitation device.

The energy dissipation rate, \( W = \Delta P \times Q \)  

(3)

The overall cavitation yield (amount of ammoniacal nitrogen degraded per unit energy dissipation) can be written as,

\[ Y = \frac{V(C_0 - C)}{\Delta P Q \tau} \text{mg/J} \]  

(4)

Fig. 8 shows values of per pass degradation factor and energy dissipation rate for the different conditions. At higher pressure drop conditions for vortex diode at 2 bar and orifice at 5 bar, the energy dissipation rate is quite high than low pressure drop conditions. This clearly demonstrates that lower pressure drop conditions are more favorable for both vortex diode and orifice from the cavitation yield perspective. The vortex diode at 0.5 bar shows maximum per-pass degradation compared to all other pressure drop conditions.

4.7. Comparative analysis of per-pass degradation factor- without aeration and with aeration

It is instructive to quantify the effect on enhancement using per-pass degradation factor for different cases such as removal without aeration and with aeration. The analysis in this regard is shown in Fig. 9. It is evident from the values of per-pass degradation factor that aeration leads to improvement in hydrodynamic cavitation. With increasing \( C_0 \), the improvement by aeration became larger. The analysis also quantitatively reveals effectiveness, especially at low pressure drops and differentiates the impact of reactor geometry.

4.8. Reactor geometry and cavitation yield

From the results obtained for ammoniacal nitrogen removal, it is clear that the reactor geometry has a strong influence on the removal behavior. This can be quantified in terms of cavitation yield for different reactors which is the ratio of amount of pollutant degraded and product of pressure drop, flow rate and time. This analysis can be more useful since there is large uncertainty associated with the characterization of the cavitation behavior due to difficulty in obtaining number/quantity of cavities, size of the cavities or size distribution that can imply quality of the cavities and effects of various known and unknown parameters such as presence of organics, dissolved solids, other impurities, liquid viscosity, surface tension, temperature and so on. Thus, the overall performance is largely attributed to the visible and measurable parameters such as pressure drop, reactor configuration. Fig. 10 provides values of cavitation yield for different reactors- vortex diode and orifice. A comparison is also made for the large enhancement obtained for the process intensification using aeration. The energy dissipated by aeration can be given by \( g \times V_c \text{ (J/kg)} \), where \( g \) is gravitational acceleration (9.81 m/s²) and \( V_c \) is superficial gas velocity (m/s). In the present work, under experimental conditions, the energy consumption due to aeration was found to be less than 1% of the total energy consumption and hence, for simplifying and ease of comparison, energy dissipated by aeration is neglected. The values of cavitation yields were 49.2 × 10⁻⁴ mg/J and 31.4 × 10⁻⁴ mg/J for vortex diode at 0.5 bar pressure drop, 100 ppm initial concentration and for with and without aeration. The corresponding values for orifice were 8.4 × 10⁻⁴ mg/J and 4.9 × 10⁻⁴ mg/J respectively. For the initial concentration of 500 ppm, the same values for vortex diode and orifice were 261.0 × 10⁻⁴ mg/J and 73.8 × 10⁻⁴ mg/J and 59.8 × 10⁻⁴ mg/J and 6.75 × 10⁻⁴ mg/J respectively. It is evident that vortex diode as a cavitation reactor is superior to the conventional device-orifice. It can also be seen that the cavitation yield is higher for higher initial concentration. Also, cavitation yield increases significantly (up to 10 times) using aeration.

4.9. Cost considerations in removal of ammoniacal nitrogen using hydrodynamic cavitation

In view of the high efficacy of hydrodynamic cavitation technology for the treatment of industrial wastewaters containing high ammoniacal nitrogen, it would be prudent to estimate approximate costs associated with the treatment method. The cost of treatment can be obtained as [1]:

\[ \text{Cost of treatment per m}^3 \text{ of effluent} = \frac{N_x \times \Delta P \times P_x}{3600} \]

(1)

For the removal of ammoniacal nitrogen with and without aeration, the cost is estimated for the Indian scenario assuming the cost of electricity as Rs. 10 per kWh (1$ = ~70 Rs). Pump efficiency was assumed as 66%. For the similar levels of removal and for the process conditions found most favorable in the present work, 0.5 bar \( \Delta P \) and vortex diode, the cost of treatment is 7 Rs/m³ (~0.1$/m³), without aeration and 2 Rs/m³ (~0.025$/m³) for process intensification with aeration (assuming negligible cost of aeration).

The corresponding costs for the orifice are 30 and 7 Rs/m³ (approx. 0.42 and 0.1 $/m³ respectively), at 2 bar \( \Delta P \) without and with aeration respectively. For a high concentration of 500 ppm, the estimated costs are 7 Rs/m³ (~0.1$/m³) and 0.60 Rs/m³ (~0.008$/m³) for vortex diode without and with aeration while corresponding values for orifice are 30 and 3 Rs/m³ (approx. 0.42 and 0.04 $/m³ respectively). Thus, the treatment cost for vortex diode is significantly lower as compared to that of orifice.
The high effectiveness of vortex diode in the treatment of wastewaters is largely due to the flow pattern – vortex flow in the design of cavitation reactor. The rotational flow in such case is effective in removal at lower pressure drop conditions as compared to the linear flow based conventional cavitation devices.

5. Removal of ammoniacal nitrogen from real industrial wastewater- two case studies

Two different industrial wastewater samples mainly having the problem of high ammoniacal nitrogen were procured from a local distillery industry. The first sample was partially treated spent wash with initial COD of 75875 ppm and initial ammoniacal nitrogen content of 2050 ppm. The sample was dark brown in colour with intense odor, pH of the sample was 7. The second sample was of condensate water, after the biological treatment of distillery wastewater and had ammoniacal nitrogen content of 2880 ppm.

Both the samples were specifically evaluated for the removal of ammoniacal nitrogen using vortex diode and employing a pressure drop of 0.5 bar and 2 bar respectively, conditions chosen on the basis of preliminary investigations. The reduction in the ammoniacal nitrogen for the spent wash sample was ~ 36% in 60 min, indicating efficacy of the hydrodynamic cavitation technique in treating real industrial wastewater. The treatment of condensate water however was quite difficult and a high reduction of the order of 75% could be obtained (Fig. 11) only after prolonged treatment (~10 h), indicating relatively high cost of the treatment of such wastewaters. This difficulty in the treatment can be largely attributed to the nature of highly refractory compounds that remained in the wastewaters even after the biological treatment.

The results on the real industrial wastewater treatment are similar to those reported by Bhandari et al. [20] for real industrial wastewater.
treatment of fertilizer industry where ~ 37% reduction in the ammoniacal nitrogen was reported for wastewaters of high ammoniacal nitrogen content (530–1330 ppm) and ~ 87% reduction for the low ammoniacal nitrogen (276 ppm) containing wastewater. The present study on distillery wastewater samples however had significantly higher ammoniacal nitrogen content and hydrodynamic cavitation was found to be effective in treating real industrial wastewaters even at such high levels of concentrations. Essentially, higher removal to desired extent can be achieved using prolonged treatment time or using appropriate process intensification.

6. Conclusion

The present study clearly establishes methodology for improving the effectiveness of hydrodynamic cavitation especially using vortex diode as a cavitating device in wastewater treatment, specifically for the removal of ammoniacal nitrogen. Initial concentration has significant impact on the removal and quantity of ammoniacal nitrogen removed increases with the increase in the concentration for the same pressure drop and reactor conditions. Overall, 9–45% removal could be obtained only using hydrodynamic cavitation depending upon the initial concentration and reactor geometry, high removal using vortex diode for pressure drop of only 0.5 bar. Interestingly, significant improvement, up to 8 times, can be obtained using simple process intensification by sparging air or oxygen and overall extent of removal of over 80% could be accomplished, again high improvement in the case of vortex diode at significantly low pressure drop (0.5 to 2 bar compared to orifice- up to 5 bar). For the initial concentration of 500 ppm, with and without aeration, the values of cavitation yield for vortex diode at pressure drop of 0.5 bar were 261.0 × 10⁻⁴ mg/J and 73.8 × 10⁻⁴ mg/J and for orifice at pressure drop of 2 bar were 59.8 × 10⁻⁴ mg/J and 6.75 × 10⁻⁴ mg/J, clearly proving superiority of vortex diode as a cavitation reactor over conventional device-orthodox and demonstrating order of magnitude increase in the cavitation yield using aeration. The methodology of improving efficiency gets reflected in significant cost reduction due to process intensification, ranging from 200% to more than 1100%, an crucial and important aspect from industrial application point of view. A plausible mechanism to elucidate effect of aeration clearly highlighted role of oxygen for degradation by cavitation. The application of the technology for the treatment of real industrial wastewaters from distillery industry having high ammoniacal nitrogen content was equally effective in reducing ammoniacal nitrogen proving efficacy of the developed technique. The insight obtained in this study and the results are useful for real life industrial wastewater treatment and hydrodynamic cavitation technology with aeration appears to be a highly promising technology for the removal of ammoniacal nitrogen, in terms of efficiency, ease of operation, easy scale-up and cost effectiveness. The cavitation devices and aeration may be used alone or in combinations with existing established effluent treatment processes to facilitate water recycling and reuse.

Author contributions

V.M.B. and P. B. P conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. V.V.R. contributed to the data analysis. All three authors were involved in the preparation of the manuscript.

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Conflict of Interest-One of the authors (VVR) is a founder director of Vivira Process Technologies Pvt. Ltd. which commercially offers vortex diode based cavitation devices.

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