Industrial wastewater treatment for fertilizer industry- A case study

Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade
Chemical Engineering & Process Development Division
CSIR- National Chemical Laboratory
Pune-411 008. India

Corresponding author:
E-mail: laxmigayatri1@gmail.com ; vm.bhandari@ncl.res.in
Telephone: +91-020-2590-2171
Fax: +91 2025893041

Abstract

Wastewaters from chemical fertilizer industry mainly contain organics, alcohols, ammonia, nitrates, phosphorous, heavy metals such as cadmium and suspended solids. The nature of effluent streams varies in terms of its constituents and complexity. The present work attempts to fill the void in the literature that mostly reports synthetic wastewater treatment studies; by evaluating effluent treatment solutions and comparison of different methods for real wastewaters from fertilizer industry. An attempt has been made to devise suitable methodology mainly using a new device in the form of Vortex Diode for hydrodynamic cavitation and also using adsorption, for several real wastewater streams from different locations in one major fertilizer industry of Maharashtra, India. The strategy involved characterization of wastewaters, studies on effective removal of Chemical Oxygen Demand(COD) and devising solutions for effective reduction in ammoniacal nitrogen-a more serious issue in the fertilizer industry. The characterization of wastewaters from different streams revealed huge variation in COD from 50 to 140,000 ppm and ammoniacal nitrogen from 6 to 1700 ppm. Some effluent streams contained alcohol up to 5 %. Hydrodynamic cavitation using vortex diode and adsorption with modified carbons were used to treat these streams. Cavitation studies were carried out on a pilot plant and effect of pressure drop, cavitating device and process intensification were studied. It was observed that the effluent treatment strategy requires careful identification and application of suitable treatment method on the basis of nature of the effluent. Also, hydrodynamic cavitation, using vortex diode is techno-economically attractive option in treating fertilizer wastewaters giving a very high reduction in COD and ammoniacal nitrogen (up to 85%), similar to adsorption. The results clearly identify potential of newer methodologies in treatment of effluents in fertilizer industry.

Keywords: Cavitation, Adsorption, Industry, Effluent, Ammoniacal nitrogen

Introduction

Industrial wastewater treatment is a complex problem for a variety of highly polluting chemical industries such as fertilizer, distillery, dyes and pigment, textile and specialty chemical manufacturing. Generally, the industrial effluents are characterized in terms of broad parameters such as Chemical Oxygen Demand (COD), Ammoniacal nitrogen (AN), Total suspended solids (TSS), Total dissolved solids (TDS) etc. that hardly help in identifying nature of pollutants in the effluents. The complexity arises mainly from the issues pertaining to the removal of refractory pollutants that are difficult to remove/degrade using conventional methods of treatment, in general, and biological treatment, in particular. The effluents typically require COD below 250 ppm and AN below 50 ppm for discharge in surface waters, though these norms could differ on the basis of location/country/industry and many a times are even more stricter. This therefore requires development of highly specific methodologies that help in effectively removing refractory pollutants, either through the use of removal and recovery processes (e.g. adsorption) or through use of destructive methods such as hydrodynamic cavitation that destroy the pollutants and results in partial/complete mineralization of the pollutant species through advanced oxidation without employing high temperatures/pressures or catalysts. In the present work, we report studies in both removal and destructive methodologies for a specific case study on various effluent streams from a fertilizer industry, with specific focus on the effective removal of COD and ammoniacal nitrogen from various wastewater streams of this industry sector.

Industrial wastewater treatment usually requires one or more processes from Physical, Physico-chemical and Biological methods. The application of physical methods is quite straightforward for preliminary treatment- mainly for the removal of suspended solids or pH adjustment and will not be discussed here. The challenge is in the selection of most appropriate process(es) from physico-chemical methods such as adsorption/ ion exchange/ membranes, newer forms of advanced oxidation processes etc.; biological methods such as aerobic or anaerobic treatment or combination of both. The volume of effluent, nature and concentration of pollutants and total cost of treatment usually dictate the selection.

Fertilizer industry is very important manufacturing sector, especially for India due to its agricultural based economy. The growth of agricultural sector is significant and is fuelled by variety of fertilizers that includes nutrients such as nitrogen, phosphorous and potassium (N, P, K- nitrogeneous, phosphatic and potassic fertilizers). A typical fertilizer industry complex would include ammonia plant (essential for nitrogen fertilizers), acid plants such as phosphoric acid/nitric acid, solvents such as alcohol and different fertilizer units. Thus, the wastewater generated from various plants includes different contaminants such as acids, alcohols, salts and is characterized having significantly high values of COD and ammoniacal nitrogen depending upon the source of generation. Some other contaminants such as metals are also present due to the use of rock phosphate. Thus, it is necessary to classify the effluent streams generated at different points as process effluent or effluent from cleaning/ treatment stages. Wastewater treatment is a major problem in such complex fertilizer plant from environmental pollution point of view. For example, wastewater is generated from ammonia plant contains ammonia, methanol, and trace metals. Treatment involves condensate steam strippers to remove ammonia and methanol followed by ion exchange. Methanol production unit also generates wastewaters containing alcohol and is a major pollution problem.

Application of novel approaches in the existing practice such as newer modified adsorbents or intensified processes can not only improve the effluent treatment plant (ETP) operation for better performance at reduced cost, but also provide incentive for recovering part of the cost of treatment. Thus, it is important to focus on development of newer separation processes and process integration/intensification options that combine or redefine finer aspects of existing physico-chemical methods- mainly adsorption and cavitation. In this report, we present work on adsorption (newer modified adsorbents) and hydrodynamic cavitation processes (newer cavitating device with vortex flow) with specific focus on Industrial wastewater treatment in Fertilizer Industry.

Adsorption and Hydrodynamic Cavitation

The existing practices in fertilizer industry employ well established physico-chemical/biological methods of treatment. It is however, essential to evolve better techno-economic alternatives that effectively treat different effluents and reduce overall cost of ETP. Two such methods are adsorption and hydrodynamic cavitation. In adsorption, exploring newer types of adsorbents will help in realizing better capacity for removal of various organics and metals. Similarly, application of novel methodologies such as hydrodynamic cavitation is expected to provide newer options/alternatives for replacing existing methods or in process intensification.

Adsorption is a well established technique for removal of organics, metals and colour. Thus, in this regard, it can easily serve in reducing the COD of the effluent. Screening of adsorbent is very important since hundreds of commercial adsorbents of different types are available or can be made. Activated carbons are commonly employed adsorbents that are derived from variety of sources and are available from very cheap to expensive materials depending on the type. Adsorption capacity for carbons is typically in the range of 0.25-0.87 kg COD/kg [1] . Many chemical industries, in general and fertilizer industry, in particular have a peculiar problem in reducing ammoniacal nitrogen from wastewaters. Ammoniacal nitrogen (NH_3-N), is a measure for the amount of ammonia, a toxic pollutant. Ammoniacal Nitrogen removal can be carried out by biological, physical, chemical or combination of these methods. Available technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification [2] . Conventional methods, however, are not efficient and are cost intensive. Physico-chemical treatment or ion exchange/adsorption is preferred over other methods because of better stability, and reliability. Aguilar et al. [3] investigated physiochemical removal of AN by coagulation-flocculation using activated silica, powdered activated carbon and precipitated calcium carbonate. They found very low ammonia removal of around 3-17% but albuminoid nitrogen (nitrogen in the form of proteins) removal was appreciable (74-89%) and the addition of coagulant aids reduced the sludge volume to 42%. Ion exchange resins and some cheaper alternative natural and waste materials can be used to replace high cost materials. Various researchers have studied the effectiveness of a variety of low cost materials for ammonia removal such as clay and zeolite [4-8] ; limestone [4] ; natural and waste materials such as waste paper, refuse cement and concrete [9] . However, there has been not much work on treatment of industrial wastewaters for effective removal of ammoniacal nitrogen using adsorption or newer/ modified adsorbents.

Cavitation can be considered to work similar to advanced oxidation process without employing complex catalyst, high temperature and pressure. Hydrodynamic cavitation in general can be achieved for industrial wastewater treatment using simple mechanical devices such as orifice, venturi or vortex diode. The nature and operating parameters of cavitation set-up enables cavities to get generated, grow and collapse in a predefined manner. Cavities get generated when liquid is passed through a constriction which in effect increases kinetic energy associated with the liquid at an expense of the local pressure, and when the pressure at the throat or vena-contracta of the constriction falls below the vapor pressure of the liquid, the liquid flashes, generating number of cavities that subsequently collapse when the pressure recovers downstream of the mechanical constriction [10] . The cavity collapse is one of the most important aspect, usually referred as implosion of cavities, resulting in localized extremely high temperature (up to 5000 K), pressure conditions (up to 1000 atm). Under such extreme conditions, water molecules cleave consequently generating oxidizing agents e.g. hydroxyl radicals which can decompose the pollutants partially or fully- similar to oxidation process. Cavitation technology can be effectively used to treat industrial effluent for removal of COD, ammoniacal nitrogen and/or color. The geometry of cavitating device and operating parameters such as pressure drop, initial concentration play important role in process performance and optimization in terms of these is crucial. Further, cavitation can be employed alone or in combination (process integration) with other processes such as Biological treatment process, oxidation, adsorption, ion exchange or coagulation.

Hydrodynamic cavitation is an emerging technology that can be easily employed in wastewater treatment. Cavitation generates strong oxidizing conditions due to production of hydroxyl radicals and also hydrogen peroxide. Although significant work has been reported in the area of sonochemical reactors and its application in wastewater treatment, its implementation for actual industrial practice is still negligible due to the reasons of high cost of treatment and operational difficulties, especially in power dissipation. The impact of cavitation processes can be dramatically increased by combining it with other oxidation process employing catalysts or additives. It has been reported that cavitation coupled with other methods such as coagulation or adsorption, can be effective in water treatment and pollutant removal [11–16] . Thus, process intensification can work wonders if cavitation and suitable other methods are integrated, especially in treating wastewaters containing refractory pollutants and/or having unusually high COD. Sivakumar and Pandit[17] have investigated the use of hydrodynamic cavitation reactors for degradation of Rhodamine B dye solution (5–6 μg/ml). Chakinala et. al.[18]]have reported the applicability of a combination of hydrodynamic cavitation and advanced Fenton process for treatment of industrial effluents. Saharan et al.[19-20] have investigated the use of hydrodynamic cavitation reactors for degradation of Acid Red 88 dye solution using venture and for degradation of orange-G dye (30 to 150 μM) using three different cavitating device viz. a single hole orifice plate, circular venturi and a slit venturi. Hiremath et al. [21]recently reported degradation of dyes such as Auramine O using vortex diode.

There are not many reports that evaluate applications of newer cavitating devices for real industrial wastewater treatment, especially in vortex flow. In the present work, we have studied relatively less reported method of hydrodynamic cavitation for industrial wastewater treatment using a newer device-Vortex Diode and compare the results with that obtained using established methods like adsorption.

Experimental

Newer types of commercially available modified carbon based adsorbents- SHIRASAGI X7000H, GS2x, KL, GTSx, TAC, NCC (Japan Envirochemicals Ltd., Japan) were used for effluent treatment using adsorption process. The adsorbents were activated prior to their application. Characterization of the adsorbents was carried out by Scanning electron microscope, SEM (Leo-Leica, Stereoscan 440, Cambridge,UK) attached with Energy dispersive X-ray spectroscopy, EDX (Bruker,Quanrax-200,Berlin,Germany), Pan analytical XRD in the scan range of 2θ between 10-80° for all adsorbents in continuous mode using the Cu Kα radiation (LFF tube 40kV, 30 mA). Specific surface area was measured by Quantachrome Autosorb Automated Gas Sorption system and calculated by applying Brunaer-Emmett-Teller (BET) method. Surface functional groups were determined by Cary 600 Fourier Transform- Infrared, FTIR (Agilent) spectrophotometer having 4 cm^{-1} resolution using KBr pellet method in the range 400-4000cm^{-1}.

The schematic of hydrodynamic cavitation set-up used in the present study is shown in Fig.1. The setup includes a holding tank of 60 L capacity, a multistage centrifugal pump of rating 2.2 kW (2900 RPM), control valves, and vortex diode as a cavitating devices for wastewater treatment. The flow rate can be adjusted by adjusting the by-pass valve. Flow transmitter and pressure transmitter were used for measurement of flow and pressure respectively and thermocouple for measurement of temperature. The entire set-up is fabricated in SS-316.

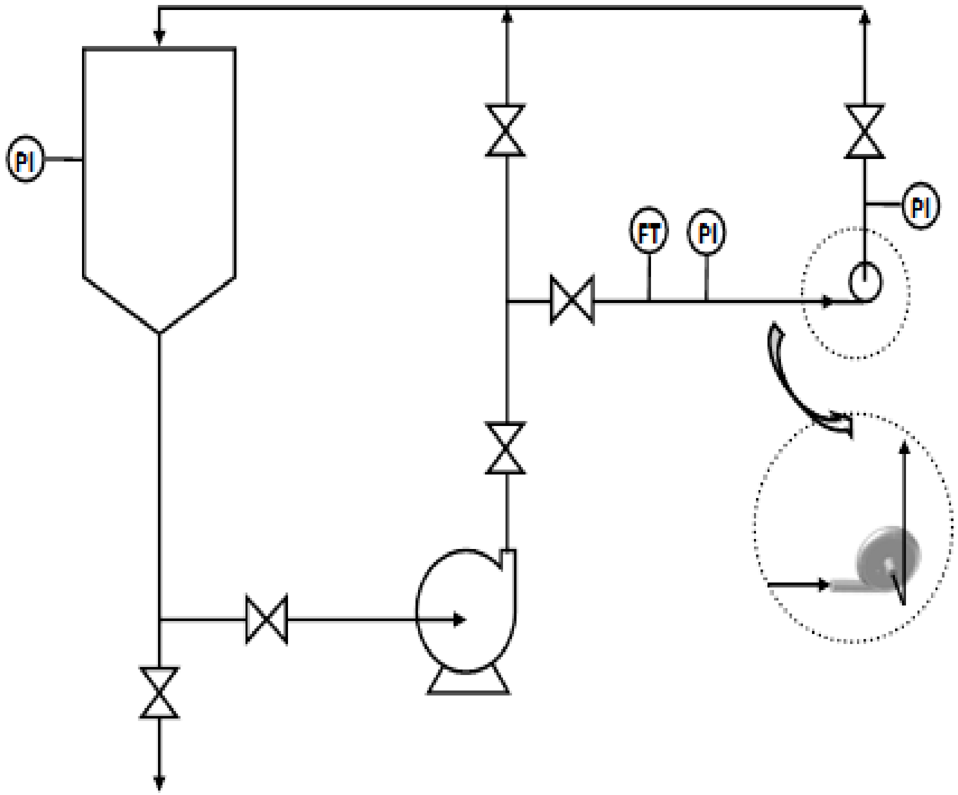

Fig. 1 Schematic of Experimental Set-up for Hydrodynamic Cavitation using Vortex Diode

Industrial wastewater samples were obtained from different locations and plants from a local Fertilizer industry and were used for effluent treatment as such without any pre-treatment or addition of chemicals. The effluents were characterized for their initial COD, ammoniacal nitrogen and other physical/chemical parameters. Adsorption equilibria studies were carried out using different adsorbents at ambient conditions. Cavitation technique was employed using Vortex Diode and using different pressure drop conditions. The temperature of bulk liquid was maintained by circulating coolant through coils in the holding tank. Cavitation was conducted using aeration for improved degradation. Effect of flow rate and pressure drop was studied and samples were withdrawn for analysis at regular intervals. Spectroquant TR 320 digester of Merck make was used for digestion for 2 hrs and then samples were analyzed for COD reduction and reduction in ammoniacal nitrogen using SpectroquantPharo 100 Spectrophotometer (Merck).

Results and Discussion

The characterization of the industrial effluent samples has been given in Table-1. The effluents included those with very high COD, but very low ammoniacal nitrogen and effluent streams with lower COD but with high ammoniacal nitrogen content. Also, the total dissolved solids (TDS) and total suspended solids (TSS) were also different in each of these effluents.

Table-1: Characterization of various effluent streams of Fertilizer Industry

Effluent Stream	Initial COD (ppm)	Initial NH_3-N (ppm)	Remarks
1	125000	2	pH 7-8, Colored, characteristic odor, low TDS/TSS, presence of alcohols/ organics
2	946	1710	Very high AN
3	460	86	pH 10.6, Low TSS, TDS<2000
4	130	1330	pH 10, High AN, Very low TDS/TSS
5	44	530	pH 9.6, Low COD
6	170	276	pH 11, TDS<2000

A detailed characterization of the adsorbents has been reported earlier [22] . All the adsorbents have large surface area close to 1000 m^2/g. The screening of the adsorbent was carried out using batch equilibrium studies. Adsorbent loading of 2.5% was used to evaluate effectiveness in removal of COD/ammoniacal nitrogen.

Hydrodynamic Cavitation for the treatment of fertilizer industry effluent

Vortex diodes employ vortex phenomena for its operation. The basic design of a vortex diode consists of cylindrical axial port, a tangential port and a chamber connecting the two ports. The chamber is characterized by its diameter and height, which decide the chamber volume. The flow entering the device through the tangential port sets up a vortex, and establishes a large pressure drop across the device[23] . A generalized form for cavitation number based on pressure drop in vortex diode can be used that defines the cavitation number σ, as below [24] .

$$\sigma = \frac{p_d - p_v}{p_u - p_d} \approx \frac{p_d}{p_u} \qquad (1)$$

Where p_d, p_u and p_v are downstream, upstream and vapor pressures of the fluid respectively. The approximation holds when $p_u >> p_d >> p_v$. An increase in upstream pressure should decrease σ and increase the number of cavitation events. This indicates increase in rate of degradation. The definition is different from conventional cavitating devices viz. orifice and venturi, where linear velocity and pressure are related to dimensionless parameter called as cavitation number (C_v). However, since in the vortex diode linear velocity does not exist because of vortex flow, Eq.1 is most appropriate and cavitation numbers obtained by both the definitions should provide similar information. Increase in liquid flow rate with an increase in the diode inlet pressure reduces the cavitation number- number of cavities generated increase with a decrease in cavitation number. Ideally, cavities are generated at a condition $C_v \leq 1$, however, cavities are also known to get generated at a value of $C_v > 1$ due to the presence of some dissolved gases and suspended particles which provide additional nuclei for the cavities to form [25] . This is one important aspect in the treatment of real industrial wastewaters that usually have high TSS. After certain value of cavitation number which depends on the specific reactor configuration, the number density of cavities increase to such an extent that cavities start coalescing forming cavity cloud that adversely affects cavitation and degradation due to choked cavitation [26] . Thus, effective degradation requires very specific conditions particular to type of effluent and operation in the range- cavitation inception and choked cavitation.

The overall cavitation process can be viewed as a combination of a Physical and Chemical processes. The physical process comprises formation of the cavities, growth of the cavitaties and subsequent collapse. It would also include physical breakdown of the pollutant species, if any due to extreme conditions of temperature and pressure. On the other hand, the chemical part of the overall process involves typical oxidation reactions involving oxidizing species (e.g. H_2O_2 and OH.) and pollutant species. As a result of physical breakdown, formation of smaller molecules that are different from parent species may be expected, while the end product of chemical oxidation is total mineralization of the pollutant species. The mineralization is therefore results in reduction in COD/ AN or colour, essential for effluent treatment.

The hydrodynamic cavitation for reduction in COD was studied in detail for effluent 1 and 2 since for other samples, initial COD was not very high, while for all the samples 2-6, cavitation was studied for reduction in ammoniacal nitrogen due to higher values for initial ammoniacal nitrogen. The process parameters were kept constant for all the runs, except for the time of treatment. The most important parameter in hydrodynamic cavitation is pressure drop across the reactor/cavitating device and is typically optimized for synthetic wastewater streams. Based on the guidelines (Ranade and Bhandari, 2014), a pressure drop of 0.5 kg/cm^2 was employed (corresponding to flow rate of 380 LPH) for 1st one hour of treatment and 2.0 kg/cm^2 for subsequent treatment (corresponding to a flow rate of 780 LPH). The results on the reduction of COD for effluent 1 and 2 indicated a very high reduction of 85 and 76% respectively (Table-2). This is significant in view of very high value of initial COD in effluent 1 and suggests that cavitation alone can be a suitable technology for treating this effluent which doesn't have appreciable ammoniacal nitrogen.

It is evident that there is substantial variation in the reduction of COD and ammoniacal nitrogen using vortex diode for different effluent samples, even when the COD values were low. Further, extent of COD reduction is found to be far less for effluents having lower initial COD. This can be mainly attributed to the type of pollutant species believed to be most refractory pollutants that remain at such low initial concentrations. However, it is also possible that the suspended solids contribute to the performance variation as the number and quality of cavities are expected to differ significantly under varying TSS or TDS conditions. It also implies that more severe conditions such as higher pressure drop may be required for effecting degradation in such cases. The effect of pH also needs careful evaluation.

Hydrodynamic cavitation with vortex diode as cavitating device is highly effective in reducing the ammoniacal nitrogen from the effluent streams. In fact, in most cases, the results compare very well with the high removal obtained using adsorption.

Effect of number of passes

The number of passes (Np), can be expressed as –

$$N_p = \frac{Volumetric\ flow\,rate \times Time\,of\ operation}{Volume\,of\ effluent\,in\,holding\ tank}$$

The extent of degradation increases with increasing number of passes. However, it is essential to optimize the number of passes for economical operation as higher number of passes directly reflects higher cost of treatment. Thus, this factor is crucial in determining the cost of operation, less number of passes- lower the cost. This, again depends on the nature of effluent, especially that for real industrial effluent for which characteristics such as COD, presence of metals, TDS/TSS are varying in most cases.

The number of passes, as indicated above, has to be optimized in all the effluent treatments. In general, for obtaining high COD and ammoniacal nitrogen reduction in effluent streams-1 and 2, number of passes was more than 100, indicating relatively high cost of the cavitation for degradation of the pollutants. This can be attributed to high COD/AN content of these streams. However, for all other effluent streams, the number of passes was close to 50 for the reduction shown in Table-2, indicating relatively lower cost of the treatment using hydrodynamic cavitation with vortex diode as cavitating device. The variation in the performance of the process, however, may have to be attributed to the variation in the nature of pollutants and concentration in different effluent streams and mere values of COD/AN will not provide information in this regard making it difficult to predict the behaviour in terms of degradation or for generalization of the results.

Adsorption Process using modified adsorbents for fertilizer industry effluents

The adsorption process can be successfully employed for reducing COD or for ammoniacal nitrogen using suitable adsorbents. The selection of suitable adsorbent is important as conventional adsorbents have limited or no capacity. Further limitations to employing adsorption include cost of adsorbent, regeneration/reactivation and rates of removal. While adsorption can certainly be useful as a polishing method for lowering COD/ ammoniacal nitrogen below the statutory limits, its use is limited for high initial COD or ammoniacal nitrogen concentrations due to requirement of excessively high adsorbent quantities, making its application techno-economically not feasible.

The results on the modified adsorbents for the treatment of various fertilizer industry effluents are shown in Fig. 2 to 5 for low COD effluent streams of 3-6. It is evident that there is significant variation in the performance of various adsorbents in spite of the fact that all of these adsorbents are modified activated carbons. Further the removal capacities are drastically different for different effluent streams. All these effluent streams are basic with pH ~10 and vary in terms of initial COD or ammoniacal nitrogen content. For the effluent stream-3, the initial COD is 460 ppm while AN value is 86. It can be seen that most of the adsorbents of this work show more or less satisfactory removal of COD and AN for this particular stream and maximum COD reduction of ~ 80% can be obtained using GS2x while ~80% reduction in AN can be obtained using TAC adsorbent. For most other adsorbents, the removal was ~60% for both COD and AN.

Effluent sample-4 has very high AN of ~1330 ppm and low COD of ~130 ppm. Thus this stream requires treatment only for the removal of ammoniacal nitrogen. However, as against effluent stream-3, all the adsorbents were less effective for the removal of AN and a maximum reduction of only ~30% could be obtained using TAC as adsorbent. Thus, adsorption here appears to be less satisfactory method for removal of ammoniacal nitrogen from such effluents.

Effluent streams 5 and 6, both have reasonably high ammoniacal nitrogen (530 & 276 ppm respectively) and low COD. Again, similar to effluent stream of 4, here too, no adsorbent is found suitable for removal of AN from stream-5 and a maximum reduction of ~35% could be obtained using TAC adsorbent. However, for effluent stream-6, near complete AN removal (~98%) could be obtained using X7000H adsorbent while TAC gave ~50% reduction. Interestingly, here even the hydrodynamic cavitation using vortex diode yields 87% removal of AN similar to adsorption.

X7000H is a coal based while TAC & NCC are coconut shell derived adsorbents. TAC has not indicated presence of metals on its surface while, X7000H has presence of potassium, which is likely to expand interlayers of adjacent hexagonal network planes consisting of C atoms, enhance pore formation and as a consequence give better adsorption. Presence of Ni in X7000H is also expected to enhance adsorption. GH2x also has much high surface area of ~1329 m^2/g and has elements like Al and Si[27] . The better adsorption behaviour for X7000H, TAC and GH2x can be attributed to these specific modifications as compared to other adsorbents.

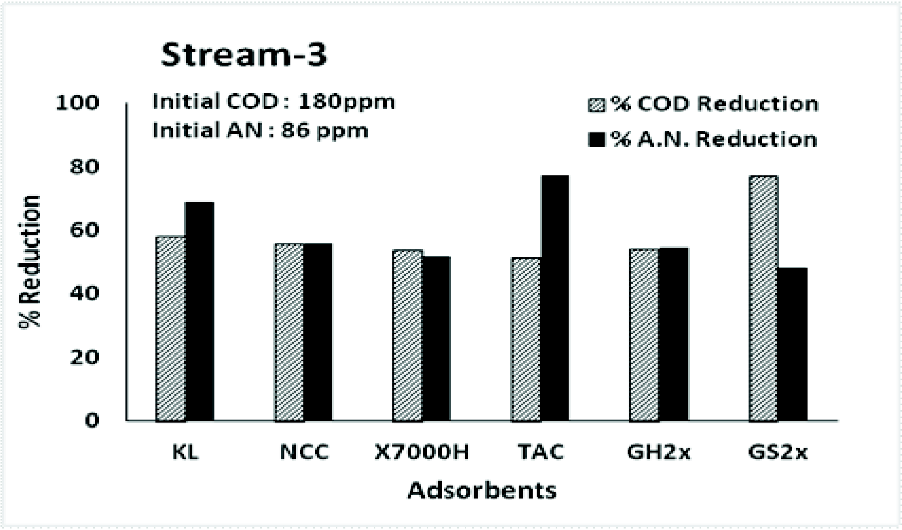

Fig. 2 Effluent-3: COD/AN reduction using adsorption with modified adsorbents

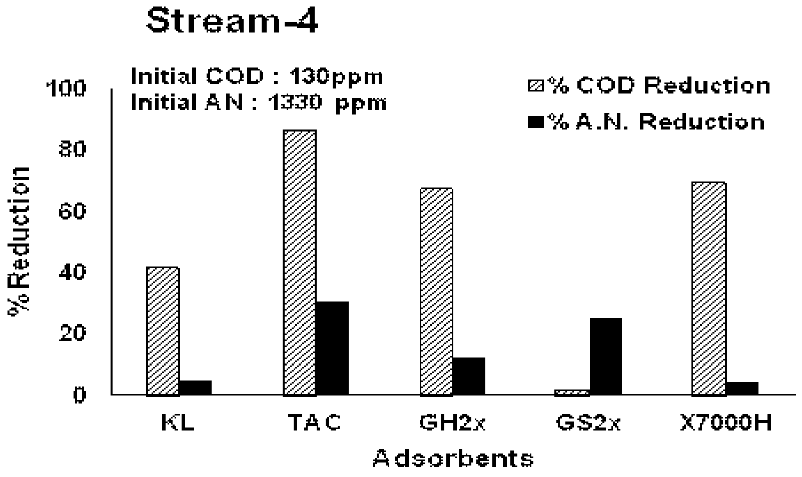

Fig. 3 Effluent-4: COD/AN reduction using adsorption with modified adsorbents

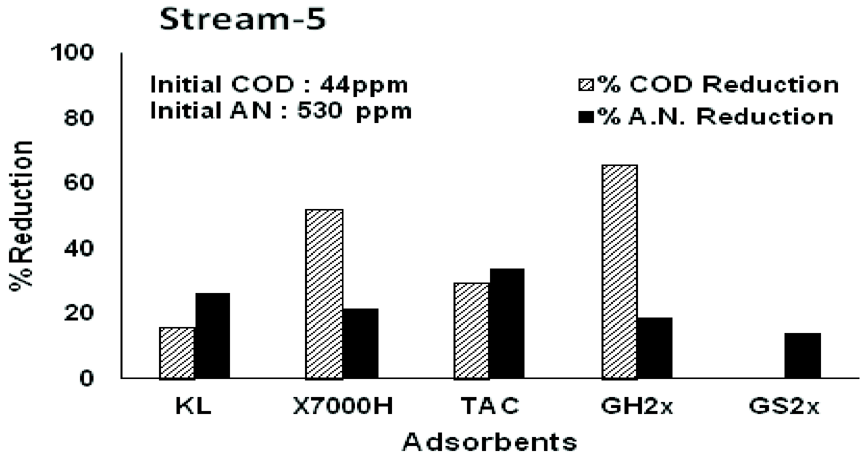

Fig. 4 Effluent-5: COD/AN reduction using adsorption with modified adsorbents

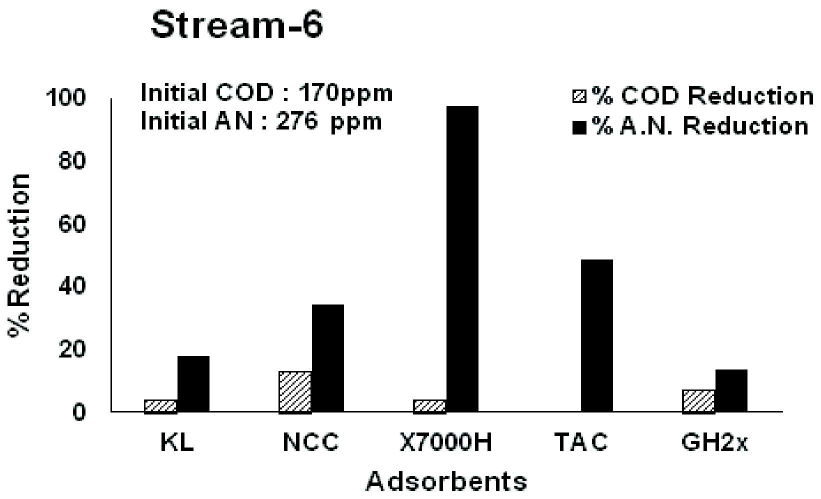

Fig. 5 Effluent-6: COD/AN reduction using adsorption with modified adsorbents

Comparison of adsorption and hydrodynamic cavitation using vortex diode

The results on cavitation and adsorption can be summarized for comparison in Table-2. Though it is not possible to directly correlate the cost of the two processes at this point, it can be seen that cavitation is effective technology in treating effluents for reducing COD and AN simultaneously. Especially for reducing ammoniacal nitrogen, cavitation appears to be more effective as compared to adsorption.

A close examination of the results on adsorption and cavitation reveals following very interesting observations:

1. Hydrodynamic cavitation using vortex diode appears to be an effective method for the treatment of industrial wastewaters.
2. Being a destructive method and requiring no regeneration/ reagents/ catalyst, hydrodynamic cavitation may be advantageous over other conventional treatment methods.
3. Hydrodynamic cavitation using vortex diode requires substantially less space as compared to methods such as coagulation/clarification, biological treatment etc.
4. A very high removal of COD and AN can be obtained using adsorption and hydrodynamic cavitation-vortex diode.
5. The energy requirements for the treatment of various effluents vary substantially depending on the nature of effluent, presence of organics/TSS/TDS and refractory pollutants and needs careful optimization in terms of processing parameters- pressure drop, number of passes etc.
6. Where, hydrodynamic cavitation, alone, is not satisfactory for complete treatment, it can be easily combined practically with all other methods of treatment- e.g. coagulation, adsorption, biological treatment etc.
7. The removal of COD and AN differs significantly for different adsorbents and for different streams indicating selection of suitable adsorbent as most crucial step in this regard.
8. Adsorption, though effective for removal of both COD and AN, can be best implemented as a polishing step for techno-economic feasibility of overall ETP operation.

Table 2. Results on Cavitation and Adsorption treatment of Fertilizer effluents.

Effluent Stream	Initial COD (ppm)	Initial NH_3-N (ppm)	% *Reduction in*			
			COD		NH_3-N	
			Adsorption	Cavitation	Adsorption	Cavitation
1	125000	2	--	85	NA	NA
2	946	1710	--	76	--	60
3	460	86	80	<10	80	41
4	130	1330	86	<10	30	36
5	44	530	65	<10	35	37
6	170	276	10	<10	98	87

Conclusions

The results of present study clearly highlight the usefulness and limitations in employing established effluent treatment method such as adsorption and relatively new method of hydrodynamic cavitation using vortex diode. Hydrodynamic cavitation using vortex diode has been found to be an effective newer technology for the treatment of various effluent streams from fertilizer industry, especially for large reduction of COD and ammoniacal nitrogen. It also can be effectively integrated with other conventional methods of treatment for overall cost optimization in ETP operation. Adsorption using modified adsorbents is effective for high COD and ammoniacal reduction for effluent streams, especially for low COD streams. However, not all adsorbents are suitable and finding most suitable adsorbent for the given stream is important. The findings are expected to be useful not just for fertilizer industry wastewater streams but also for chemical industry effluents, in general.

Acknowledgements

The authors wish to acknowledge financial support from IndusMagic (CSC0123) and SETCA (CSC0113) of Council of Scientific & Industrial Research(CSIR), India for the research work.

References

1. Guyer, P. An Introduction to Advanced Wastewater Treatment. *Eng. Edge, LLC PDH Prof. Train.* 1–6 (2011). at <http://www.cedengineering.com/courseoutline.asp>

2. Tchobanoglous, G., Burton, F. L., Metcalf & Eddy. *Wastwater Engineering: Treatment, Disposal,Reuse*. (McGraw-Hill Int., 1991).

3. Aguilar, M. Nutrient removal and sludge production in the coagulation–flocculation process. *Water Res.* **36,** 2910–2919 (2002).

4. Aziz, H. A., Adlan, M. N., Zahari, M. S. M. & Alias, S. Removal of ammoniacal nitrogen (N-NH3) from municipal solid waste leachate by using activated carbon and limestone. *Waste Manag. Res.* **22,** 371–5 (2004).

5. Sarioglu, M. Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Sep. Purif. Technol.* **41,** 1–11 (2005).

6. Demir, A., Gunay, A. & Debik, E. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA* **28,** 329–336 (2002).

7. Çelik, M. S. *et al.* Removal of ammonia by natural clay minerals using fixed and fluidised bed column reactors. *Water Sci. Technol. Water Supply* **1,** 81–88 (2001).

8. Rozic, M. Ammoniacal nitrogen removal from water by treatment with clays and zeolites. *Water Res.* **34,** 3675–3681 (2000).

9. Ahsan, S. Use of some natural and waste materials for waste water treatment. *Water Res.* **35,** 3738–3742 (2001).

10. Gogate, P. R. & Pandit, A. B. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Environ. Res.* **8,** 501–551 (2004).

11. Wang, X., Jia, J. & Wang, Y. Degradation of C.I. Reactive Red 2 through photocatalysis coupled with water jet cavitation. *J. Hazard. Mater.* **185,** 315–21 (2011).

12. Mishra, K. P. & Gogate, P. R. Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives. *Sep. Purif. Technol.* **75,** 385–391 (2010).

13. Chakinala, A. G., Gogate, P. R., Burgess, A. E. & Bremner, D. H. Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing. *Chem. Eng. J.* **152,** 498–502 (2009).

14. Ranade, Vivek Vinayak Pandit, A. B., Anil, Agra Chandrashekar Sawant, S. S., Ilangovan, D., Madhan, R. & Pilarisetty, V. K. Apparatus for filtration and disinfection of seawater/ship’s ballast water and a method of same. (2008).

15. Ranade, V. V., Kulkarni, A. A. & Bhandari, V. M. Vortex diodes as effluent treatment devices. (2013).

16. Ranade, V. V. & Bhandari, V. M. *Industrial Wastewater Treatment, Recycling and Reuse*. *Ind. Wastewater Treat. Recycl. Reuse* (Elsevier, 2014). doi:10.1016/B978-0-08-099968-5.00001-5

17. Sivakumar, M. & Pandit, A. B. Wastewater treatment: a novel energy efficient hydrodynamic cavitational technique. *Ultrason. Sonochem.* **9,** 123–31 (2002).

18. Chakinala, A. G., Gogate, P. R., Burgess, A. E. & Bremner, D. H. Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process. *Ultrason. Sonochem.* **15,** 49–54 (2008).

19. Saharan, V. K., Pandit, A. B., Satish Kumar, P. S. & Anandan, S. Hydrodynamic Cavitation as an Advanced Oxidation Technique for the Degradation of Acid Red 88 Dye. *Ind. Eng. Chem. Res.* **51,** 1981–1989 (2012).

20. Saharan, V. K., Rizwani, M. A., Malani, A. A. & Pandit, A. B. Effect of geometry of hydrodynamically cavitating device on degradation of orange-G. *Ultrason. Sonochem.* **20,** 345–53 (2013).

21. Hiremath, R. S., Bhandari, V. M. & Ranade, V. V. Effluent Treatment Using Hydrodynamic Cavitation: Vortex Diode As a Cavitating Device. in *AIChE 2013 Annu. Meet.* (2013).

22. Pund, A., Sorokhaibam, L. G., Bhandari, V. M., Patil, V. . & Ranade, V. V. Newer adsorbents and cavitation intensified process for dye wastewater treatment. in *Int. Conf. Environ. Ecol.* (2015).

23. Kulkarni, A. A., Ranade, V. V., Rajeev, R. & Koganti, S. B. Pressure drop across vortex diodes: Experiments and design guidelines. *Chem. Eng. Sci.* **64,** 1285–1292 (2009).

24. Suslick, K. S., Mdleleni, M. M. & Ries, J. T. Chemistry Induced by Hydrodynamic Cavitation. *J. Am. Chem. Soc.* **119,** 9303–9304 (1997).

25. Shah, Y. T., Pandit, A. B. & Moholkar, V. S. *Cavitation Reaction Engineering*. (Springer US, 1999). doi:10.1007/978-1-4615-4787-7

26. Sawant, S. S. *et al.* Effect of hydrodynamic cavitation on zooplankton: A tool for disinfection. *Biochem. Eng. J.* **42,** 320–328 (2008).

27. Patil, S. V., Sorokhaibam, L. G., Bhandari, V. M., Killedar, D. J. & Ranade, V. V. Investigating role of sulphur specific carbon adsorbents in deep desulphurization. *J. Environ. Chem. Eng.* **2,** 1495–1505 (2014).