Real Life Solutions for Industrial Wastewater Treatment for Different Industry Sectors

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CSIR- National Chemical Laboratory

Water & Wastewater Treatment

Water Usage (India Scenario)

- Drinking/Domestic [< 10 %]
- Agriculture [> 80 %]
- Industry [~ 10 %]

- Since 1950, world population has doubled – water consumption has increased SIX fold, Industrial consumption is expected to grow
- Industrial Wastewater Treatment is essential
- Disinfection of water is essential for removing pathogenic microorganisms

Key Issues

- Can we avoid liquid discharge?
  - Dream of zero liquid discharge
- Can we reuse treated water?
  - At least as cooling water or boiler make-up if not as process water
- How to manage process economics?
  - In terms of money & space

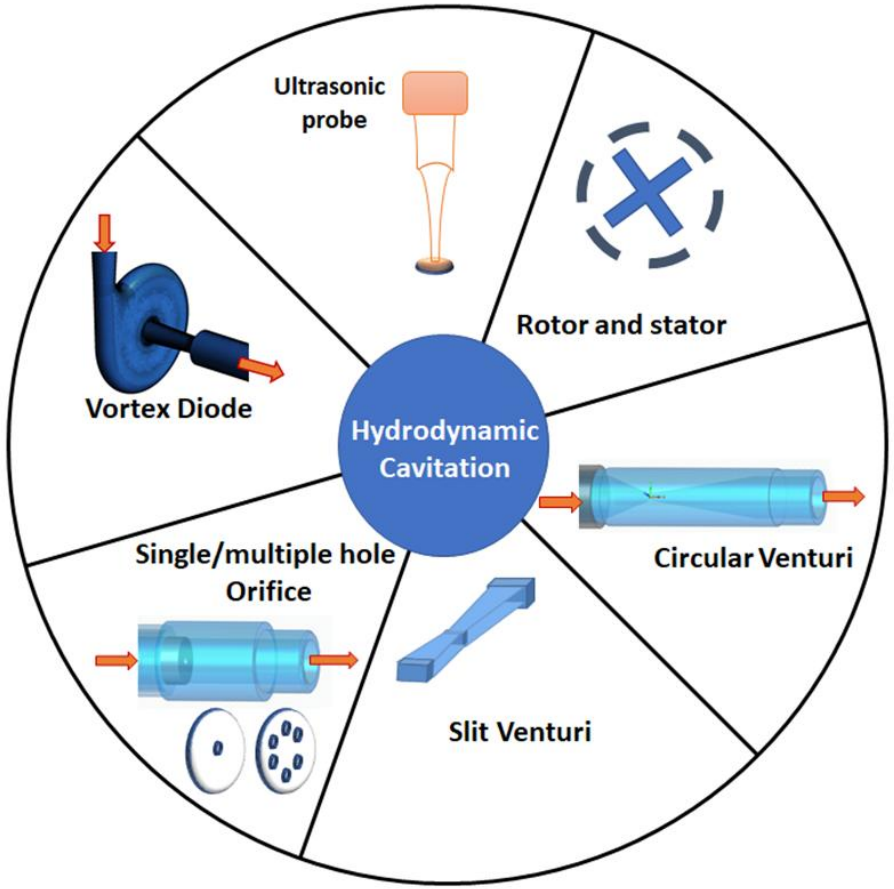
Where is space for process plant?

Treatment cost: ~ X paise/lit

Key Technologies

- Coagulation
- Membranes
- Adsorption
- Biological
  - Anaerobic/ aerobic
- Oxidation
  - Fenton, WAO
- Hydrodynamic Cavitation

Cavitation- Conventional Format



Acoustic Cavitation

- Not very Useful

Hydrodynamic Cavitation

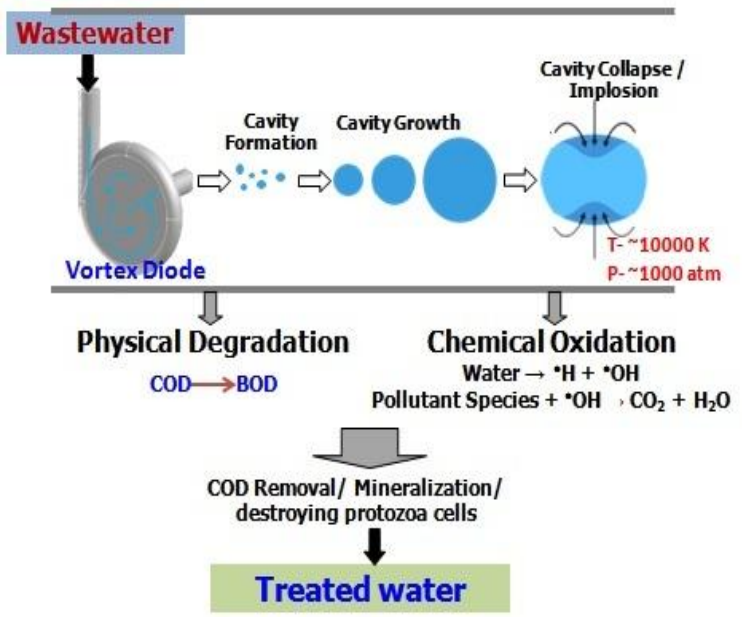
- Many limitations

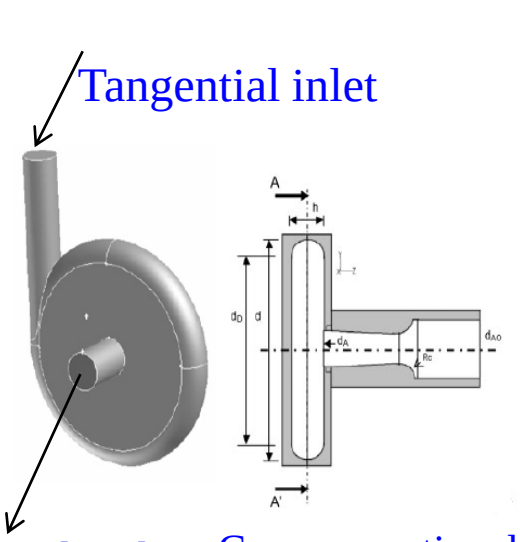
Conventional Devices

- Orifice with single hole of different hole diameter
- Orifice/ valves with variations in the open area of constriction
- Venturi cavitation reactors with different convergent- divergent sections
- Vortex diode with vortex flow- tangential and inverse flow

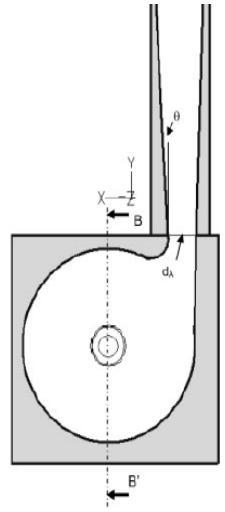
Orifice reactors (49%), Venturi (10%), high pressure homogenizers (10%)
Rotor-stator type (13%), blenders (8%), liquid whistle reactor (3%), Vortex diode (~5%).

CSIR-NCL's Technology : Hydrodynamic Cavitation-Vortex Diode for Water & Wastewater Treatment





Cross sectional view- axial outlet

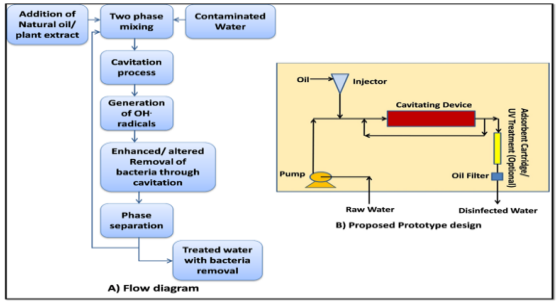


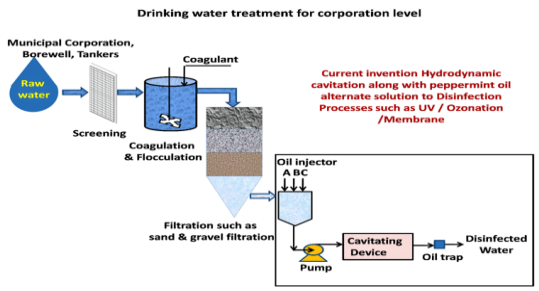
Cross sectional view - Tangential inlet

Pilot Plants at CSIR-NCL

CSIR-NCL's Green Technology for disinfection of Water

Safe Water and Sustainable Technology Initiative from Indian Knowledgebase (SWASTIIK)





Household to corporation water treatment

A Novel Hydrodynamic Cavitation Process can Provide Complete & Cost-Effective Disinfection of Water along with Health Benefits of Natural Oils

Patent: Bhandari V. M., Maya Mane and Kshama Balapure. A novel process for enhancing and altering removal of bacteria by use of natural oils derived from plant or extract in cavitation 2019-NCL-0026; 2019-NF-0085, Appl. No. 201911024544, filed on 20th June 2019.

Bhandari et al.,

IN397769
US9422952B2
EP2766314
PCT/IN2012/000676
US9725338B2
IN338553
PCT/IN2020/051007
WO 2021/111476 A1
US2021111476.

Industrial Wastewater Treatment- Pharmaceutical Industry

Background / Importance/ Relevance of the study

- **Patancheru**, Hyderabad: One of the world's largest "**bulk drug**" manufacturing hubs, supplying to markets across Europe and USA
- October 2017: > **200,000 dead fish** were observed in Gandigudem Cheruvu lake due to exposure of API Pollutants

'Contamination of water sources with drugs has had grave consequences in India, where an estimated 58,000 new-borns die from multidrug-resistant infections every year'- Lancet Report, 2013

2009: Patancheru-Bollaram zone was classified as 'Critically Polluted'.

In 2016, the country's Supreme Court ordered pharma companies to implement a Zero Liquid Waste Policy.

Larsson, 2014

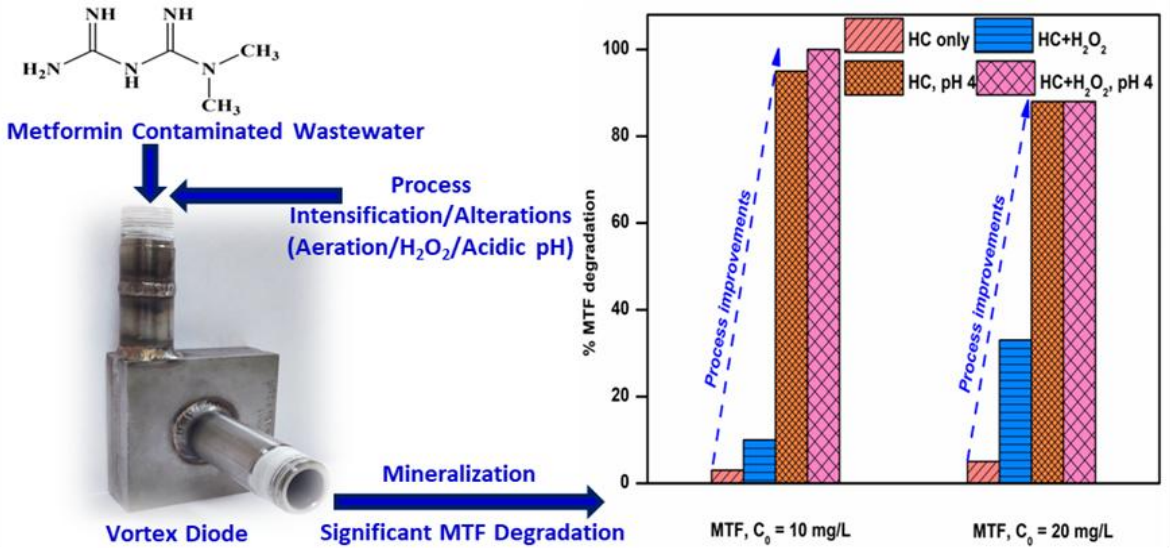
The concentration of ciprofloxacin, a broad-spectrum antibiotic, was as high as 31 ppm, and estimated total release of ciprofloxacin for 1 day was 44 kg, ***which is sufficient to treat everyone in city with 44 000 inhabitants.***

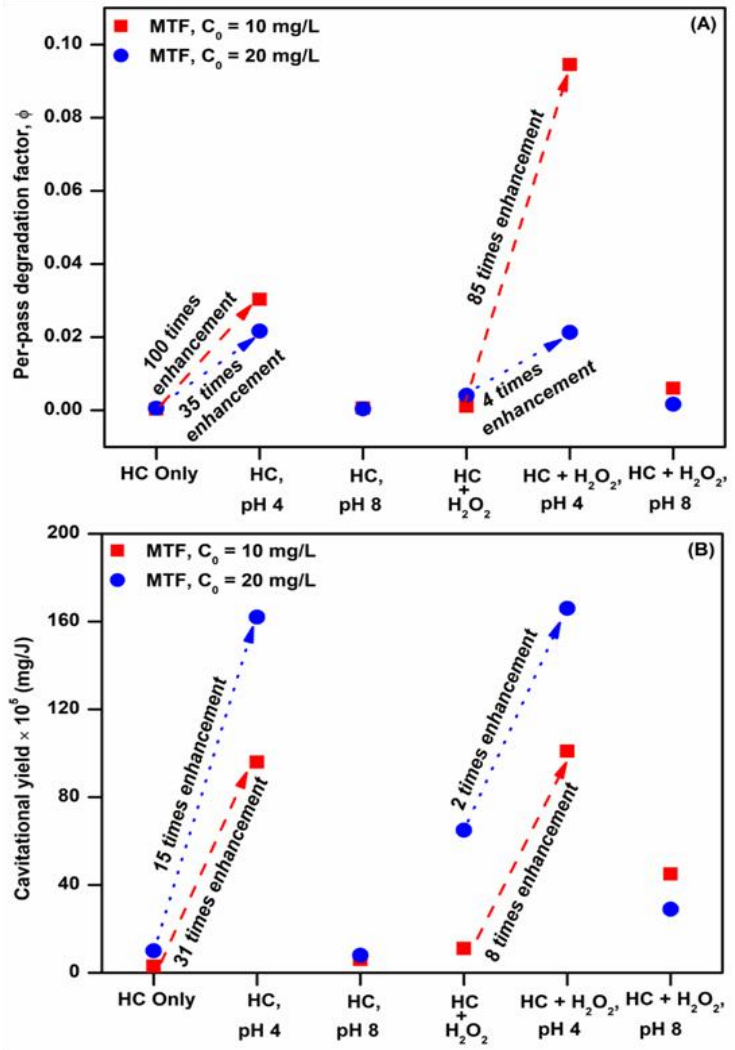
To ensure safe discharge levels from drug manufacturing, developing efficient wastewater technologies is essential.

Country	API Pollutant	~ Concentration	year
India	salicylic acid— Anti inflammatory	2270 mg/L	1988
China	oxytetracycline— antibiotic	1065 mg/L	1993
India	ciprofloxacin	31 mg/L	2007
China	oxytetracycline	19.5 mg/L	2008
Israel	Venlafaxine	11.7 mg/L	2013

Hydrodynamic Cavitation for Pharmaceutical Wastewater Treatment

Removal of API Pollutants -Metformin





Highlights

A strategy for complete degradation of metformin using hydrodynamic cavitation

- Process intensification using H_2O_2 and acidic pH conditions favour high degradation
- The synergy can be drastically enhanced by process modifications for 100% removal
- Per pass degradation enhanced 100 times with major cost reduction compared to HC

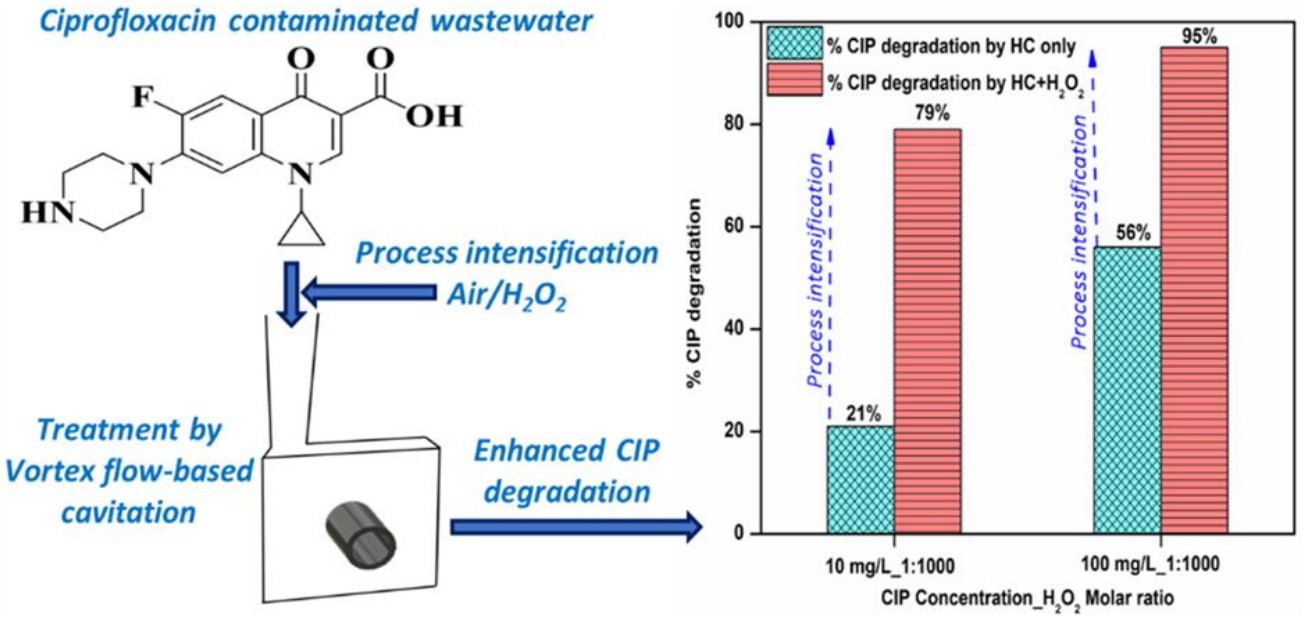
- Degradation of metformin, an antidiabetic drug
- Successful demonstration at <u>pilot plant scale (1m³/h) and for high concentrations, 10-20 mg/L.</u>
- <u>Enhancement due to Process Intensifications up to 900%.</u>

Typical cost
45 to 75 Rs/m³

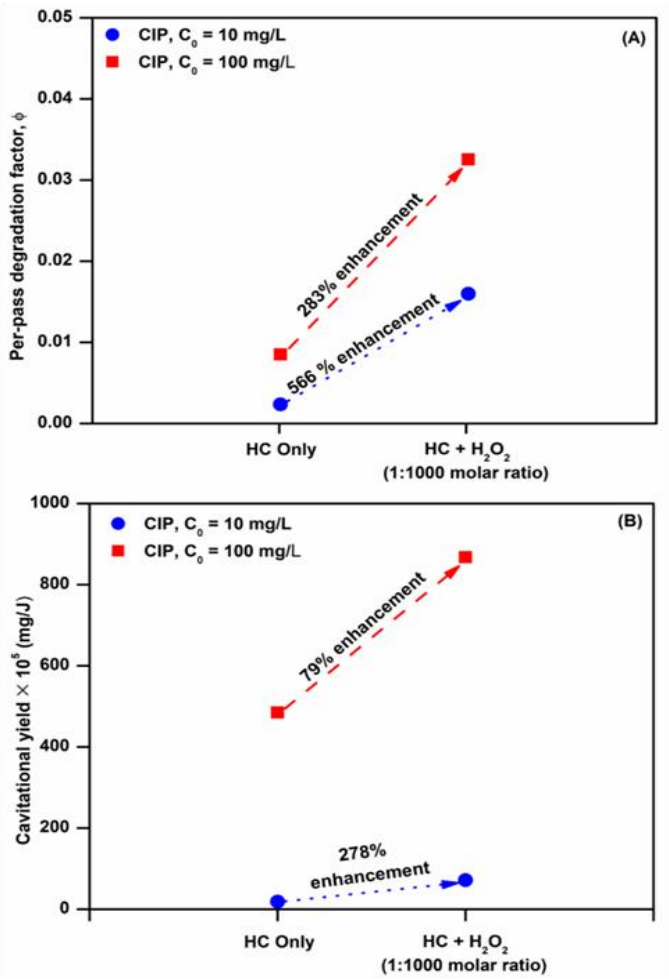
Patil et al., IEC Res., 2022

Hydrodynamic Cavitation for Pharmaceutical Wastewater Treatment

Removal of API Pollutants -Ciprofloxacin



- The hybrid approach showed the highest per-pass degradation factor with 283% and 566% enhancement compared to HC alone.
- The hybrid method is superior to the single method in terms of cavitational yield with 79% and 278% enhancement compare to HC alone.
- Cost for HC alone 41 Rs/m^3, 22 Rs/gm for 10 mg/L and for hybrid approach 38 Rs/m^3 and ~8 Rs/gm

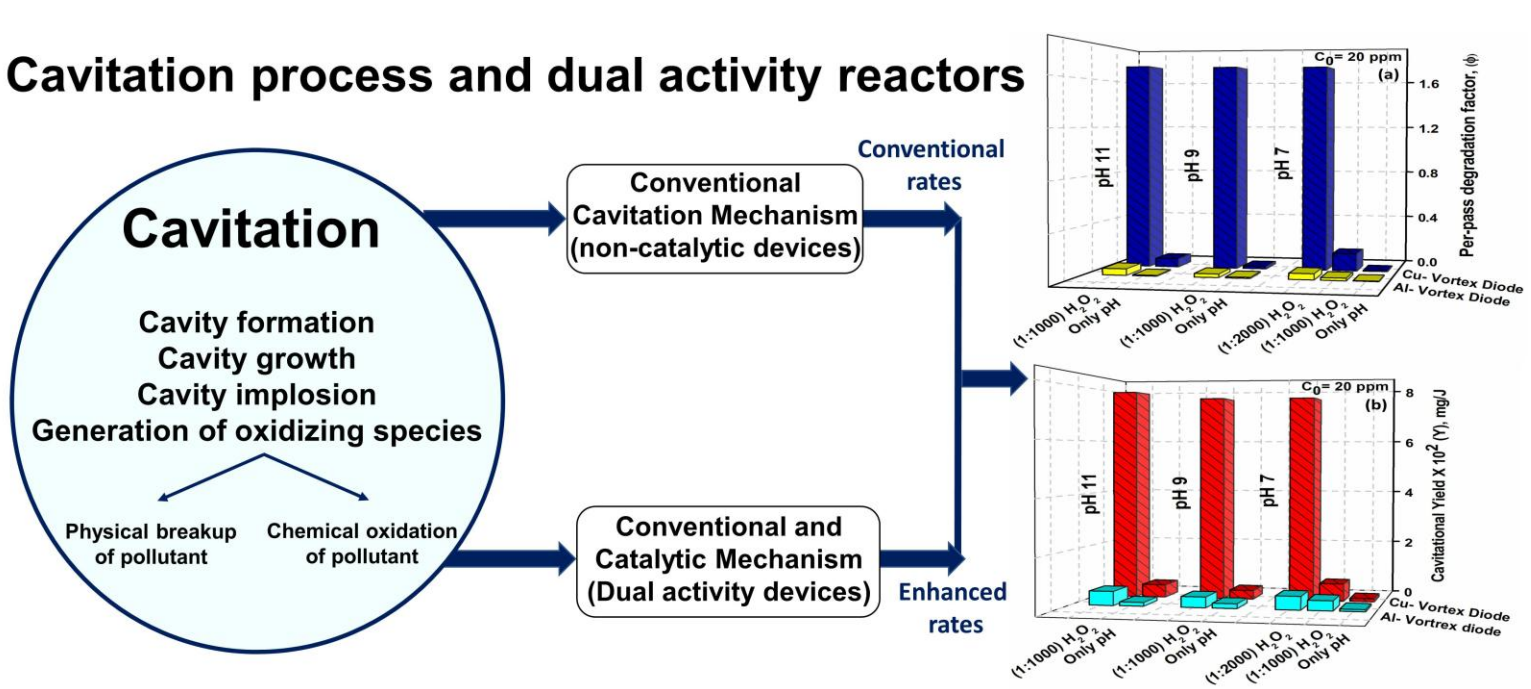


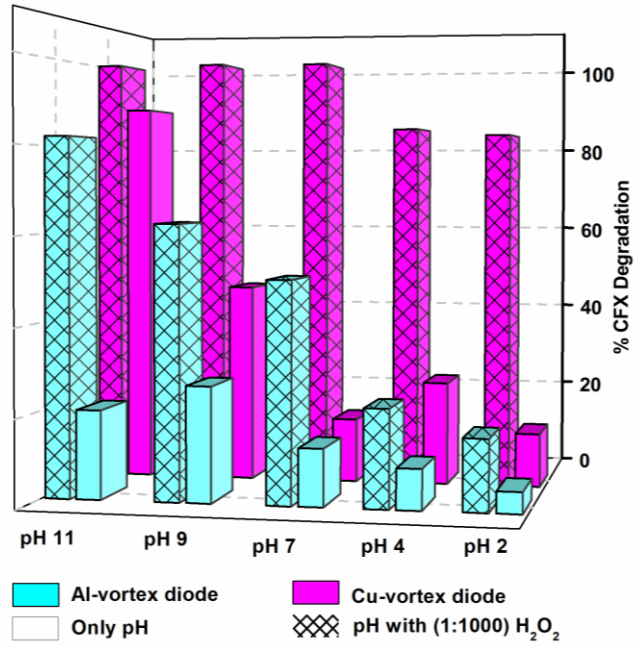
Per-pass degradation factor

Patil et al., CEPPI, 2022

Hydrodynamic Cavitation for Pharmaceutical Wastewater Treatment

Dual Activity Cavitation Reactors- Removal of Cephalexin



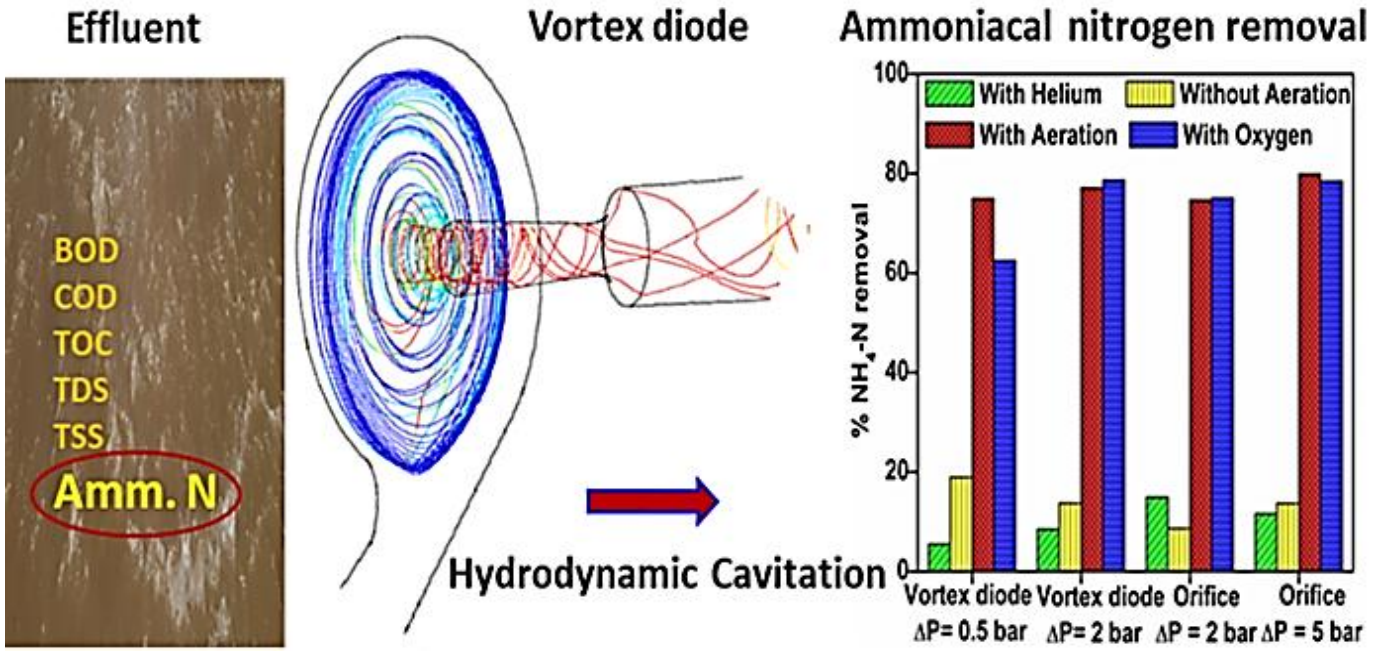


Highlights:

- Dual function cavitation reactors and novel reactor-induced catalytic oxidation
- Degradation of cephalexin using a novel dual function cavitation reactors
- 100% degradation in 5 minutes for copper device, an order of magnitude enhancement
- Huge enhancements in per pass degradation factor and in cavitational yields
- Potential applications in wastewater treatment and also in catalysis

Divya et al., CHERD, 2023

Real Life Solutions for Industrial Wastewater Treatment for different Industry Sectors- Removal of Ammoniacal Nitrogen

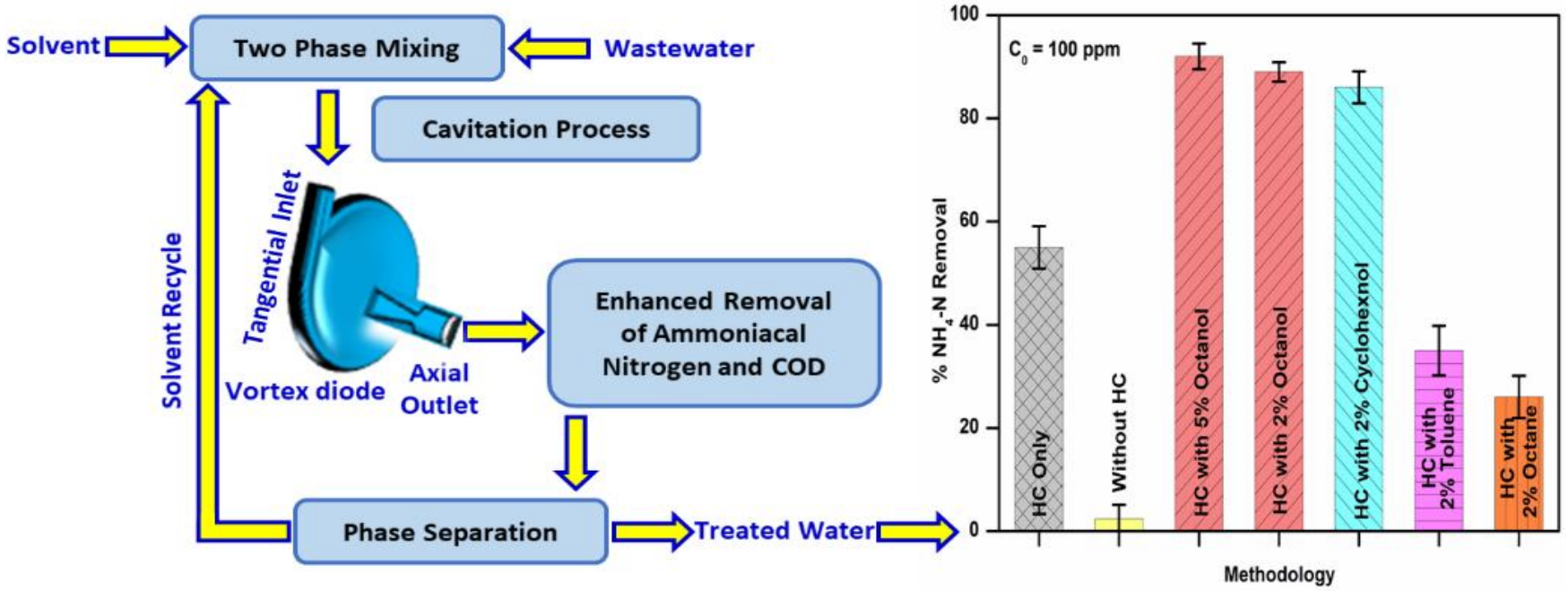


- IN397769
- US9725338B2
- WO 2013054362 A2 20130418
- US9422952B2
- EP2766314
- PCT/IN2020/051007
- WO 2021/111476 A1
- US2021111476

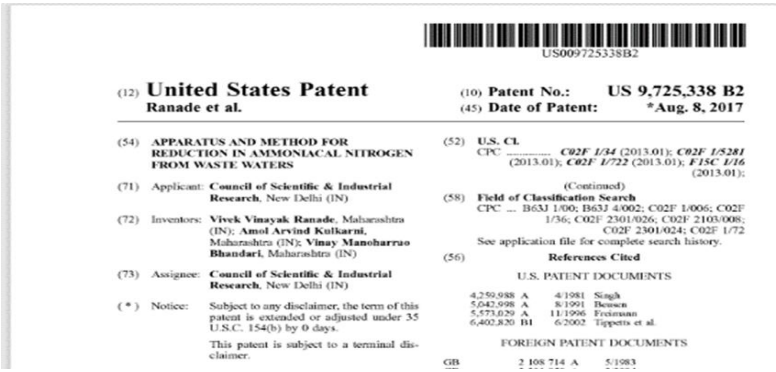
- Hydrodynamic cavitation especially using vortex diode is highly effective for the removal of ammoniacal nitrogen.
- Initial concentration has significant impact on the removal
- Up to 8 times, can be obtained using simple process intensification by sparging air or oxygen and overall extent of removal of over 80% could be accomplished
- Cost reduction due to process intensification, ranging from 200% to more than 1100%

Patil et al., Ultrasonics Sonochem, 2021

New Technology: Solvent Assisted Cavitation Removal of Ammoniacal Nitrogen



- A proof of concept with significantly improved efficiency using solvent-assisted hydrodynamic cavitation
- Relatively polar solvents increase the efficiency (>65%) and also increase the rates to an extent of more than 200%, compared to only HC.
- More than 90% removal was obtained for solvents 1-octanol and cyclohexanol, indicating the importance of the selection of solvent.


US009725338B2

(12) **United States Patent**
Ranade et al.

(10) **Patent No.: US 9,725,338 B2**
(45) **Date of Patent: *Aug. 8, 2017**

(54) APPARATUS AND METHOD FOR REDUCTION IN AMMONIACAL NITROGEN FROM WASTE WATERS

(71) Applicant: **Council of Scientific & Industrial Research**, New Delhi (IN)

(72) Inventors: **Vivek Vinayak Ranade**, Maharashtra (IN); **Amol Arvind Kulkarni**, Maharashtra (IN); **Vinay Manoharrao Bhandari**, Maharashtra (IN)

(73) Assignee: **Council of Scientific & Industrial Research**, New Delhi (IN)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(52) U.S. CL
CPC *C02F 1/34* (2013.01); *C02F 1/5281* (2013.01); *C02F 1/722* (2013.01); *F15C 1/16* (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC ... B63J 1/00; B63J 4/002; C02F 1/006; C02F 1/36; C02F 2301/026; C02F 2103/008; C02F 2301/024; C02F 1/72
See application file for complete search history.

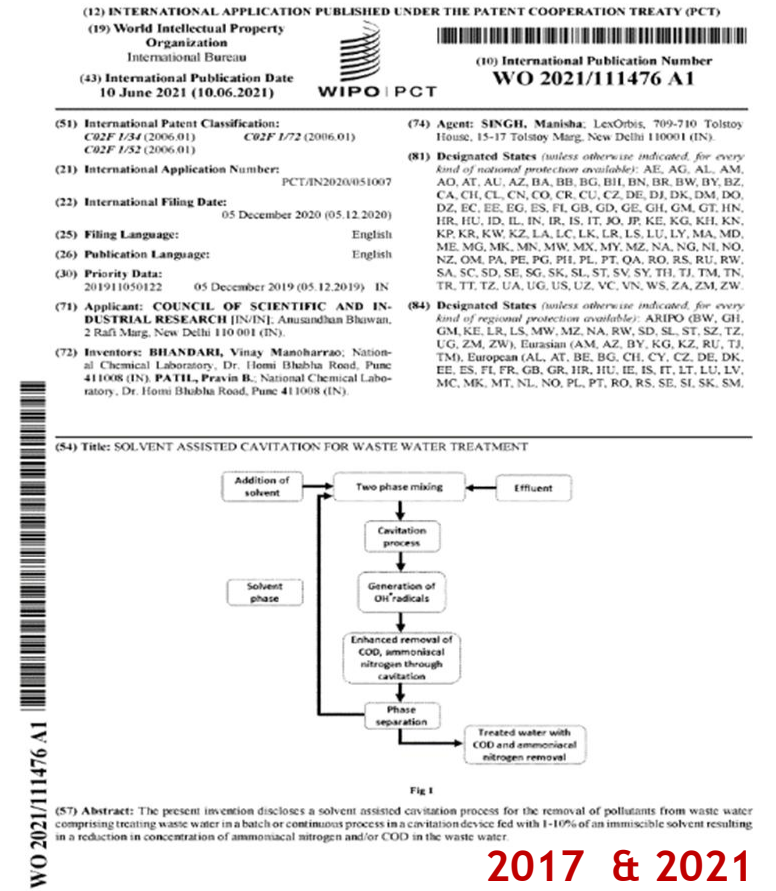
(56) **References Cited**

U.S. PATENT DOCUMENTS

4,259,988 A 4/1981 Singh
5,042,998 A 8/1991 Beusen
5,573,029 A 11/1996 Freimann
6,402,820 B1 6/2002 Tippetts et al.

FOREIGN PATENT DOCUMENTS

GB 2 108 714 A 5/1983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(30) Priority Data:
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(71) Applicant: **COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH** [IN/IN]; Anusandhan Bhawan, 2 Rafi Marg, New Delhi 110 001 (IN).

(72) Inventors: **BHANDARI, Vinay Manoharrao**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008 (IN). **PATIL, Pravin B.**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008 (IN).

(74) Agent: **SINGH, Manisha**; LexOrbis, 709-710 Tolstoy House, 15-17 Tolstoy Marg, New Delhi 110001 (IN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM.

(54) Title: SOLVENT ASSISTED CAVITATION FOR WASTE WATER TREATMENT

Fig 1

(57) Abstract: The present invention discloses a solvent assisted cavitation process for the removal of pollutants from waste water comprising treating waste water in a batch or continuous process in a cavitation device fed with 1-10% of an immiscible solvent resulting in a reduction in concentration of ammoniacal nitrogen and/or COD in the waste water.

WO 2021/111476 A1

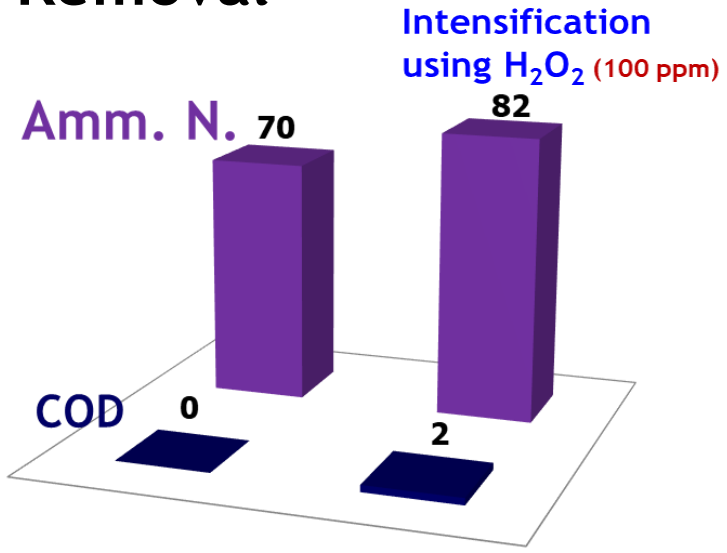
2017 & 2021

Real Life Solutions for Industrial Wastewater Treatment for different Industry Sectors- Removal of Ammoniacal Nitrogen

Dye Industry Effluent

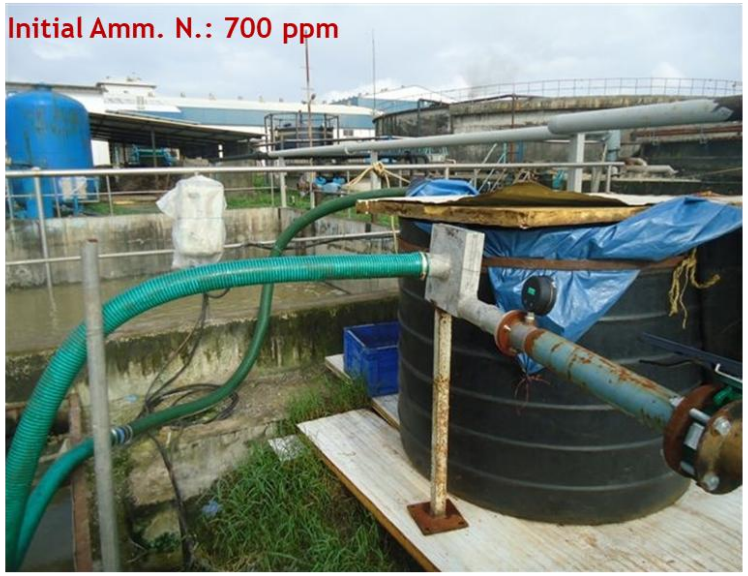
- Amm. N- 38200 ppm

% Removal



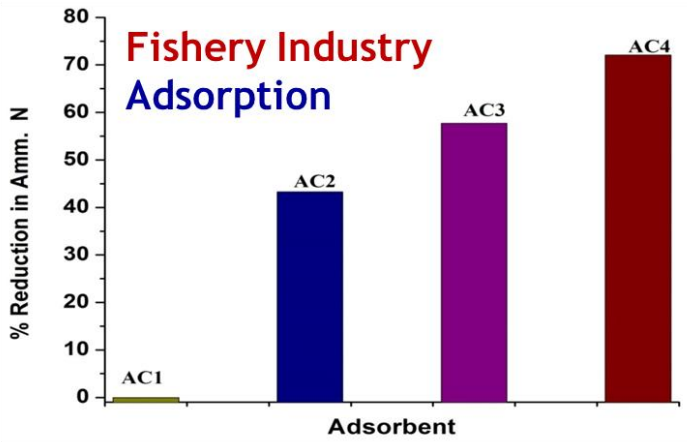
- A very high reduction using HC
- 80% using intensified cavitation

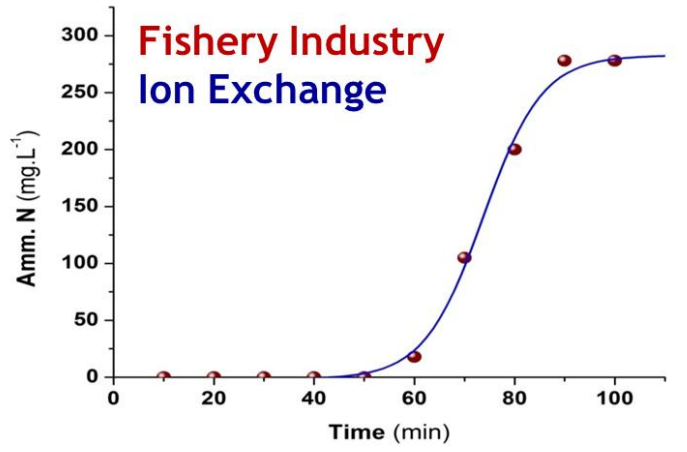
Fishery Industry Effluent



Cavitation shows ~33% Reduction

Pilot Plant Studies using Process Intensification indicated very high reduction (~80% -synthetic wastewaters)





Real Life Solutions for Industrial Wastewater Treatment for different Industry Sectors- Fertilizer Industry: Removal of COD/Ammoniacal nitrogen

Adsorption & Ion Exchange Methods -Suitable for Low Concentrations

- **Presence of –**
  - **Organics, alcohols**
  - **Ammonia**
  - **Nitrates**
  - **Phosphorous**
  - **Heavy metals**

Fertilizer Industry- 6 effluent samples from different locations

Adsorption & Cavitation

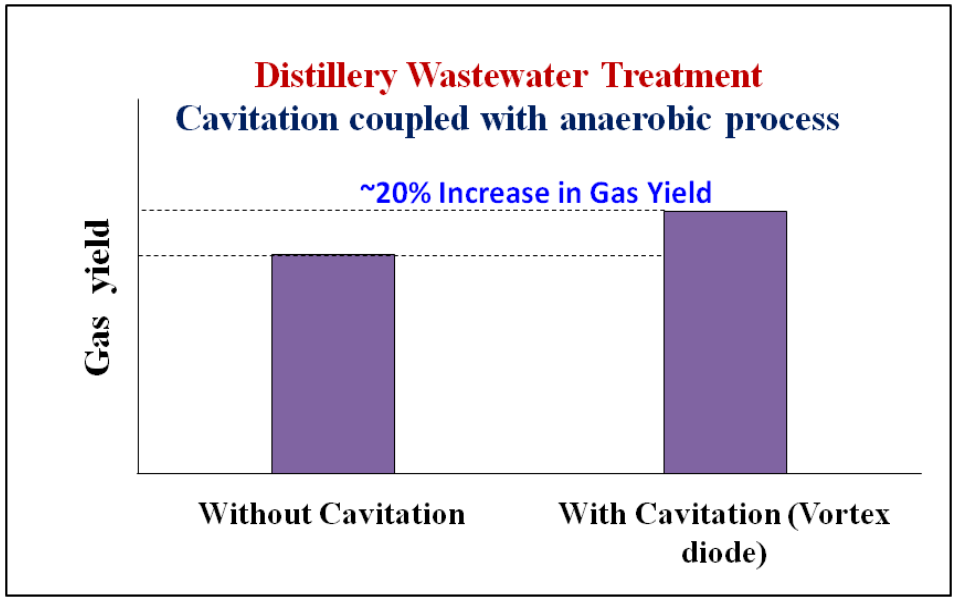
Effluent Stream	Initial COD (ppm)	Initial NH_3-N (ppm)	% Reduction			
			COD		NH_3-N	
			Adsorption	Cavitation	Adsorption	Cavitation
1	125000	2	--	85	NA	NA
2	946	1710	--	76	--	60
3	460	86	80	<10	80	41
4	130	1330	86	<10	30	36
5	44	530	65	<10	35	37
6	170	276	10	<10	98	87

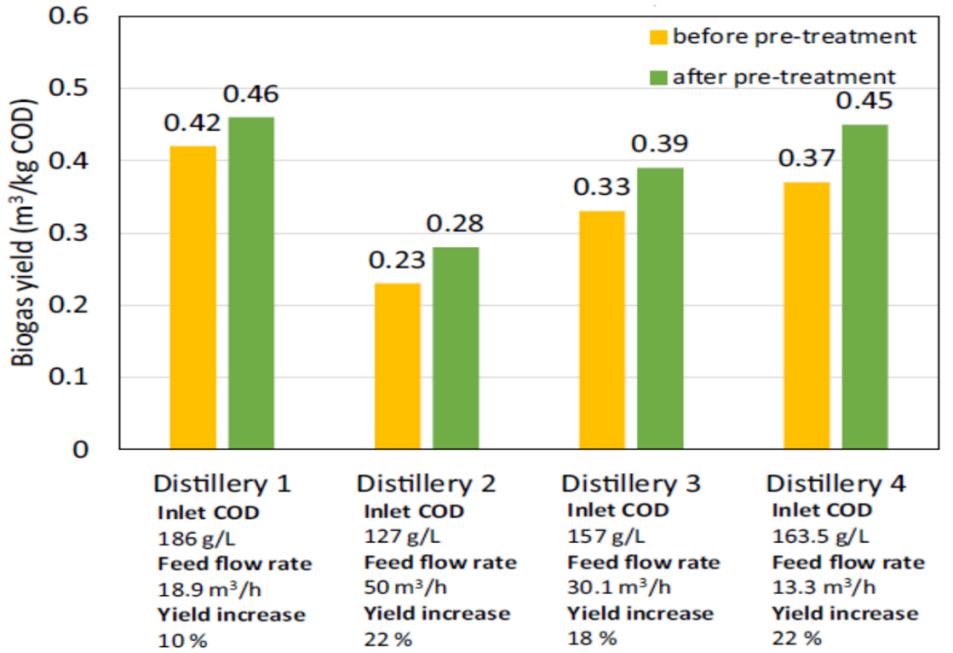
Existing practices employ different physico-chemical/ Biological methods….

Bhandari et al., Desalination and Water Treatment, 2016

Real Life Solutions for Industrial Wastewater Treatment for different Industry Sectors- Enhancing Gas Yield in Distillery Industry

Wastewater as a source of energy is being increasingly considered





Plant data from four digesters (single pass through cavitation device)

Courtesy Dr. VV Ranade, VIVIRA

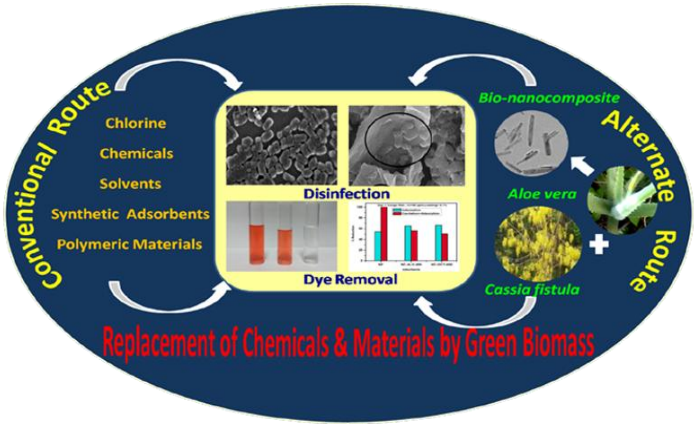
Breaks down refractory Pollutants to enhance gas yield

Results of REAL Plant Installations (2022)

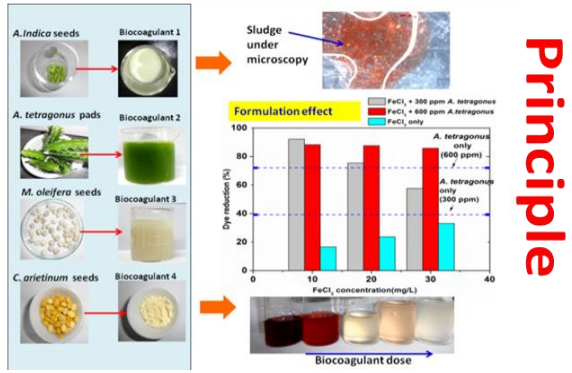
Future Trends - Hybrid technologies
Materials, Emerging Technologies & Process Integration

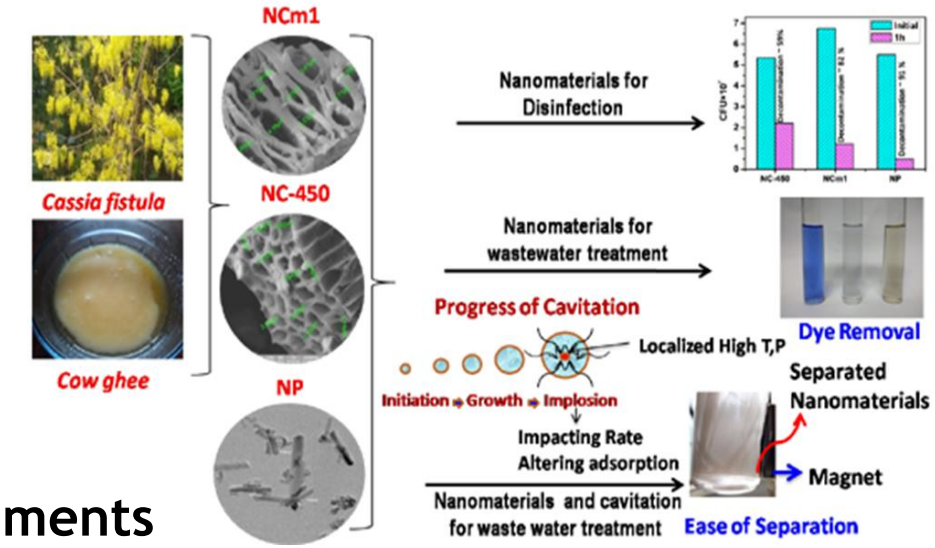
Bioadsorbents, Biocoagulants, Nano-biocomposites

Philosophy



Principle





Improved Efficiency & Economics through Newer Developments

- *Clean Technologies and Environmental Policy, 2018*
- *J. Environ. Management, 2019*
- *Int. J. Env. Sci. Technol., 2021*

Deliverables

- ✓Prototype- Newer Materials
- ✓Implementation at Industry
- ✓Installations at different levels

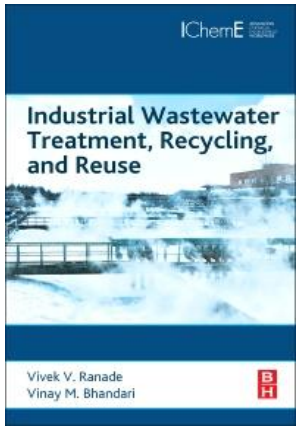
Industry/ Societal Benefits

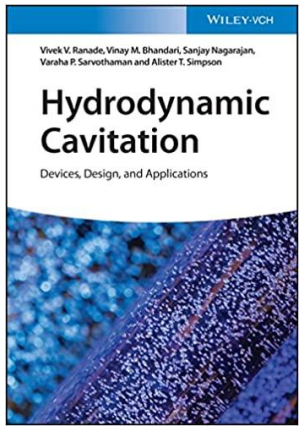
- ✓ Reduced Pollution
- ✓ Recyclable Water
- ✓ Preserving Ecology

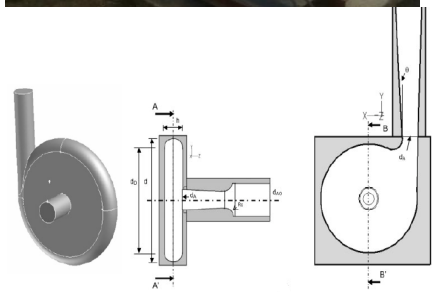
➢ **Cavitation**

+ Adsorption/ ion-exchange
+ Coagulation
+ Oxidation
+ Biological treatment
+ Membrane separation

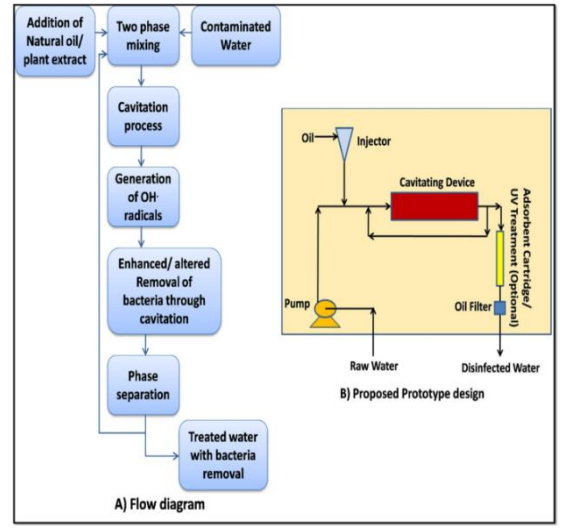
CSIR-NCL's TECHNOLOGIES FOR WATER & WASTEWATER TREATMENT

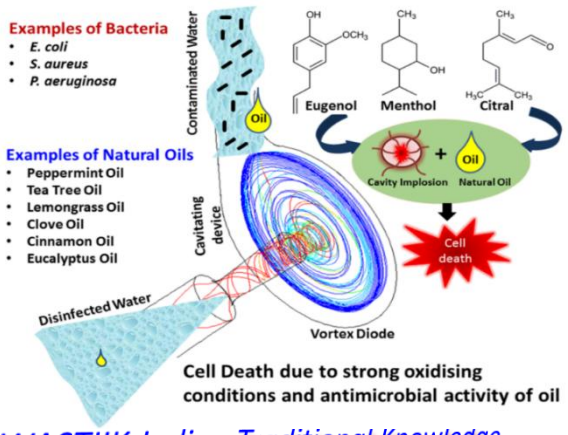






- Application of CSIR-NCL's Cavitation Technology to Industry (**TRL 9**)
  - ✓ For removal of COD and Ammoniacal nitrogen
- Development of Industry Specific solutions (**TRL 9**)
  - ✓ Distillery wastewater Treatment increases gas yield~20%.
  - ✓ Dye wastewater treatment
  - ✓ Pharmaceutical industry Effluent
- Development of Water Treatment Technology from TRL 4 to TRL 9.
  - ✓ Safe Water and Sustainable Technology Initiative from Indian Knowledgebase **(SWASTIIK)**
- Develop advanced oxidation processes or hybrid processes





SWASTIIK-Indian Traditional Knowledge

Technology Licensed to VIVIRA Technologies

➢**CSIR- NCL's Device for Wastewater Treatment Commercialized in 2015**
➢**Running in ~ 50 installations/ Industries**
➢**~ 30 units were sold till 2020 with total flow rate of 330 m^3/h or nearly 8 MLD**

US9422952B2 (2016); US9725338B2 (2017), EP2766314 (2019), Appl. No. 201911024544 (2019), Appl. No. 201911050122, (2019), PCT/IN2020/051007; WO 2021/111476 A1 (2021)

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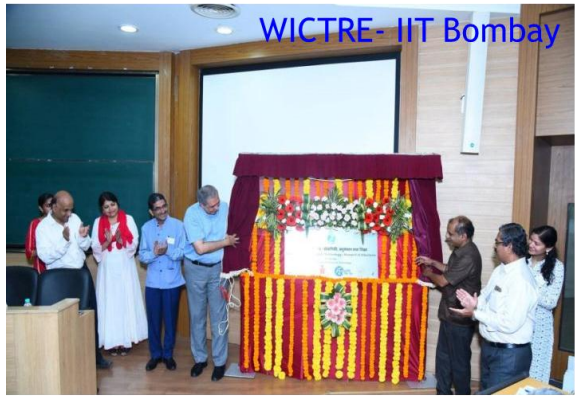
Students: Nalinee Suryawanshi; Maya Mane; Pravin Patil; Divya Dixit



Saumaya Kirti; Pooja Jain; Chethana; Monal; Pravin Suryawanshi; Sarika; Anamika & Others

Societal Commitments



Hon. Minister (Science & Technology) visiting our Pilot Plant

DD News http://ddnews.gov.in/sci-tech/modern-technology-indian-traditional-knowledge-combines-bring-safe-healthy-drinking-water

Rajya Sabha TV https://youtu.be/2qfy3iR4MWI

DST PIB https://pib.gov.in/PressReleasePage.aspx?PRID=1723634
https://pib.gov.in/PressReleaseIframePage.aspx?PRID=1723594

Digital India
https://twitter.com/indiadst/status/1399956079543418881?s=24
https://www.livemint.com/news/india/csirncl-lab-leverages-ayurveda-for-safe-drinking-water-technology-11622617458721.html

TECHNOLOGY AWARD- June, 2019

SRISTI-Gandhian Young Technological Innovation Awards

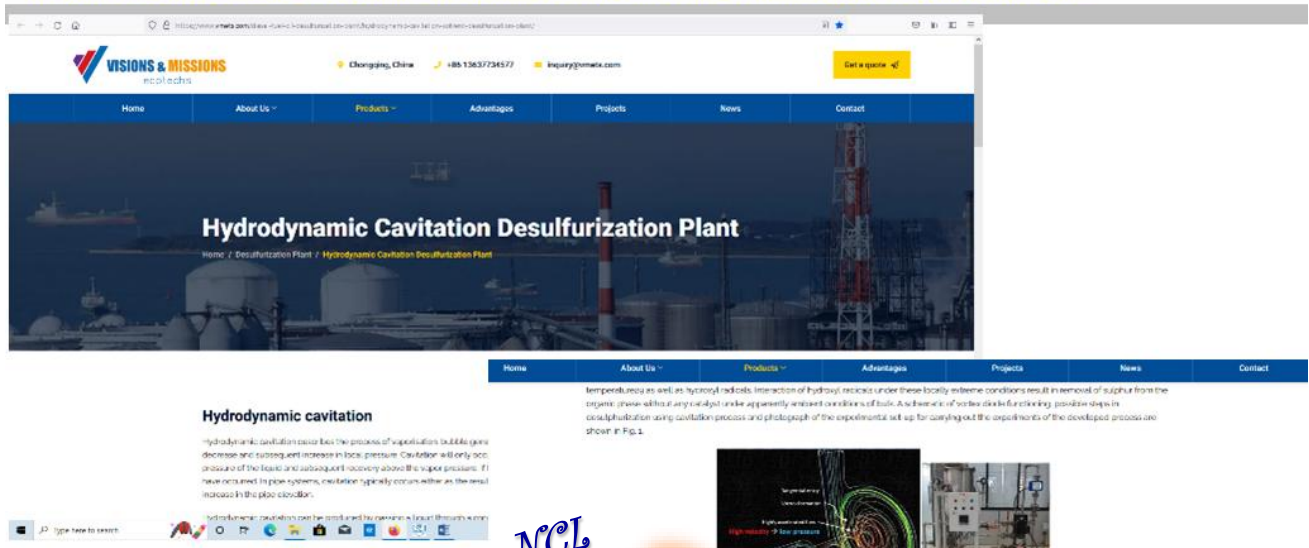
GYTI -2019

Hydrodynamic Cavitation for Deep Desulfurization of Fuels

Chinese Website citing Hydrodynamic Cavitation Technology based Plant

https://www.vmets.com/diesel-fuel-oil-desulfurization-plant/hydrodynamic-cavitation-solvent-desulfurization-plant/

Viewed on 3 Aug. 23)



This Photo of pilot plant is from NCL and the Figure was published by us in Nature- Scientific Reports, 2016