Report of the work done	
Project number & Title of the Project	T4E, Development of Water Treatment System Based on Advanced Oxidation Process (AOP) for the Removal of Emerging Contaminants in Water
Name and Address of the PI & Co-PIs	Dr. V. Sivanandan Achari Professor & Dean Principal Investigator RUSA 2.0 Project T4E School of Environmental Studies Cochin University of Science and Technology, Kochi-682022 Dr. G. Madhu Professor & Co-PI RUSA 2.0 Project T4E Division of Safety & Fire Engineering School of Engineering Cochin University of Science and Technology, Kochi-682022 Dr. Renu Pawels Professor & Co-PI RUSA 2.0 Project T4E Division of Civil Engineering School of Engineering Cochin University of Science and Technology, Kochi-682022
RUSA grant allotted	Hard components: 2,50,000/-
	Soft components: Computer/software/minor components – 2,00,000/- Manpower – 2,10,000/-
Expenditure as on May 31, 2024	Hard components: 2,49,073/-
	Soft components: Computer/software/minor components – 1,99,962/- Manpower – 1,48,385/- More than 95% of fund utilized from Hard Component and Soft Components allotted.
Total Amount Withdrawn through SR	5,97,420/-
Expenditure as on May 31 through adjustment CB	5,97,420/-

Brief report of the work done (500 words)	Separate Sheet attached
Milestones achieved:	i.The project RUSA 2.0, T4E, Development of Water Treatment System Based on Advanced Oxidation Process (AOP) for the Removal of Emerging Contaminants in Water Has been initiated and is under progress. Under this project, One project staff was appointed on 19/08/2023. ii. Purchases of various items under different heads were Carried out. Tenders were invited for the purchase of Ultrasonic Probe Sonicator, Model PS Advance 20-500. The equipment purchased from the firm (SCIENTIFIC ENTERPRISES) that quoted the most suitable technical Specification with lowest quoted amount as we required. The equipment installed on 06/10/23. iii. Quotations were invited for purchase of laptop and printers under the head computer/software/minor Components. Laptop and printers purchased from the firm (M/S EXTREMEIT SOLUTIONS) that quoted the most suitable specification with lowest quoted amount as we Required. Iv. The SR's taken under the heads of Hard component, computer/software/minor components, Manpower were utilised and settled before 29/02/2024 1. C.B No. Adj- CB/320/2023-24/139 for SR/320/2023-24/27 dated 19/09/2023 Amt:2,13,108/- 2. C.B No. Adj- CB/320/2023-24/140 for SR/320/2023-24/34 dated 27/09/2023 Amt:36,692/- 3. C.B No. Adj- CB/320/2023-24/141 for SR/320/2023-24/28 dated 27/09/2023 Amt:1,63,270/- 4. C.B No. Adj- CB/320/2023-24/170 for SR/320/2023-24/35 dated 29/09/2023 Amt:35,965/- 5. C.B No. Adj- CB/320/2024-25/3 for SR/320/2023-24/16 dated 08/09/2023 Amt:1,48,385/- Intimation slip received for the SR drawn: 1. SR/320/2023-24/27 Amt: 2,13,108/- (Intimation Slip No. 128 dated 15/11/2023) 2. SR/320/2023-24/34 Amt: 36,692/- (Intimation Slip No. 141 dated 23/11/2024)

	3. SR/320/2023-24/28 Amt: 1,63,270/- (Intimation Slip 140 dated 23/11/2023) 4. SR/320/2023-24/35 Amt: 35,965/- (Intimation Slip No. 22 dated 26/03/2024)
Publications	Submitted: NIL
	Accepted: NIL
Patents	Applied: NIL
	Approved: NIL

WORK REPORT

Introduction

Advanced Oxidation Processes (AOPs) are a group of water treatment techniques that involve the generation of highly reactive hydroxyl radicals (•OH) to degrade and remove various pollutants from water. These processes are particularly effective in treating recalcitrant and persistent organic pollutants, such as pharmaceutical compounds and endocrine-disrupting chemicals. One such pharmaceutical compound of concern is bisphenol A (BPA), a synthetic compound commonly used in the production of plastics and resins.

AOPs typically involve the use of powerful oxidizing agents or methods to generate hydroxyl radicals, which then react with the target pollutants, leading to their degradation into simpler and less harmful substances. Common AOPs include ozonation, photocatalysis, sonocatalysis, Sono-Fenton, Fenton and photo-Fenton processes, and advanced oxidation with hydrogen peroxide (H_2O_2).

Several research papers have focused on the application of AOPs for the removal of bisphenol A and other pharmaceutical compounds from water. The efficiency of these processes is often assessed by measuring the degradation percentage, which represents the extent to which the target compound is broken down during treatment. The degradation percentage is influenced by factors such as the type of AOP used, reaction conditions, concentration of oxidants, and the characteristics of the target pollutants.

Objective

- To study the degradation percentage of Bisphenol A using the oxidant H_2O_2 and Fenton Oxidation Process.
- To synthesize Cr doped TiO_2 catalyst to use it as a photocatalyst and Sonocatalyst for the removal of bisphenol A

- To study the effect of dopant concentration on the removal efficiency of bisphenol A
- To compare the effect of reaction time, reaction process, pH of the medium, and initial concentration of the pollutant.

Materials and Methods

The Chemical reagents used were all analytical grade. Hydrogen peroxide is used as the source of oxidants like hydroxyl radical in the advanced oxidation process. H_2O_2 (30.0% w/v) analytical grade from Merck India was used in the study. Sodium sulphite (Na_2SO_3) analytical grade was used as the peroxide quencher in the process. Ferrous Sulphate heptahydrate ($FeSO_4.7H_2O_2$) was used as the iron source. Hydrochloric acid and NaOH were used for pH adjustments.

For the preparation of catalyst, Chromium doped titanium dioxide, the chemicals Such as TiO_2 (Degussa P25), Chromium Nitrate hexahydrate Cr $(NO_3)_2.6H_2O$ and Methanol (99%) used as the solvent.

Experimental Procedure

100 ml synthetic sample of bisphenol A (BPA) with initial concentration of 15 ppm was taken in a 250 ml pyrex glass reactor, and the initial pH of the sample is adjusted to the required value by using Hyrochloric acid and NaOH. Initial sample pH of 3 was noted using Scientific Tech Advanced pH system for the experiments to analyze the pH effect. For fenton process, the catalyst added in required concentration followed by oxidant. The contents in the reactor were mixed continuously using a magnetic stirrer (Fig 1). Addition of the oxidant was considered as the start time of reaction. Fixed volume of sample was withdrawn at regular intervals of time and analysed the TOC content using a Vario TOC Analyser (Fig 2.). One drop of 0.1 N sodium sulphite solution was added to each sample taken to quench the action of any excess H_2O_2 present in the sample. For degradation using Ultrasonic waves, Ultrasonic Probe Sonicator (Model PS Advance 20-500) is used for about 1 hour (Fig 3.)

Fig 1.Fenton process in magnetic stirrer

Fig 2. Vario TOC Analyzer

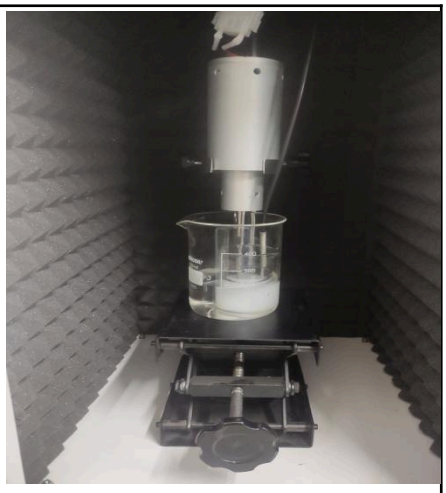


Fig 3. Sonication of BPA with Cr-doped TiO_2

Synthesis of Cr doped TiO_2 Catalyst

The co-doped TiO_2 nanopowder was prepared using the method discussed by Garg *et al*. with a little modification wherein methanol was taken in place of water for suspension of TiO_2. Degusaa P25 TiO_2 5g has been suspended in 100 ml of methanol, followed by the addition of Chromium nitrate hexahydrate solution. The obtained slurry was well stirred followed by ultrasonication for 10 minutes and kept at rest for 24 hours. The obtained slurry has been washed thoroughly with distilled water and for removal of undoped ions before drying in hot air oven at 100°C for overnight. The solid particles were grounded in agate mortar followed by calcinations at 400 degree Celsius for 2 hours in muffle furnance. The co-doped TiO_2 catalyst were prepared with co-dopant concentration of TCr_x(X=0.5, 1, 1.5). The prepared catalysts are shown in Figure 4.

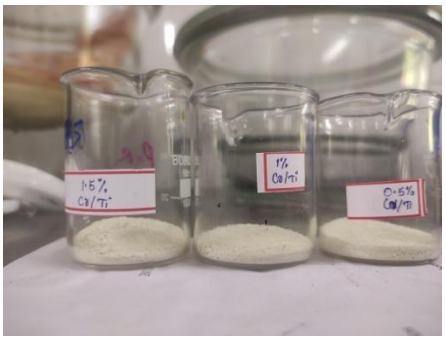


Fig 4. Prepared Cr-doped TiO_2

Prepared Catalyst	Initial yield (g)	Yield after calcinations (g)
0.5% Cr/Ti	4.6013	4.5024
1% Cr/Ti	4.7325	4.7633
1.5% Cr/Ti	4.7554	4.6611

Table1. Yield of catalysts.

Results

The prepared catalysts were characterized using Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS) analysis, Fourier Transform Infrared Spectroscopy and X-ray diffraction (XRD) analysis. The spherical shape morphology is analyzed from SEM images. The crystal structure of doped and undoped TiO_2 catalyst was detected by XRD. The influence of Chromium ion incorporation on the chemical composition was analysed by EDS. Hence by EDS spectra presence of chromium in the doped catalyst were confirmed. FTIR patterns of the doped and undoped TiO_2 particles were taken to get the information on the surface chemistry of the particles.

Fenton Process: The Fenton process was conducted in the molar ratio 0.7:1 and the pH were adjusted to 3 using 0.1 M hydrochloric acid. The Contents in the beaker stirred uniformly using a magnetic stirrer. In this reaction H_2O_2 used as the oxidant and Ferrous Sulphate

heptahydrate ($FeSO_4.7H_2O_2$) used as the catalyst. The molar ratio of H_2O_2:Fe^{2+} is an important factor influencing the degradation efficiency. Fixed volume of samples withdrawn from the reaction system and analyzed using TOC Analyzer. The degradation efficiency is only 24 % even after 120 minutes of reaction time.

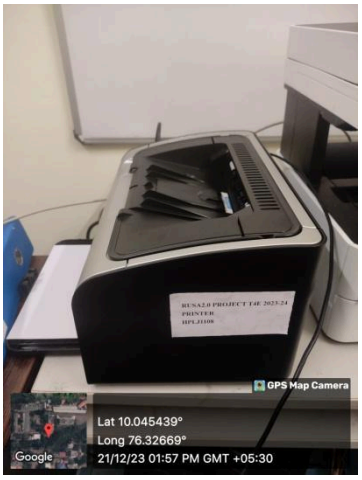
Sonolysis: During sonolysis, the same operational parameters were taken as fenton process and reaction time choosed as 1 hour. Results from TOC value shows sonolysis alone doesn't show any advanced degradation. Only 5% degradation of initial concentration of BPA is obtained. Further studies were conducted with different pH ranging from 3 to 11. Maximum degradation is obtained at pH 3. Sonolysis with different initial concentration of BPA of 5, 10, 15, 20, 25, 30 ppm shows the maximum degradation at initial concentration of 15 ppm.

Sonocatalysis: Sonocatalytic degradation of BPA was studied with the prepared Cr-doped TiO_2 and pure TiO_2 powder. 50 mg/L of catalyst was added to BPA solution of initial concentration of 15 ppm and pH 3. From the comparative study of pure TiO_2 and different Cr-doped TiO_2, 1%Cr-doped TiO_2 shows maximum degradation efficiency of 81%. Further studies were conducted with the 1%Cr-doped TiO_2. The influence of pH of the reaction mixture on degradation efficiency of BPA conducted with different pH ranging from 3 to 11. From the results, the degradation efficiency decreases as pH increases from 3 to 11. The effect of pollutant dose on degradation was further studied with initial BPA concentration of 5, 10, 15, 20, 25, and 30 ppm. The maximum BPA removal efficiency obtained with initial pollutant concentration of 15 ppm. Further studies were conducted on the effect of catalytic dose on removal of BPA. Different reactions with varying adding amount of 1%Cr-doped TiO_2 of 10, 30, 50, 75, 100, 120 and 150 mg/L were employed. TOC removal efficiency of 81% obtained when 50mg/L of catalyst used.

Future Works

- Advanced Oxidation of bisphenol A using ozone as the oxidant and compare the reaction procedures.
- Study of effect of oxidant, catalyst, pH, reaction time on Fenton Oxidation process.
- Advanced Oxidation of bisphenol A by UV/Fenton, Photolysis and Photocatalytic reaction
- Preparation of Photocatalysts and degradation of BPA using UV rays.
- Degaradation of the organic pollutant Chlorophene using H_2O_2, ozonation, fenton, sono-fenton, and sonocatalysis.

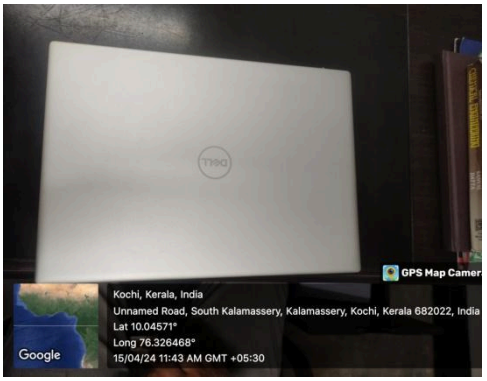
Equipments purchased and Installed



HP Laserjet 1108 printer

Ultrasonic Probe sonicator (Model: PS Advance) Of Rs. 2, 13,108/-

Epson L6460 series Printer



Laptop (DELL inspiron)

International Conferences Attended by the Project Assistant

1. T4E Project staffs, Anjana P S, RUSA 2.0, T4E, participated in one day workshop and International Conference- **Energy Summit 2023 at Indian Institute of Technology, Madras, 5-7th December 2023.**
2. T4E Project staffs, Anjana P S, RUSA 2.0, T4E, participated in a one day workshop and Skill Training-"Functional Materials & Systems for Environmental & Energy Applications: Pollution Reduction and Control" on 23/02/2024 at **School of Environmental Studies, Cochin University of Science and Technology**

Papers Published by Principal Investigator RUSA2.0 T4E from May 2023 to upto March 2024

1. Krishna, B., Achari, V.S., 2023. Groundwater chemistry and entropy weighted water quality index of tsunami affected and ecologically sensitive coastal

region of India. Heliyon 9 (10), e20431, Elsevier Publications. https://doi.org/10.1016/j.heliyon.2023.e20431 . Impact factor: 4.0

2. Krishna, B., Achari, V.S., 2023. Groundwater for drinking and industrial purposes: A study of water stability and human health risk assessment from black sand mineral rich coastal region of Kerala, India. J. Environ. Manage. 351, 119783. https://doi.org/10.1016/j.jenvman.2023.119783 . Elsevier Publications, Impact factor: 8.9
3. Mohanadas, M., Achari, V.S., Lekshmy, J., Namboothiri, Y.K., Sathyachandran, A., 2023. The hidden impact of seafood processing on coastal aquifers: Hydrogeochemistry and water quality assessment. Mar. Pollut. Bull. 196, 115611. https://doi.org/10.1016/j.marpolbul.2023.11561, Elsevier Publications, Impact factor: 5.8

4. Rajalakshmi A.S, Achari V S, Sekkar V, Organo-inorganic hybrid IPN sourced porous carbons and their lead decontamination perspectives, Surfaces and Interfaces 48 (2024) 104196, https://doi.org/10.1016/j.surfin.2024.104196, Elsevier Publications, Impact factor: 6.2

Papers Published by the Co-PI –Dr. G Madhu from May 2023 to upto March 2024

1. G. Sanoop, Sobha Cyrus and G. Madhu. Sustainability Analysis of Landfill Cover System Constructed Using Recycled Waste Materials by Life Cycle Assessment, Nature Environment and Pollution Technology, Volume 23, Issue No 1, Mar 2024. DOI Number: 10.46488/NEPT.2024.v23i01.035

2. Sahadev, Saurabh.; Madhu G.; Thomas, Roy M. Modelling of Activated Sludge Process Using Artificial Neuro-Fuzzy Inference System. Indian Journal of Environmental Protection, Volume 43, Issue 8, Pages 686 - 6961 August 2023.

3. Uday Sankar, K. Bhasi, M. Madhu,G. A hybrid bacterial foraging – simulated annealing framework for improving road networks. Measurement: Sensors, 2023, 26, 100704.

4. Sahadev, S. Madhu, G. Roy Thomas, M. Modeling of Activated Sludge Process Using Multi-Layer Perceptron Neural Networks. Nature Environment and Pollution Technology, 2023, 22(1), pp. 445–461.

5. Ravindran, K. Madhu, G. Renjith, V.R. Rugmini, S. Performance of the ρ- Al2O3 based Ag promoted Pd/ Al2O3 catalyst during Acetylene hydrogenation with an ideal feed
Journal of the Indian Chemical Society, 2023, 100(2), 100884.
.
6. Sankar, K.U, Bhasi, M., Madhu, G. A modified bacterial foraging algorithm for improving road networks. Optik, 2023, 273, 170377

Thesis submitted under the supervision of the Co –PI -Dr. G Madhu

Deepa, R. Studies on the Removal of the Emerging Contaminant – Mefenemic acid from aqueous media using Advanced Oxidation Processes (Open defence and Viva -voce examination held on 26.02.2024)

Thesis submitted by Principal Investigator RUSA2.0 T4E on April 2024

PhD Thesis submitted to Cochin University of Science and Technology, Kochi on April 2024 by Balamuralikrishna under the supervision of **Dr. V Sivanandan Achari, PI, RUSA2.0, Project T4E**, "Groundwater chemistry, industrial and irrigation suitability of water: A hydro geoanalytical study from placer mineral enriched coastal regions of Kerala, India".

Acknowledgement

Principal Investigator is thankful to the Rasshtriya Uchchatar Shiksha Abhiyan (RUSA 2.0), Government of India, New Delhi for financial support through RUSA2.0, Major project T4E as per the order No. CUSAT/PL(UGC).AI/2314/2023 dated 24/05/2023