UNIVERSITÀ DEGLI STUDI DI UDINE

Advanced Oxidation Processes For The Treatment of Liquid Wastes

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PhD Course : Environemntal and Energy Engineering Science

Cycle : XXXIII

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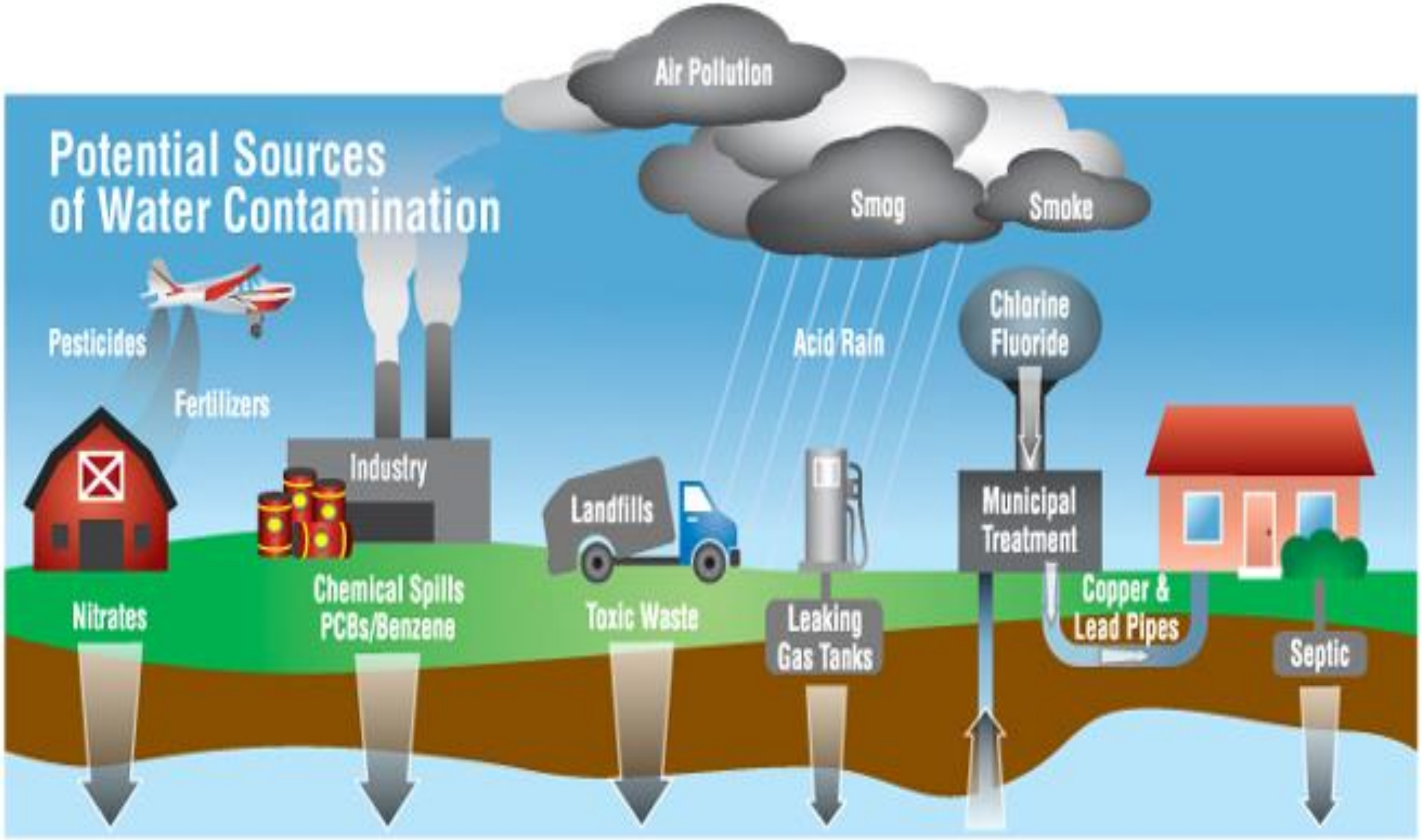
Water Contaminants

1- Organics

2- Inorganics



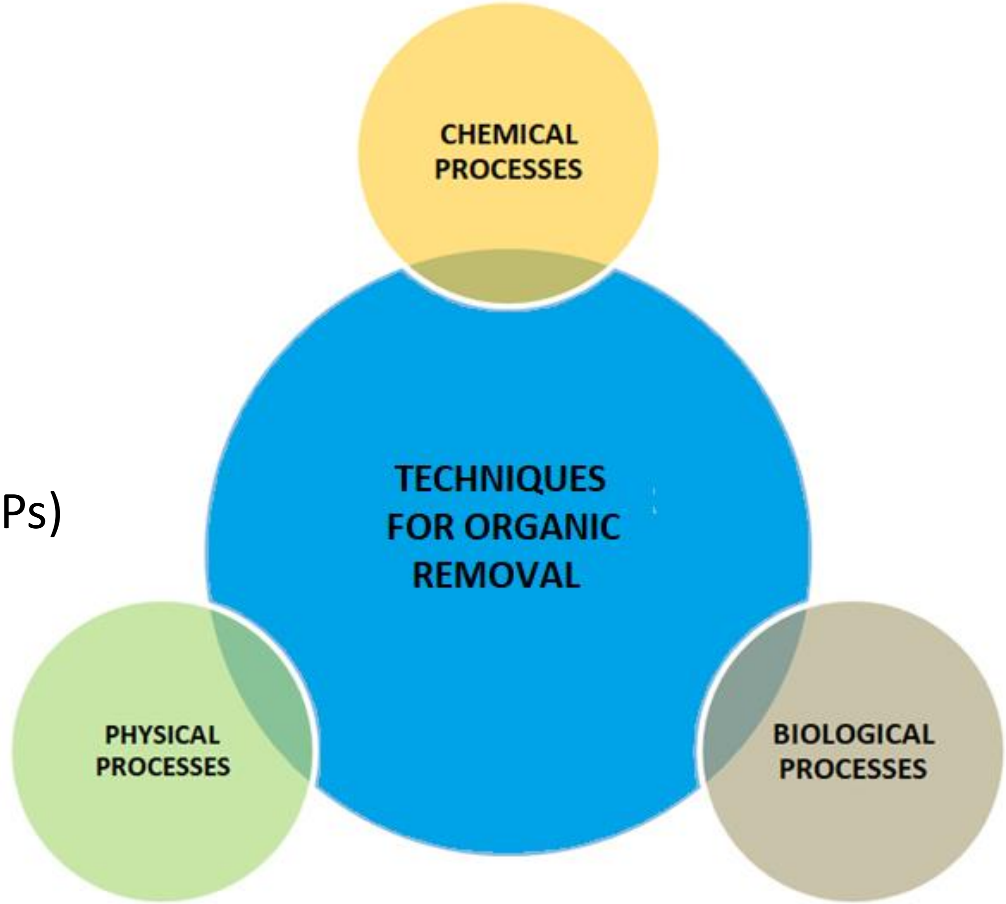
https://www.waterwise.com/think-before-you-drink/

REMOVAL OF ORGANICS

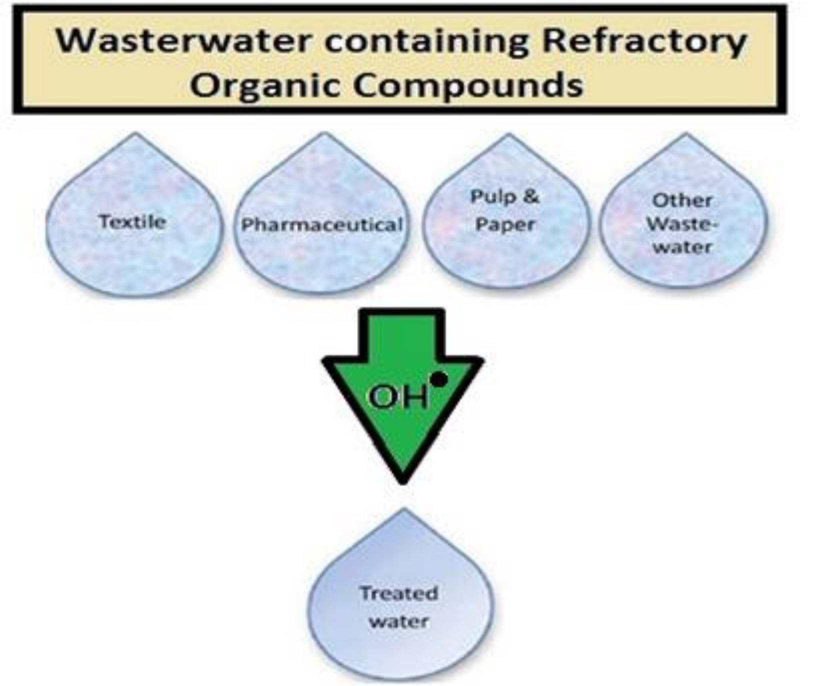
1- Physical Processes
Filtration, Air Stripping, Adsorption

2- Biological Processes
Activated Sludge Process

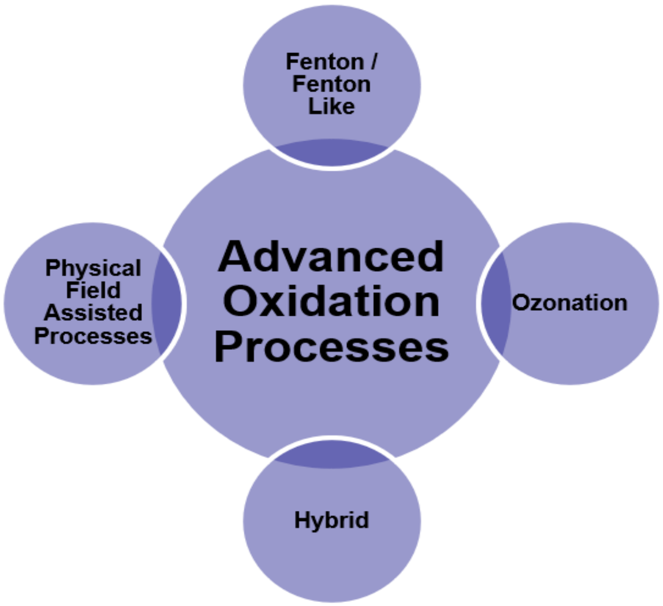
3- Chemical Processes
Advanced Oxidation Processes (AOPs)



ADVANCED OXIDATION PROCESSES



Advanced Oxidation Processes (AOPs): Chemical processes in which organic pollutants are abated by Hydroxyl Radicals (OH•).



FENTON PROCESS

Homogeneous Phase Reaction

$$Fe^{+2} + H_2O_2 = Fe^{+3} + OH^{\bullet} + OH^{-}$$

FENTON LIKE PROCESS

Heterogeneous Phase Rection

Cu / Zr Catalysts at 70 °C

RESEARCH OBJECTIVES

To Develop AOPs / Heterogeneous Fenton Like

Efficient

- Maximum organic abatement
- Organic mineralization into H_2O & CO_2
- Organic degradation into less toxic metabolites

Feasible

- Diverse Liquid Wastes
- Highly Polluted Wastewaters
  Landfill Leachate
- Industrial Effluents

Sustainable

- Scalable
- Cost Effective
- Environment Friendly

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STEP BY STEP PROGRESS OF THE PROJECT

Phase-I Catalyst Selection over model pollutant	Fe, Cu, Ag, and Ce based catalysts	Activity / Mineralization	Activity / Degradation of Ibuprofen
Phase-II Process Optimization & Treatment of Real Liquid Waste	pH, oxidant dose, catalyst dose, temperature.	Activity of Recycled Catalyst	Treatment of landfill leachate (Site I)
Phase-III Activity Enhancement of the Catalysts	Monometallic catalysts (5-10%)/Cu(or Fe)/ZrO_2	Bimetallic catalysts Cu+Fe/ZrO_2 with variable ratio	Minimal deactivation and catalyst loss
Phase-IV Waste for the Treatment of Waste	Iron slag particle sizing	Treatment of landfill leachate (Site II)	Activity analysis / Mineralization

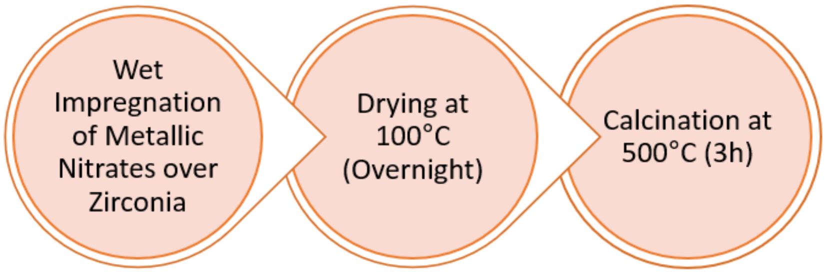
MATERIALS AND METHODS

❑ Materials

Metallic Nitrates of Cu, Fe and Sr	Zirconium Hydroxide	H_2O_2 (3 - 30%)
Ibuprofen Sodium Salt (IBP)	Landfill Leachate (Site I and Site II)	Iron Slag (Waste from Steel Industry)

❑ Methods

- **Catalyst Preparation**



- **Fenton Like Oxidation**

Fenton-like reactions were performed by means of Omni Reaction Station with continuous stirring and reflux, on 100 ml of samples investigating several variables:

pH (3-8), temperature (25-90 ºC),
catalyst dose (0.1-2 g/l), H_2O_2 dose (10-40 ml/l)
time (30-150 min)

MATERIALS AND METHODS

❑ Catalyst characterization

- **XRD** — X-ray diffraction
- **BET** — Surface area
- **H_2-TPR** — Temperature programmed reduction

❑ Catalytic activity

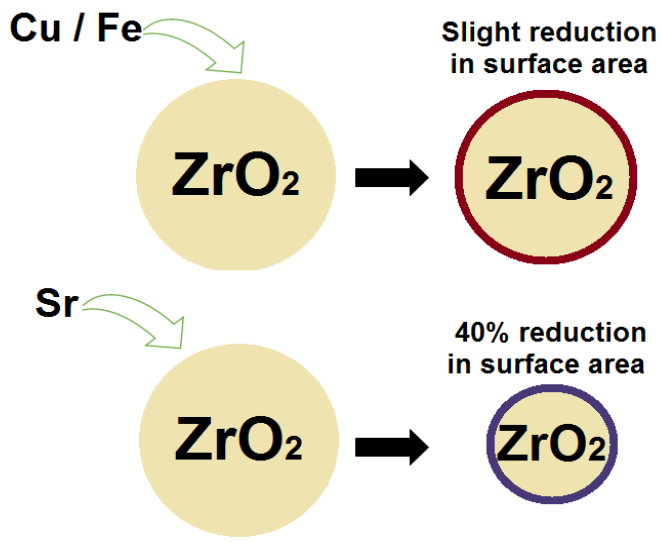
Mineralization
- **TOC** — Total organic carbon
- **COD** — Chemical oxygen demand

Indirect determination of organic matter

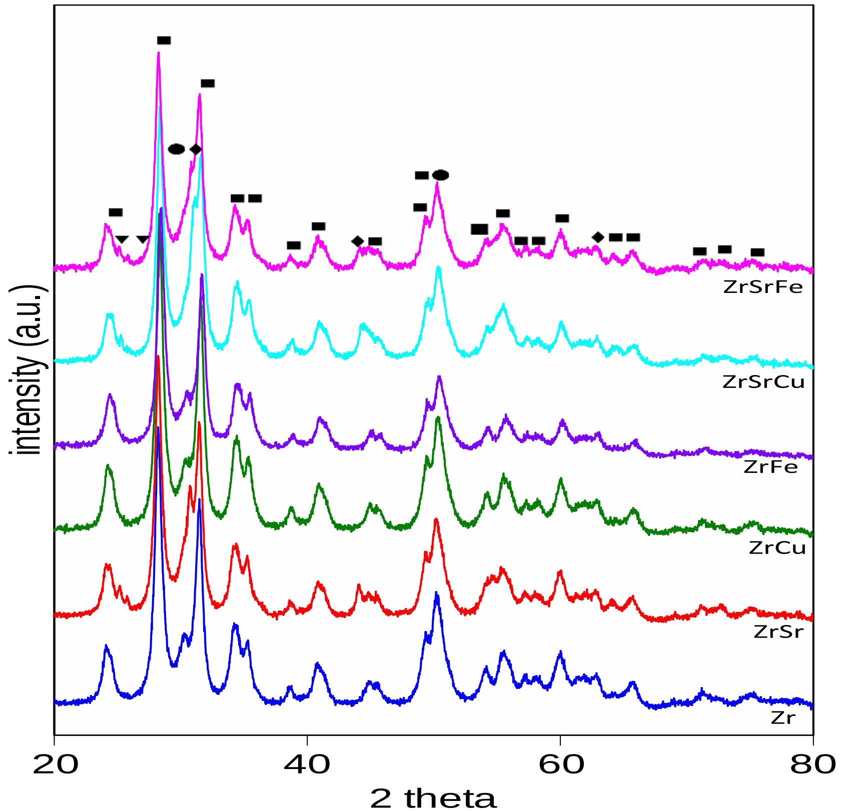
Degradation
- **HPLC MS** — High performance liquid chromatography-mass spectrometry
- **ICP** — Inductively coupled plasma
- **UV-Vis** — Ultraviolet–visible spectroscopy
- **NMR** — Nuclear Magnetic Resonance Spectroscopy

CATALYSTS CHARACTERIZATION

Catalysts: Cu(5%)/ZrO_2; Fe(5%)/ZrO_2; Cu(5%)-Sr(10%)/ZrO_2; Fe(5%)-Sr(10%)/ZrO_2



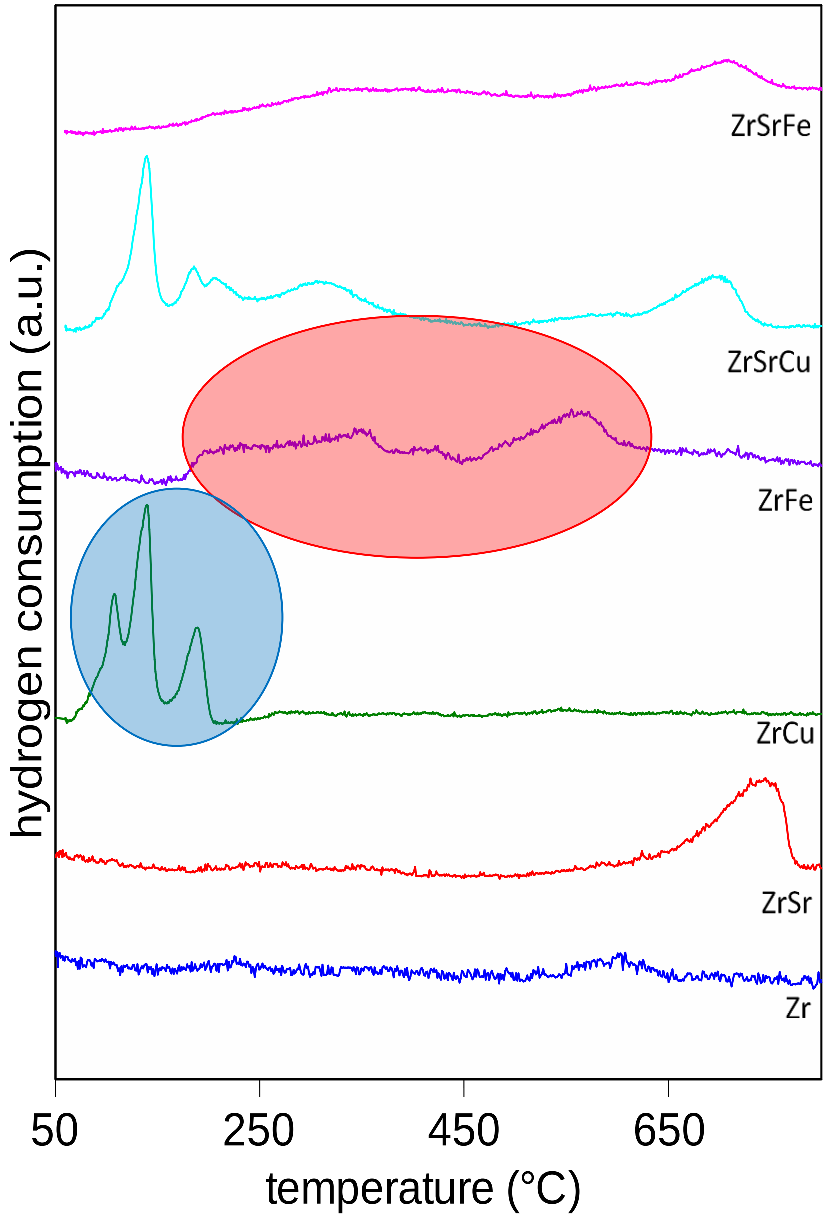
Sample	Composition	Surface Area (m^2/g)
Zr	ZrO_2	64
ZrCu	Cu(5%)/ZrO_2	55
ZrFe	Fe(5%)/ZrO_2	53
ZrSr	Sr(10%)/ZrO_2	40
ZrSrCu	Cu(5%)-Sr(10%)/ZrO_2	36
ZrSrFe	Fe(5%)-Sr(10%)/ZrO_2	35



Simultaneous presence of tetragonal (●) and monoclinic (■) ZrO_2.

No evidence for any copper or iron phase was found suggesting that Fe or Cu are homogeneously dispersed on the surface.

CATALYSTS CHARACTERIZATION

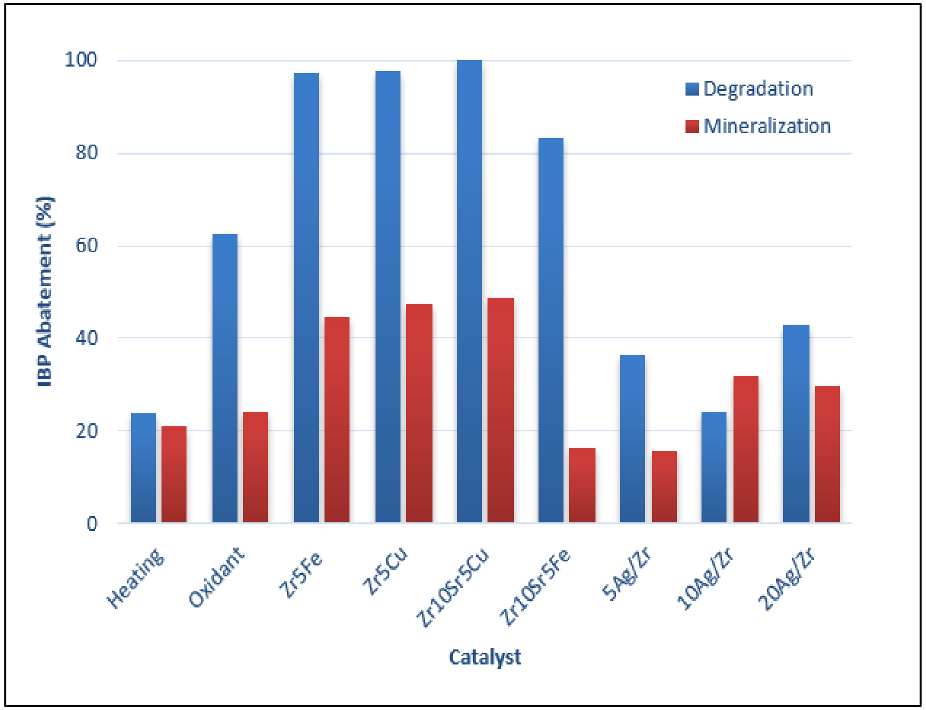


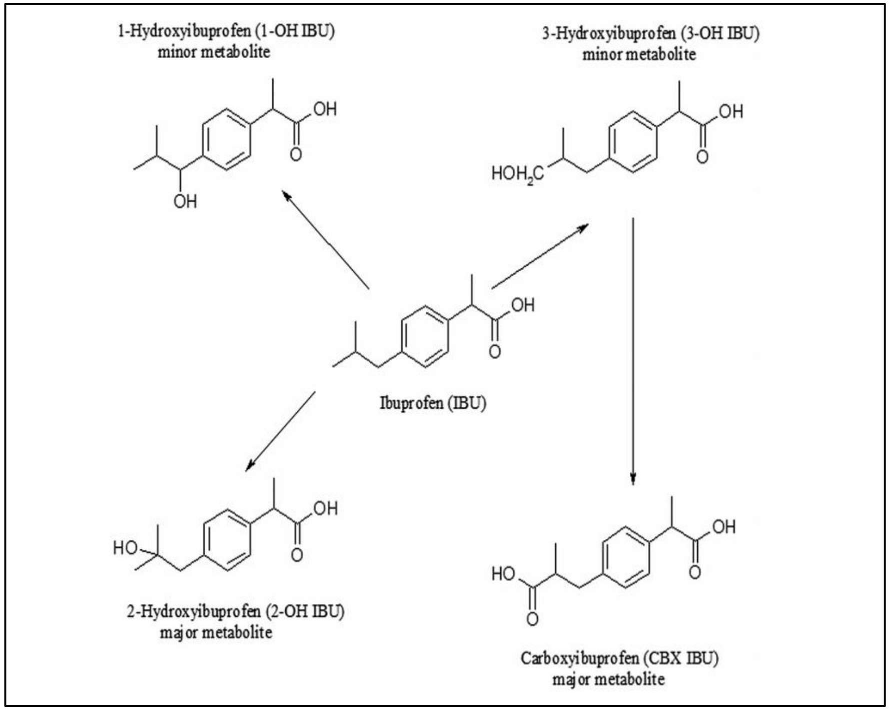
Peaks at 250-350 and 550 ºC could be correlated to the existence of free Fe_2O_3 on the zirconia surface

Peak at 190 ºC: reduction of crystalline CuO.
Peaks at 110 and 140 ºC: reduction in two steps of highly dispersed Cu^{2+} to Cu^0.

PHASE-I: SELECTION OF ACTIVE CATALYSTS

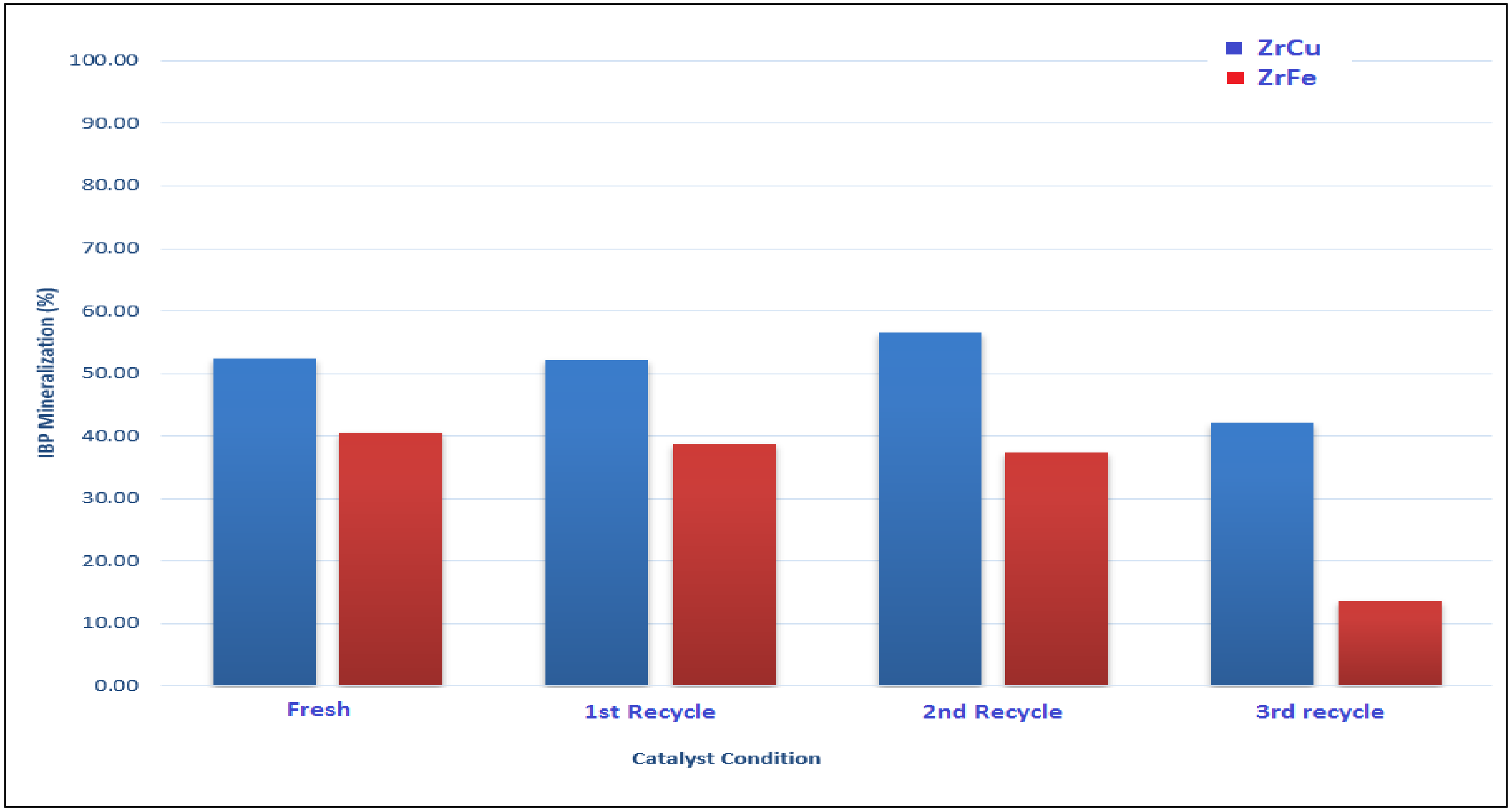
- Fenton like oxidation was performed using aqueous solutions of model pollutant ibuprofen (10 mg/l).
- ZrFe, ZrCu and ZrSrCu showed ~50% IBP **mineralization** (TOC analysis).
- These catalysts showed ~100% IBP **degradation** (HPLC-MS analysis).
- However, ZrSrCu produced toxic metabolites (HPLC-MS analysis).





PHASE-I: SELECTION OF ACTIVE CATALYSTS

ZrCu showed stable activities after three recycles while ZrFe showed stable activates until two recycles while in 3rd recycle the activity is diminished sharply.



PHASE-I: SELECTION OF ACTIVE CATALYSTS

ZrCu is a very active catalyst.

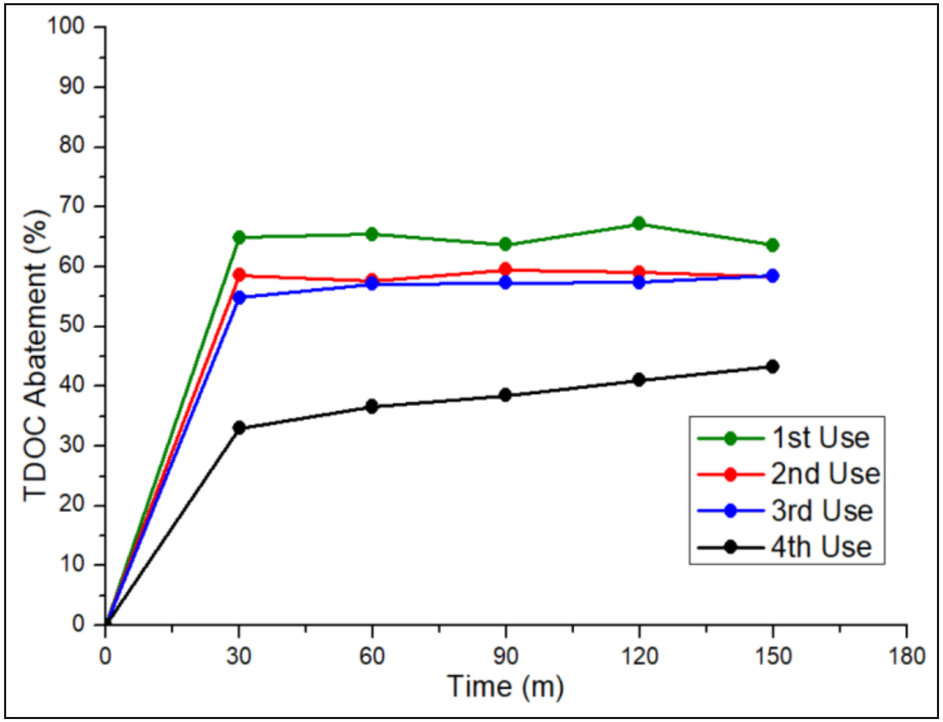
IBP amount (mg/L)	H_2O_2 dose (mM)	Catalyst dose* (mg/L)	Catalyst	Reaction	T (° C)	pH	Degradation (%)	Mineralization (%)	Ref
10	24,5	12,5	Cu/ZrO_2	Het.	70	5	100	53	This study
20	6,4	7,5	$FeSO_4$	Hom.+US	25	2,6	100	40	[69]
20	6,4	7,5	$FeSO_4$	Hom.	25	2,6	100	10	[69]
10	10	50	γ-Cu–Al_2O_3	Het.	r.t.	7	98	63	[83]
10	24,5	12,5	Fe/ZrO_2	Het.	70	5#	97	40	This study
50	3,5	430	$FeSO_4$	Hom.+UV	r.t.	-	93	90	[84]
20	6,4	163	Fe-MFI zeolite	Het.	25	3,3#	88	27	[87]
10	/	5	$FeSO_4$	Hom.+O_3	r.t.	6,5	85	3	[88]
10	/	5	Fe(OH)O goethite	Het.+O_3	r.t.	6,5	80	30	[88]
180	0,32	67	$FeSO_4$	Hom.+UV	30	6,25	80	40	[85]
60	8,9	25,2	$FeSO_4$	Hom.	20	3	80	15	[86]
50	/	5	Zervo valent iron	Het. O_3	r.t.	6,5	79	41	[88]
180	0,32	67	$FeSO_4$	Hom.	30	6,25	60	10	[85]

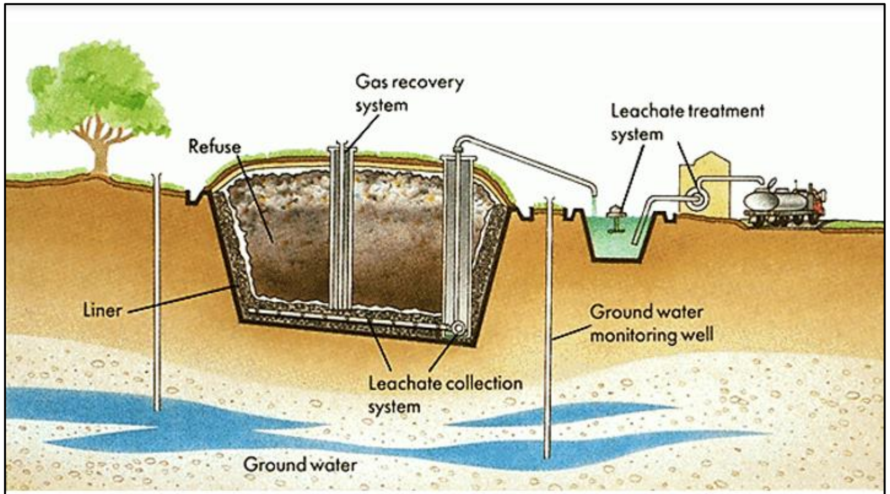
PHASE-II:TREATMENT OF LEACHATE

❑ Process optimization

Heterogeneous Fenton like process is optimized using IBP solutions at following conditions:

- pH- 5.5,
- catalyst dose (0.2 g/l) ,
- H_2O_2 dose (30 ml/l),
- temperature (70 ºC)
- 150 minutes.





Landfill site and leachate recovery and treatment system

❑ Treatment of landfill leachate

"Landfill leachate is a complex liquid waste produced when rainwater runs through the landfill site and is a very toxic and recalcitrant waste".

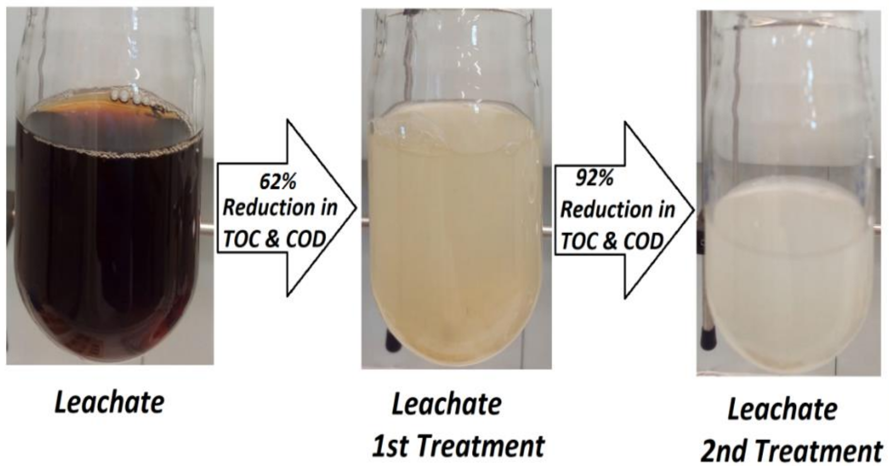
Landfill leachate is treated by applying optimal conditions of Fenton like process.

- TOC Reduction: 62%
- COD Reduction: 70%

http://www.oocities.org/green_juris/landfil.html

PHASE-II:TREATMENT OF LEACHATE

Two step oxidation is carried out to assess the catalyst ability to further increase the organic abatement.



Two step oxidation with measured abatements

Table 2: Characteristics of landfill leachate before and after Fenton like oxidation

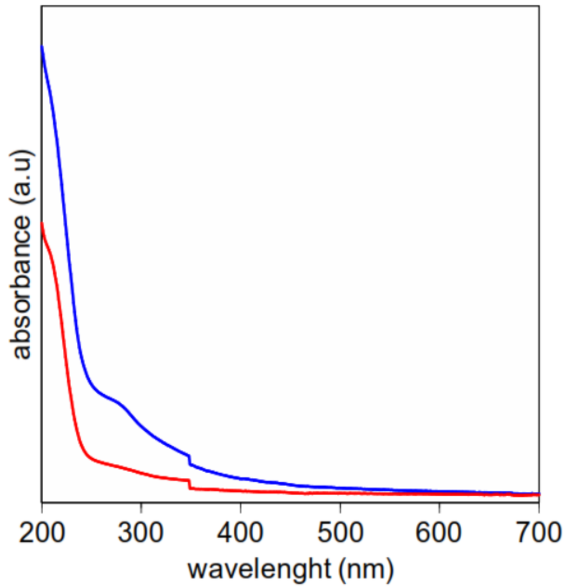
Parameters	Before Treatment (mg/L)	After Treatment (mg/L)	Removal Efficiency (%)
COD (Single Treatment)	8700	2610	70
TOC (Single Treatment)	970	368	62
AOX	13	4.8	63.07
Total Nitrogen (TN)	1.94 g/L	1.86 g/L	4.12
Color	Dark brown	Light Yellow	-----
Al	5	0.3	94
Ca	38.2	37.5	1.83
Cr	0.7	0.6	14.29
Fe	2.7	0.1	96.3
Mn	0.1	0	100
Mg	55.8	50.3	9.86
Ni	0.4	0.3	25
Zn	0.3	0.1	66.6

The process also removed 63% of adsorbable organic halogens (AOX).

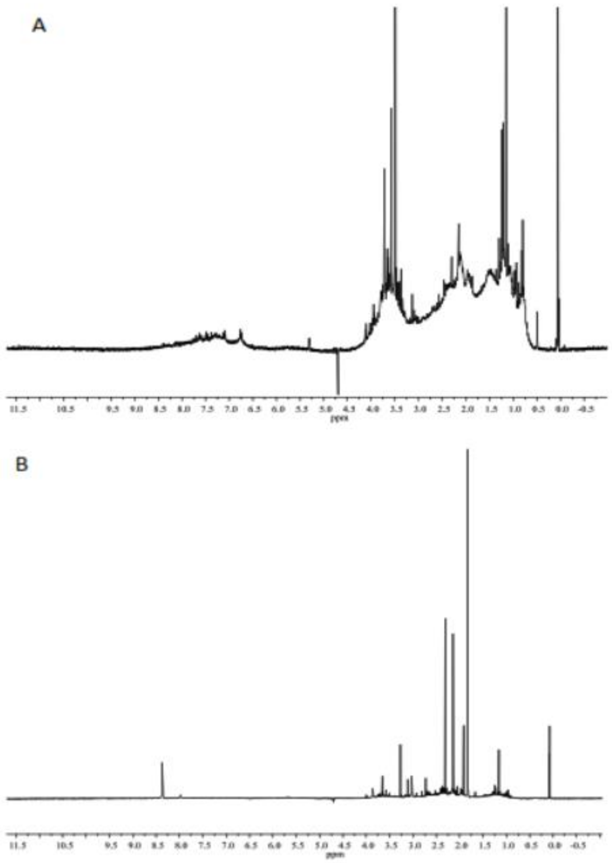
PHASE-II: TREATMENT OF LEACHATE

Qualitative monitoring of organic abatement

The **UV-Vis** and **H1 NMR** analysis indicates that specific organic compounds especially aromatic compounds have been eliminated after Fenton like oxidation.



UV-Vis spectrum of leachate before (blue line) and after treatment (red line)

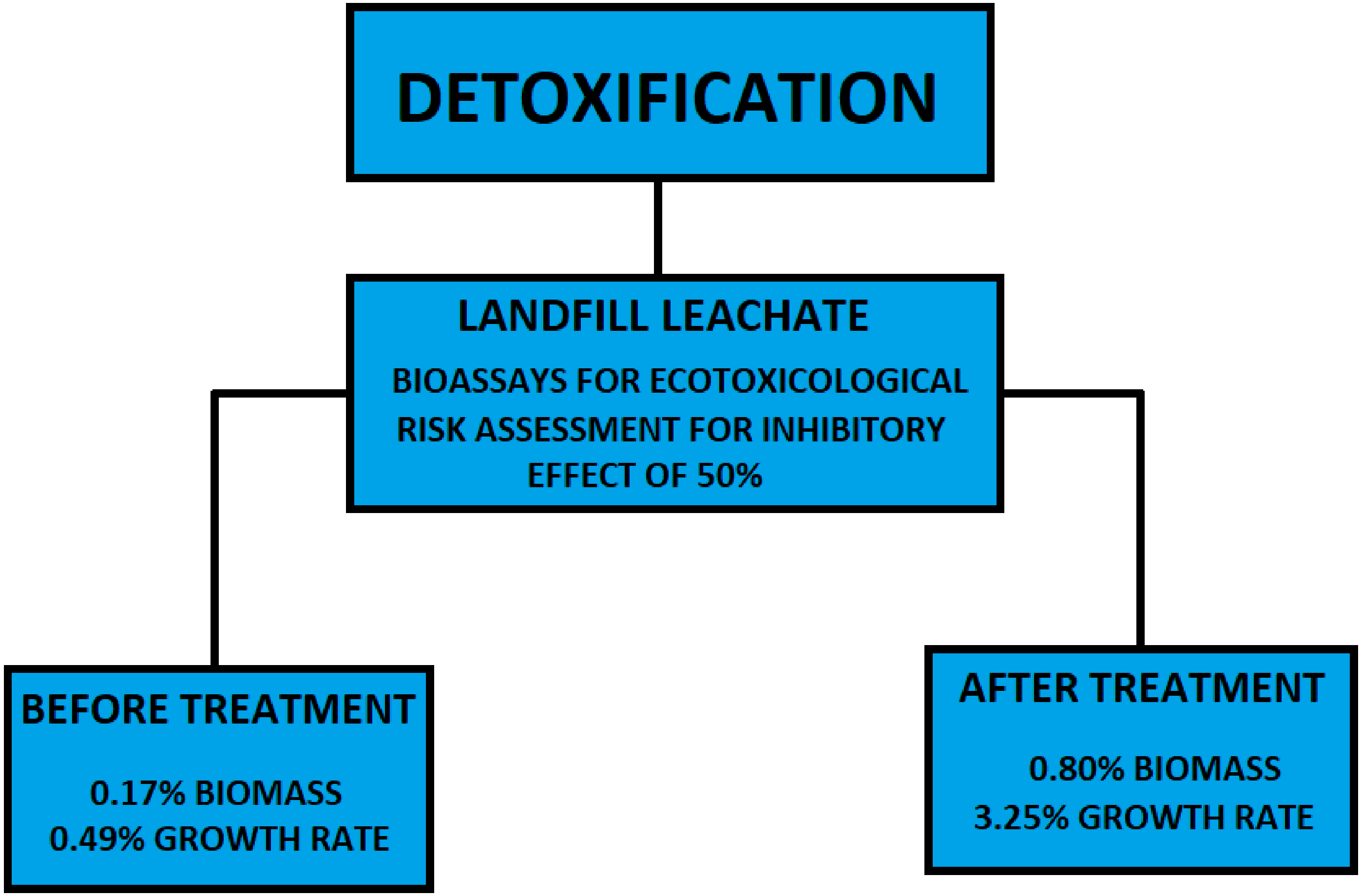


[1]H NMR spectrum of landfill leachate before (A) and after (B) Fenton treatment.

PHASE-II: TREATMENT OF LEACHATE

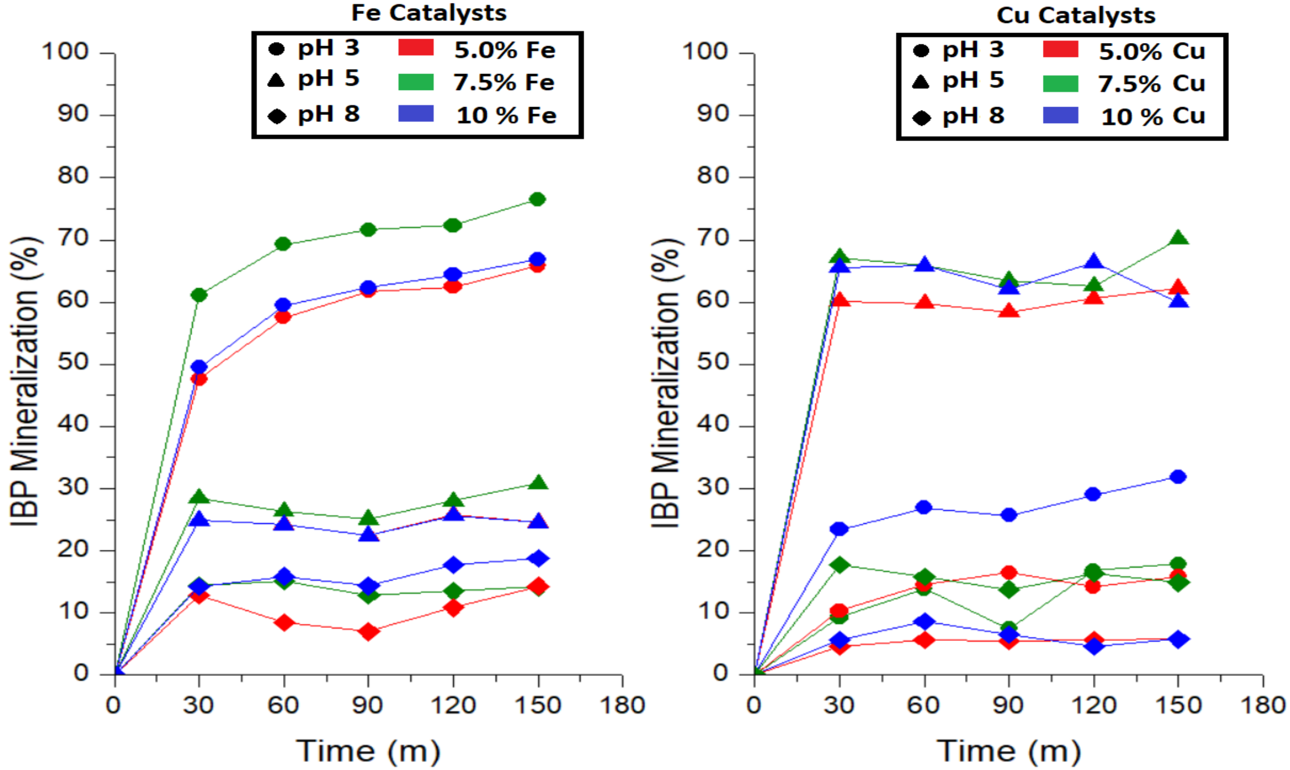
Toxicity Analysis

Bioassays – Direct toxicity measure

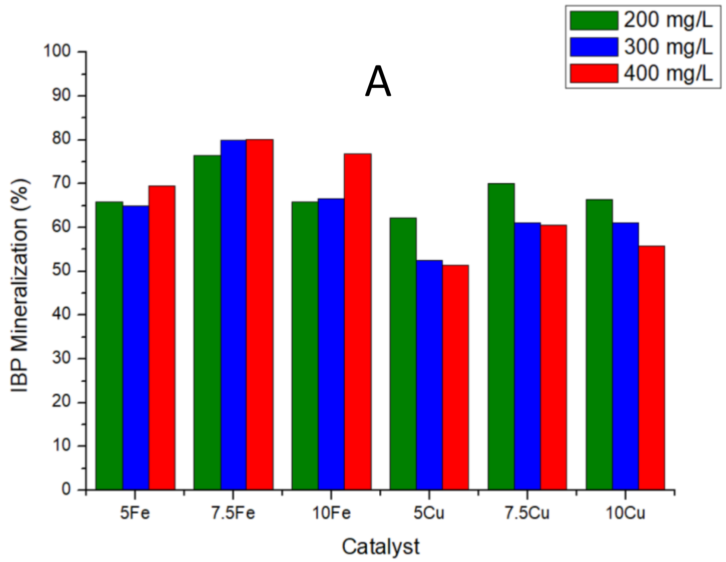


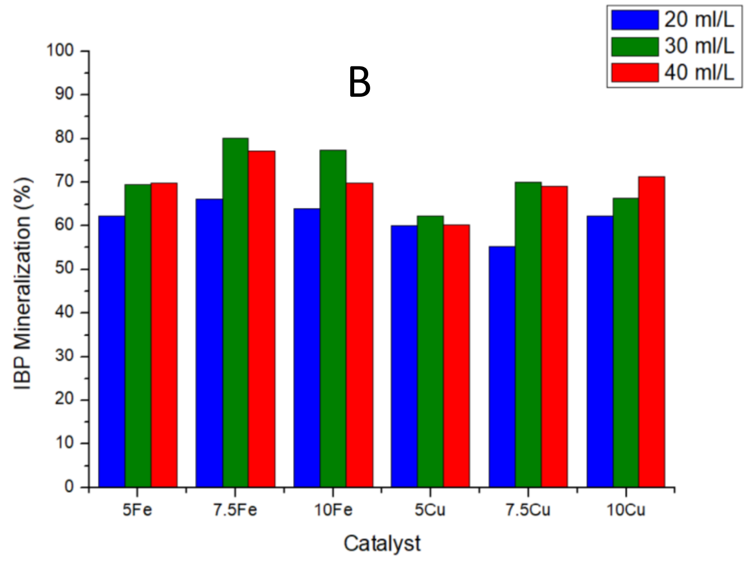
PHASE-III: ENHANCEMENT OF ACTIVITIES

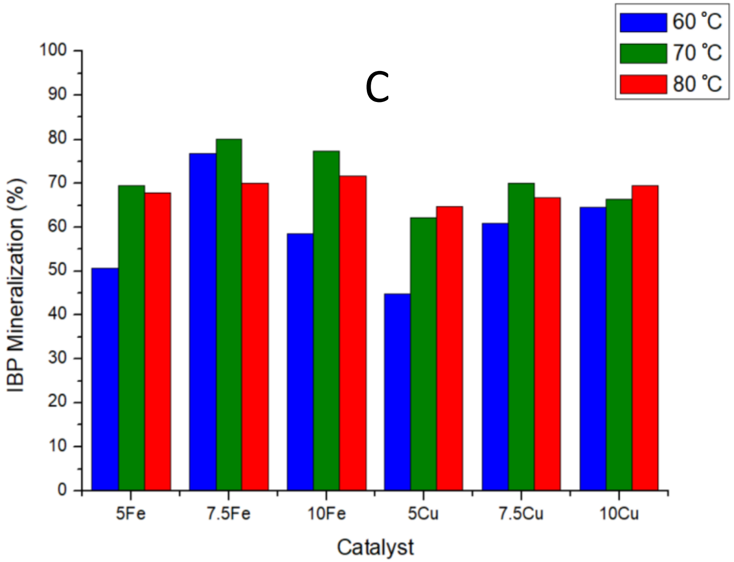
- **Monometallic catalysts (**5-10%Cu (or Fe)/ZrO_2**)**
- Cu/Zr catalysts afford maximum activty at pH 5 while Fe/Zr catalysts yield better activities at pH-3.
- The optimal loading of Cu and Fe over zirconia is 7.5%.
- The optimal reaction dose for Cu based catalysts is 200 mg/L while for Fe based catalyst 400 mg/L.
- The catalytic performance of Fe catalysts is slightly higher than that of Cu catalysts.

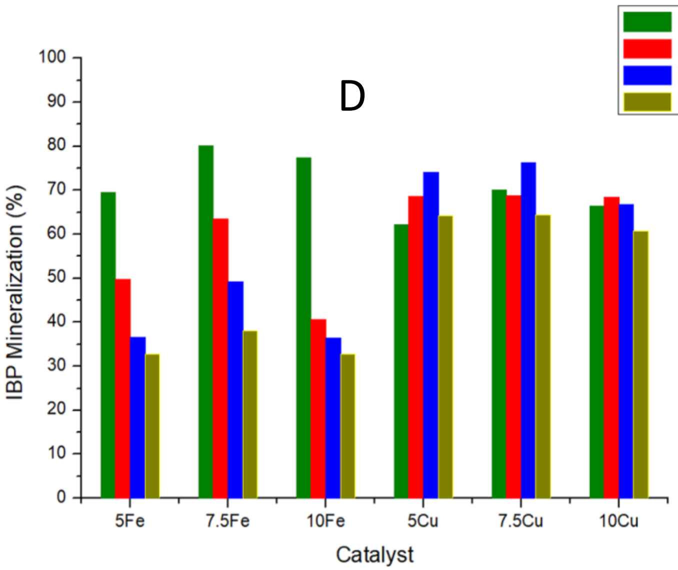


PHASE-III: ENHANCEMENT OF ACTIVITIES



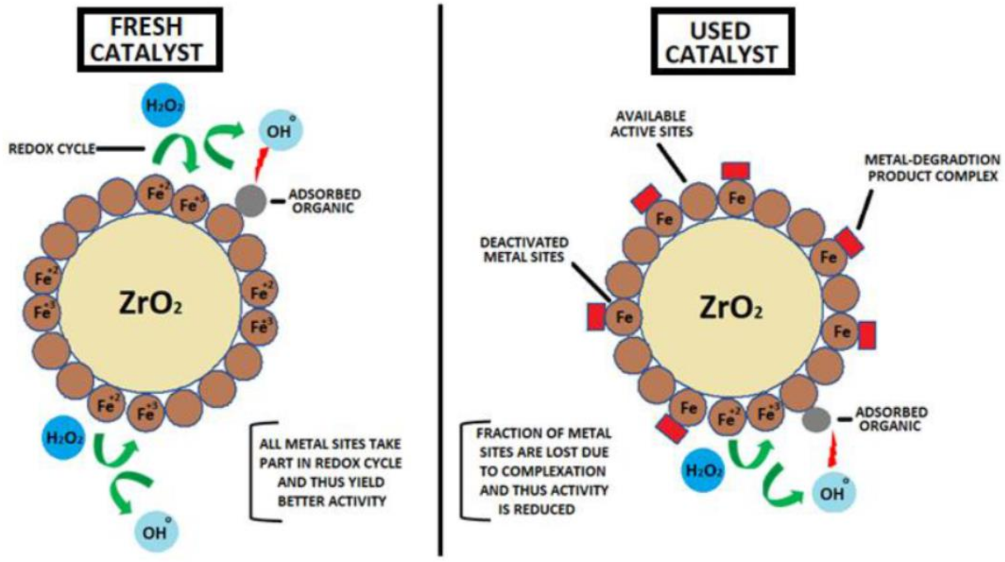




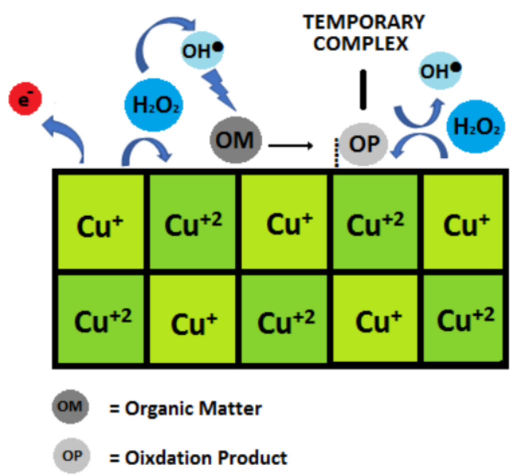


PHASE-III: ENHANCEMENT OF ACTIVITIES

- Iron based catalysts form stable complexes with degradation products
- Copper based catalysts form temporary complexes with degradation products.



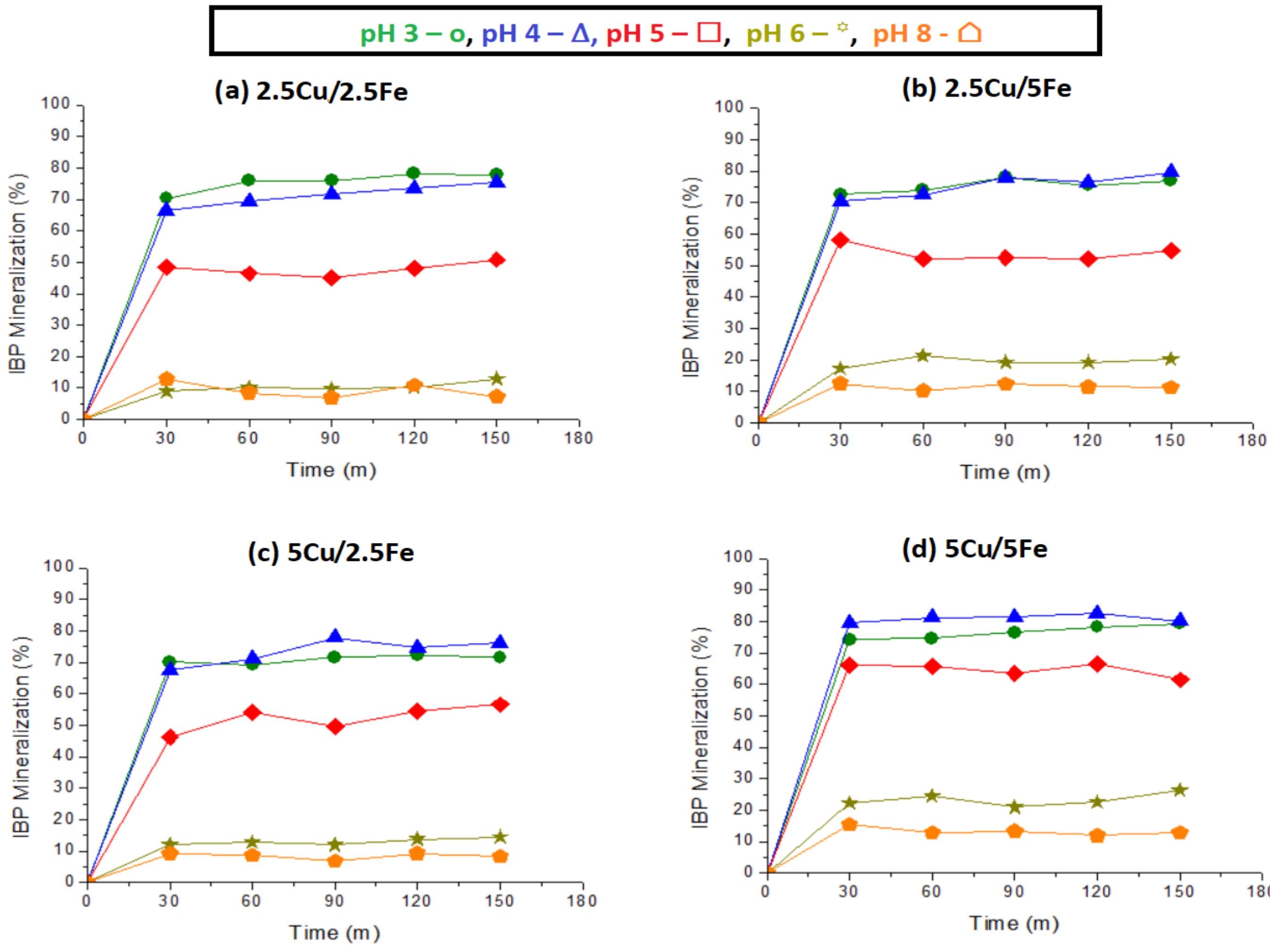
Representation of catalytic activities of fresh and used iron catalysts in heterogeneous Fenton process



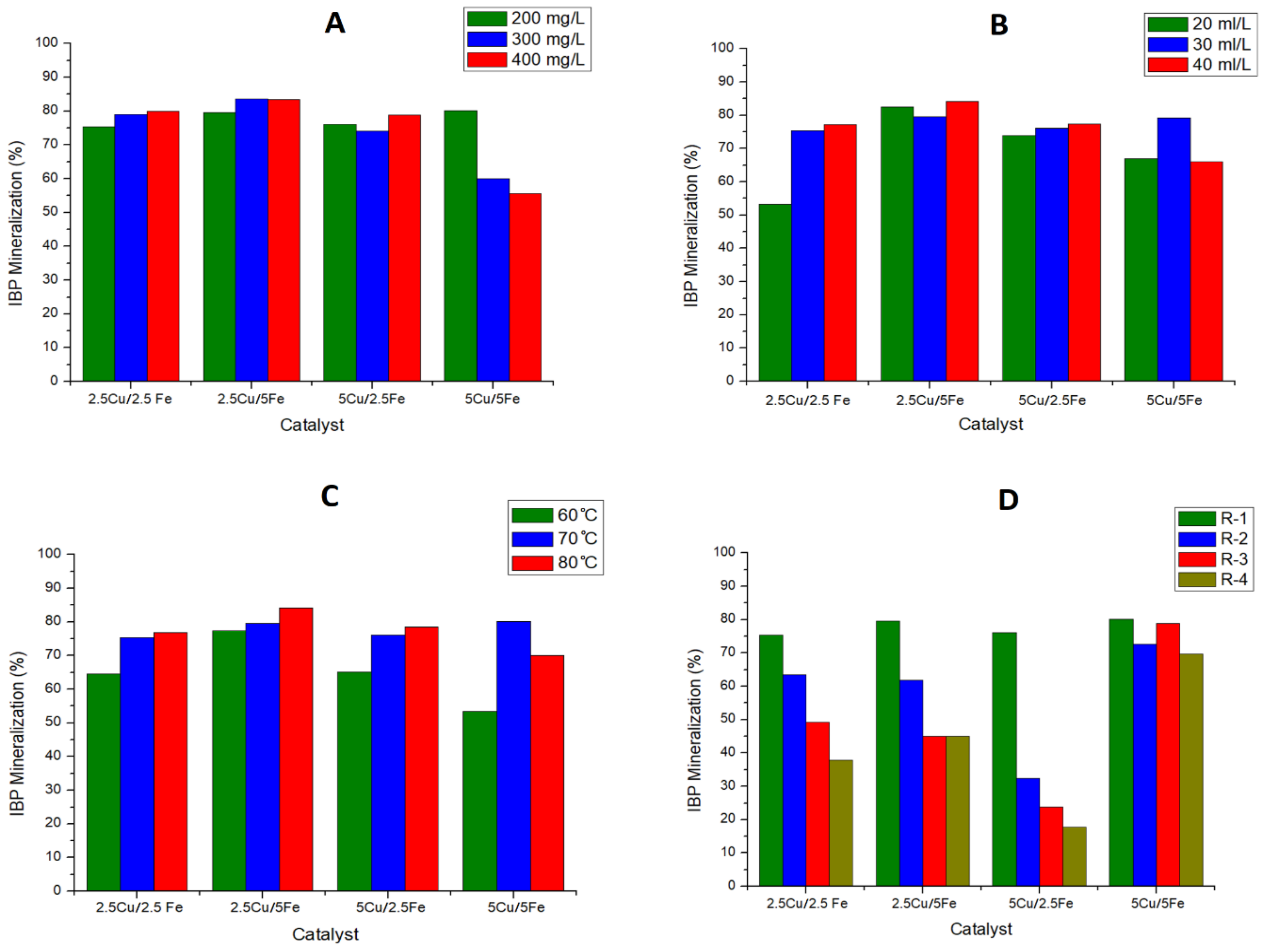
Complex formation of copper with oxidation products.

PHASE-III: ENHANCEMENT OF ACTIVITIES

- **Bimetallic catalysts** (2.5Cu5Fe, 2.5Cu2.5Fe, 5Cu2.5Fe and 5Cu5Fe)/ZrO_2.
- 2.5Cu5Fe and 5Cu5Fe afford maximum activty at pH-4 while 2.5Cu2.5Fe, 5Cu2.5Fe yield better activities at pH-3.
- Catalytic activities of all catalysts at optimal conditions are almost the same (~80%).

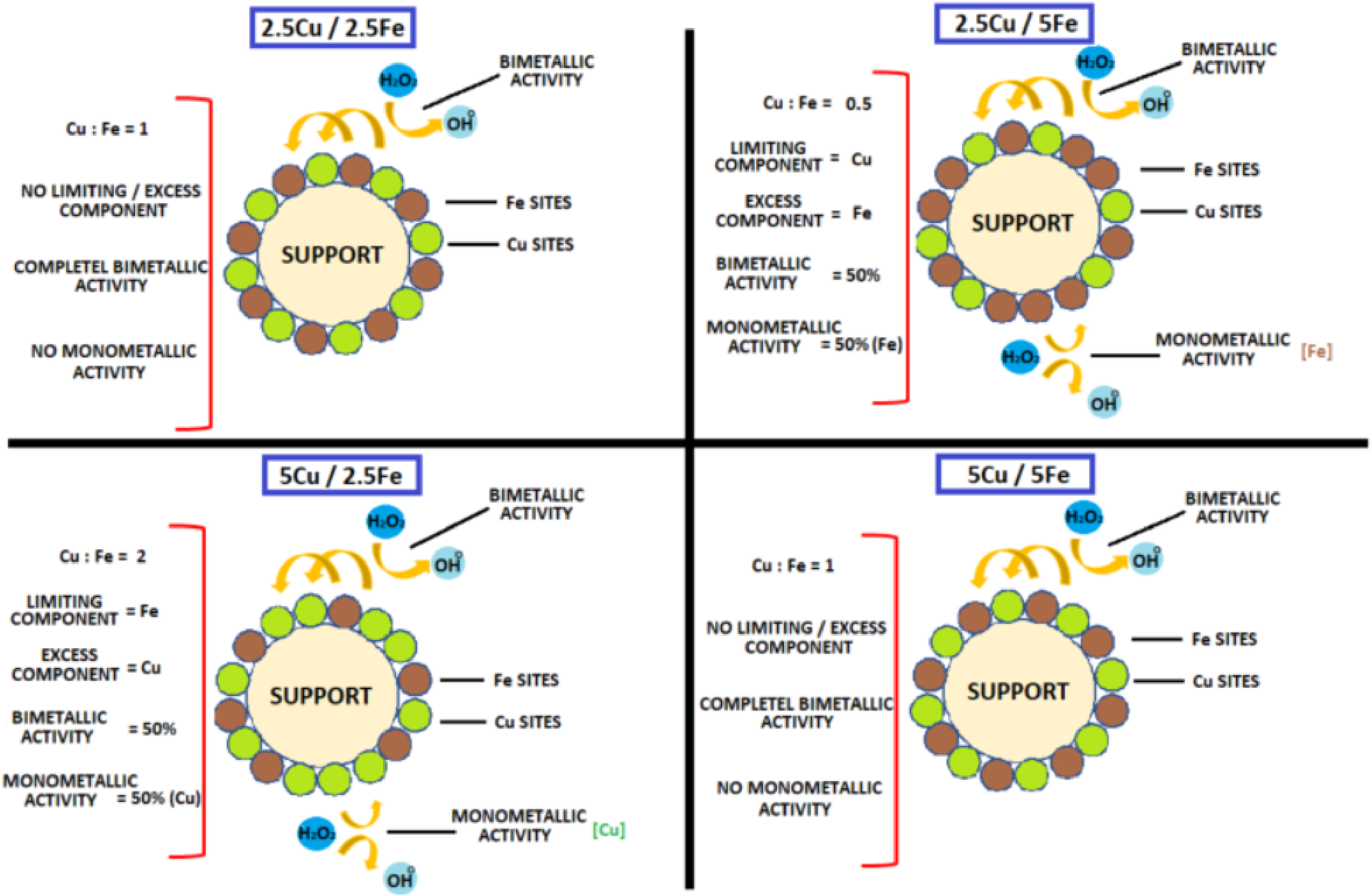


PHASE-III: ENHANCEMENT OF ACTIVITIES



PHASE-III: ENHANCEMENT OF ACTIVITIES

Cu : Fe determines the extent of bimetallic and monometallic activity of the catalyst composites

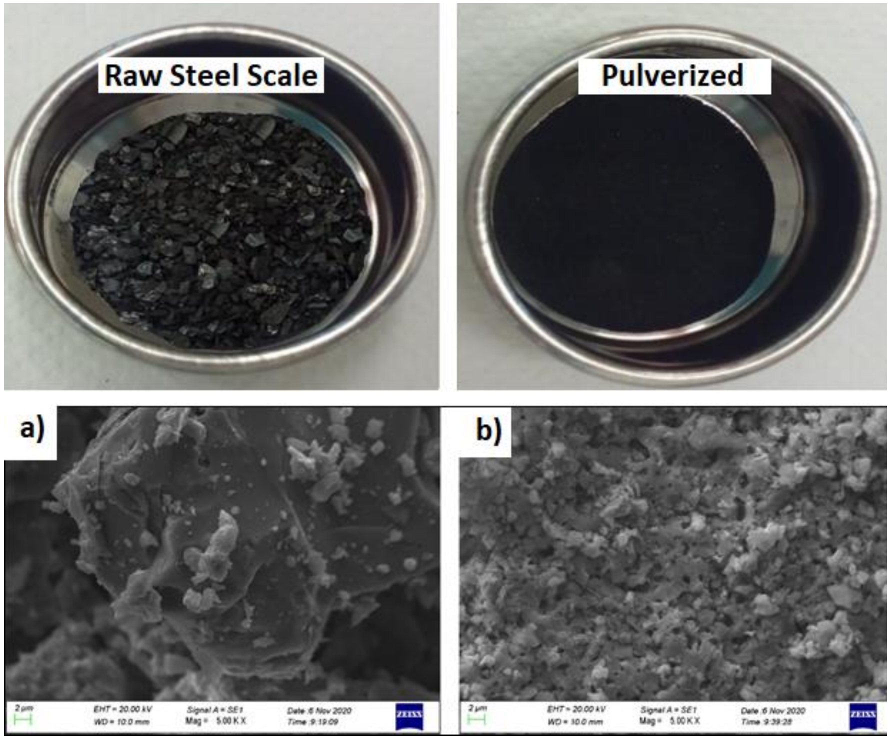


The extent of bimetallic and monometallic catalytic activity of the employed catalysts

PHASE-IV: IRON SLAG CATALYST

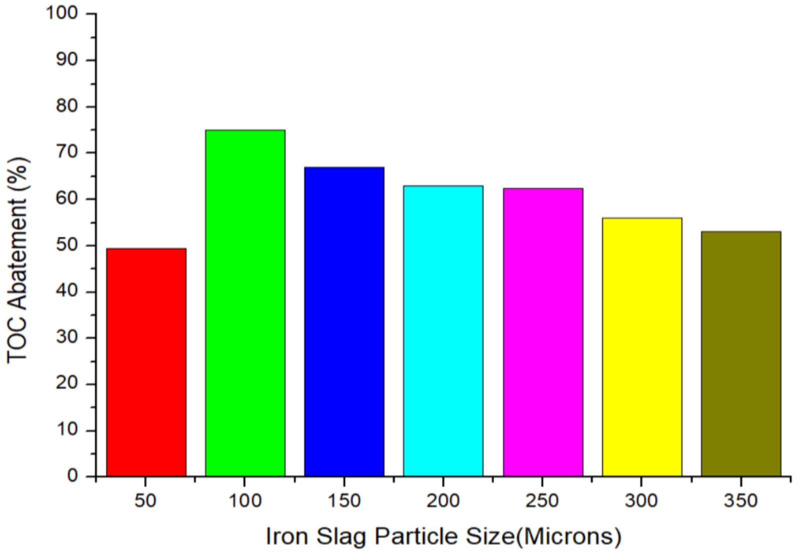
We used a **waste for the treatment of liquid waste** (circular economy).
Iron slag is the waste material of steel industry and is mainly composed of Iron and carbon with trace amounts of other metals / metal oxides.

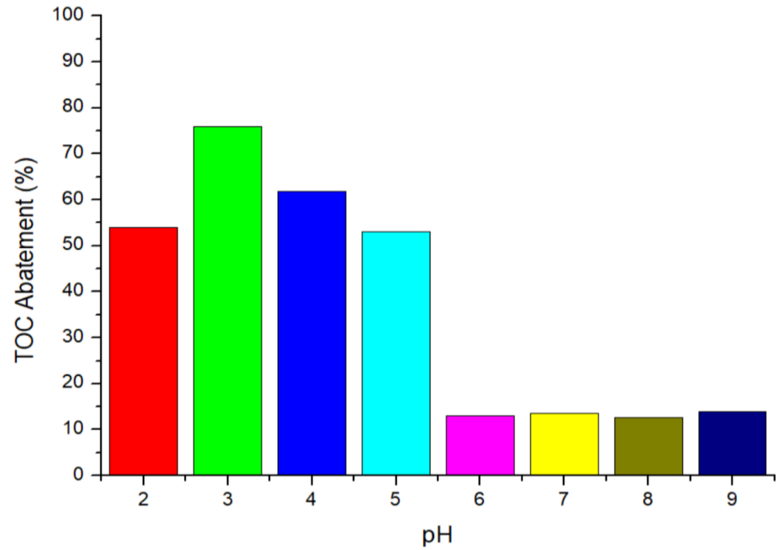

Iron Slag (Waste Material of Steel Industry)

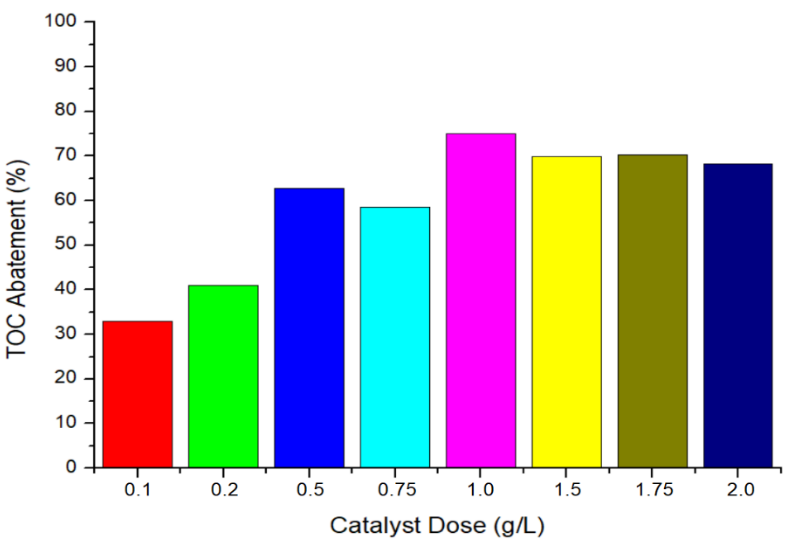


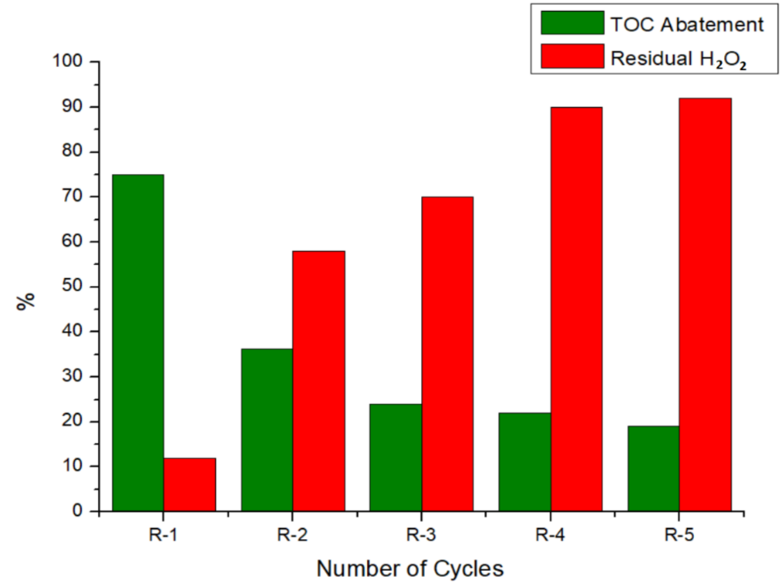
- Iron slag is grinded to obtain seven different particle sizes.
- The Fenton like process is optimized using ibuprofen solutions at pH-3, catalyst dose - 1g/l, H_2O_2 dose – 40 ml/l, particle size – 100 micron and temperature – 70 ºC.

PHASE-IV: IRON SLAG CATALYST









CONCLUSIONS

1. Cu based catalysts: Afford high organic abatement (98% degradation and 65-70% mineralization). Effective for the treatment of synthetic and real liquid wastes. Detoxify the treated effluent (50-63%).

2. Unlike other catalysts, the Cu/ZrO_2 catalysts yield maximum activity under mild acidic to near neutral conditions, reducing the chemical costs and likelihood of metallic leaching.

3. The optimal loading of Cu (7.5%) over ZrO_2 not only increases the catalytic activity but also enhances its stability.

4. The bimetallic catalysts bearing proportionate amounts of Cu and Fe i.e. 5Cu-5Fe not only result in higher organic abatement but also prevent the formation of stable complexes with Fe sites in the catalyst.

5. Iron slag has very high potential as heterogeneous Fenton catalyst for the treatment of liquid wastes to achieve the goal of sustainable circular economy.

FUTURE PERSPECTIVES

1. Increment of the surface area of the Cu-supported catalysts using high surface area supports.

2. Preparation of bimetallic catalysts by putting together copper and other suitable heavy metals which do not form stable complexes with organics.

3. Scaling up the heterogeneous Fenton like process.

4. Employment of other available solid waste materials as heterogenous catalysts.

5. Application of innovative techniques for the preparation of highly active and stable catalytic materials for Fenton like process.

PARTNERSHIPS & COLLABORATIONS

- Mario Negri Institute for Pharmacological Research – IRCCS Milan, Italy

ISTITUTO DI RICERCHE FARMACOLOGICHE MARIO NEGRI · IRCCS

- ARPA-FVG: Regional Agency for the Protection of the Environment

arpa FVG
agenzia regionale per la protezione dell'ambiente del Friuli Venezia Giulia

SCIENTIFIC PUBLICATIONS

1- Enhanced ibuprofen removal by heterogeneous-Fenton process over Cu/ZrO_2 and Fe/ZrO_2 catalysts
Sajid Hussain, Eleonora Aneggi, Sara Briguglio, Michele Mattiussi, Vito Gelao, Igino Cabras, Luciano Zorzenon, Alessandro Trovarelli, Daniele Goi
Journal of Environmental Chemical Engineering: Published (https://doi.org/10.1016/j.jece.2019.103586)

2- Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review
Sajid Hussain, Eleonora Aneggi, Daniele Goi
Environmental Chemistry Letters: Published (https://doi.org/10.1007/s10311-021-01185-z)

3- Application of Steel scale waste as a heterogeneous Fenton like catalyst for the treatment of landfill leachate
Sajid Hussain, Eleonora Aneggi, Stefano Maschio, Marco Contin, Daniele Goi
Industrial & Engineering Chemistry Research: (Minor Revision requested by the Editor)

4- Iron and copper-based catalysts for Fenton-like oxidation of ibuprofen
Sajid Hussain, Eleonora Aneggi, Alessandro Trovarelli, Daniele Goi
Journal of Water Process Engineering: ((Minor Revision requested by the Editor (Submitted and Under Review))

5- Treatment of landfill leachate through heterogeneous Fenton like oxidation using copper supported over zirconia and qualitative monitoring of the organic abatement with 1H NMR spectroscopy
Sajid Hussain, Eleonora Aneggi, Clara Comuzzi, Diego Baderna, Daniele Goi
Journal of Environmental Management: (Under Review)

6- Iron and copper-based bimetallic catalysts for Fenton-like oxidation of ibuprofen
Sajid Hussain, Eleonora Aneggi, Alessandro Trovarelli, Daniele Goi
To be Submitted

7- Heterogeneous-Fenton Process Over Cu/ZrO_2 For Enhanced Liquid Waste Treatment
Sajid Hussain, Eleonora Aneggi, Daniele Goi
SIDISA 2021 – XI International Symposium On Environmental Engineering, Turin, Italy: (Oral presentation (Presented: 1 July 2021))

8- Liquid waste treatment by Fenton-like process over copper-based catalyst
Sajid Hussain, Eleonora Aneggi, Daniele Goi
5th IWA Conference, Milan, Italy: ((Poster Presentation (Presented: 24 June 2021))

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3- Prof. Marco Contin, Dr. Diego Baderna, Prof. Clara Comuzzi and Prof. Stefano Maschio.

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5- Aldo Bertoni, Pierluigi Polese, Dr. Rosario Figliolia.

6- All the people who have been of any help to me in University of Udine.

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