Hydrothermal dechlorination of polyvinyl chloride for chemical recycling

The single and interactive effect of nickel and iron on urea-assisted hydrothermal treatment of polyvinyl chloride

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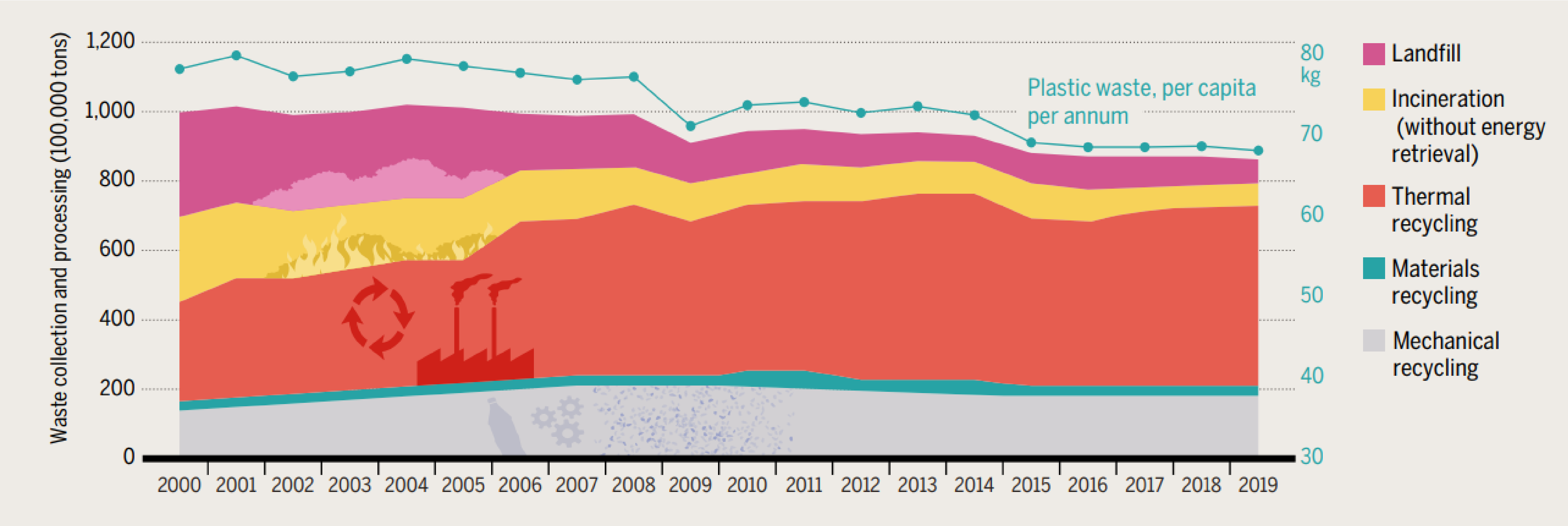
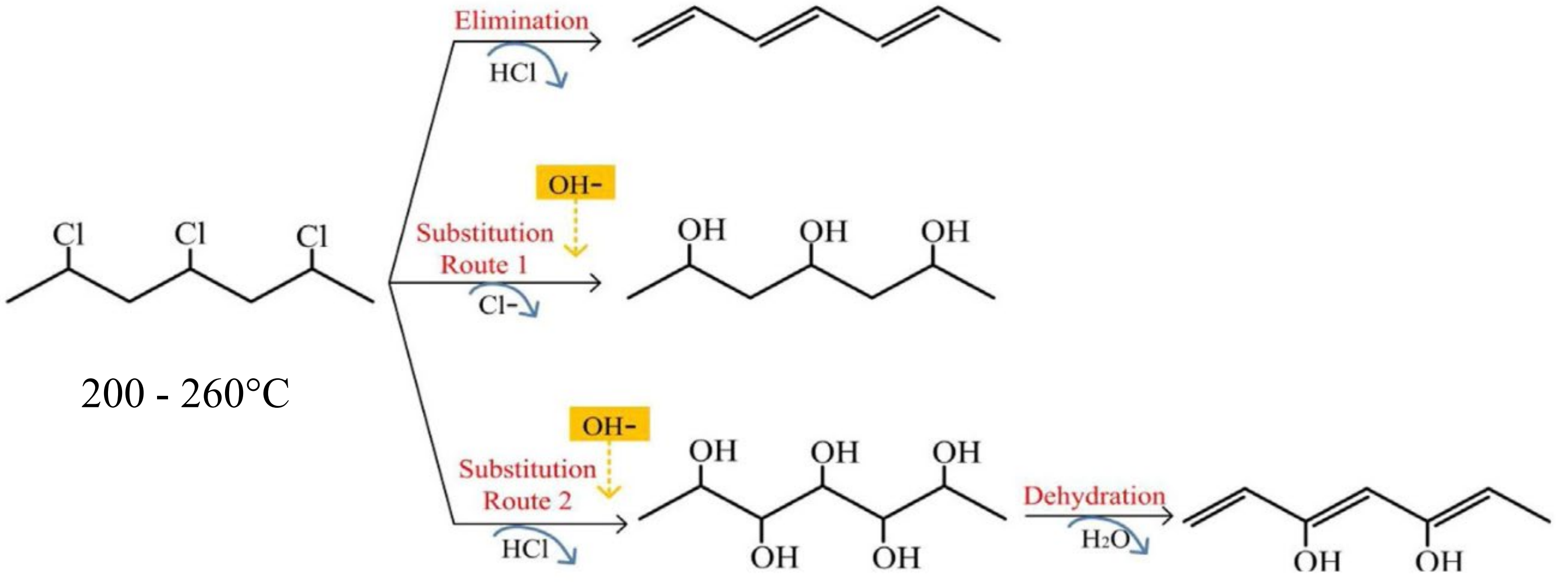
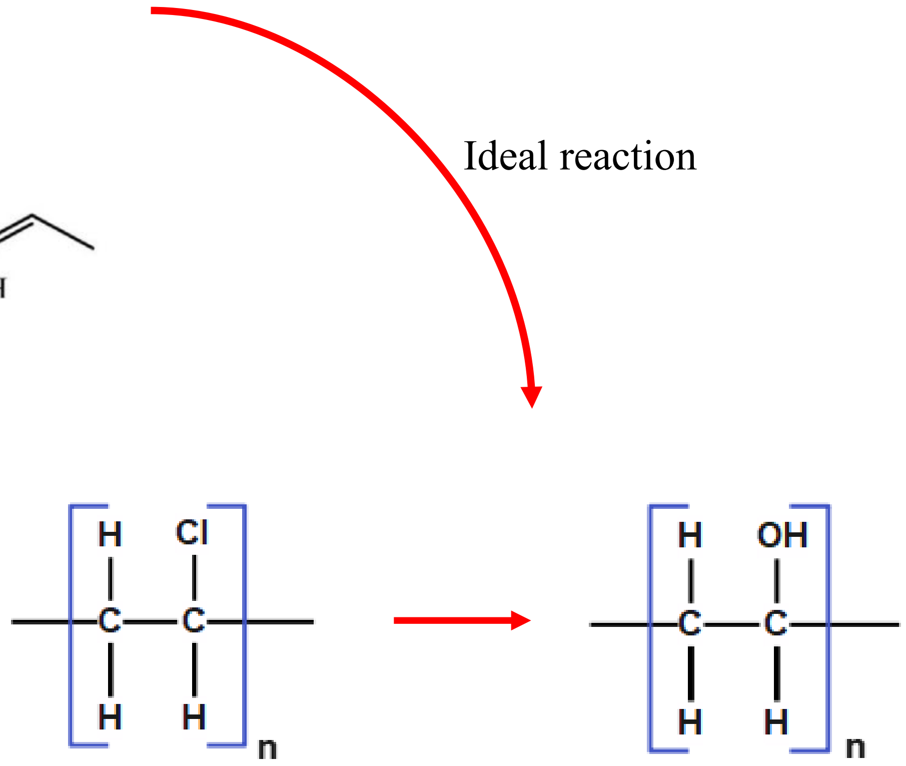
Waste Collection and Processing in Japan

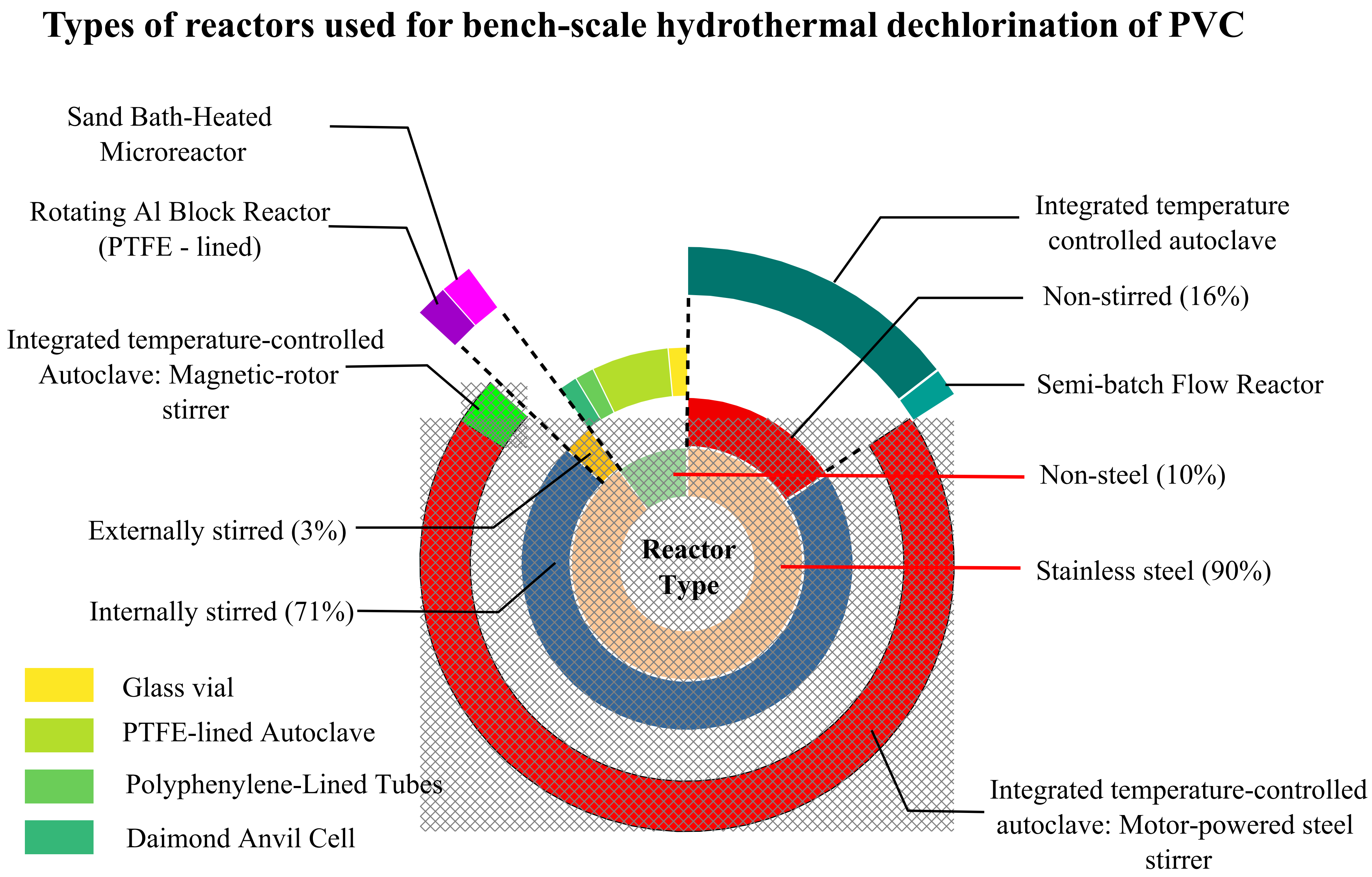


Hydrothermal dechlorination of Polyvinyl chloride



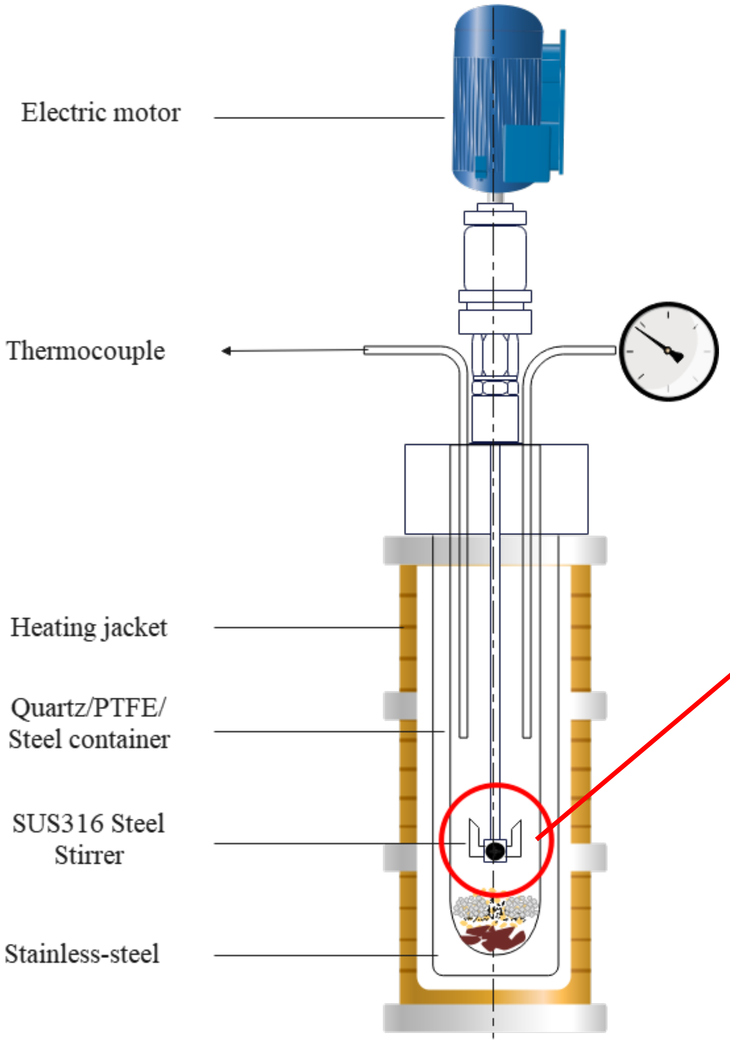
Chemical pathway for dechlorination of PVC in hydrothermal treatment

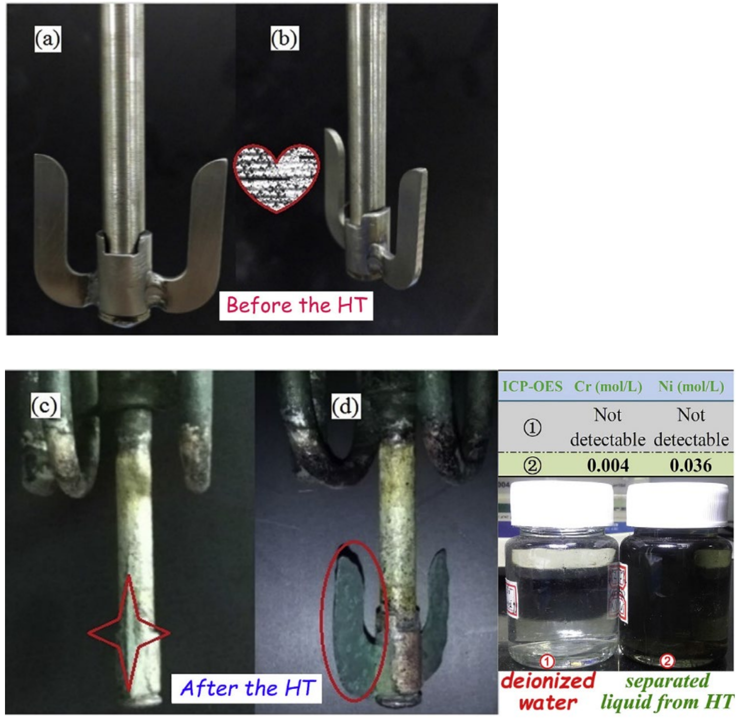




Types of reactors used for bench-scale hydrothermal dechlorination of PVC
Sand Bath-Heated Microreactor
Rotating Al Block Reactor (PTFE - lined)
Integrated temperature-controlled Autoclave: Magnetic-rotor stirrer
Externally stirred (3%)
Internally stirred (71%)
Glass vial
PTFE-lined Autoclave
Polyphenylene-Lined Tubes
Daimond Anvil Cell
Reactor Type
Integrated temperature controlled autoclave
Non-stirred (16%)
Semi-batch Flow Reactor
Non-steel (10%)
Stainless steel (90%)
Integrated temperature-controlled autoclave: Motor-powered steel stirrer

Typical Reactor Problem: Chlorine-induced corrosion





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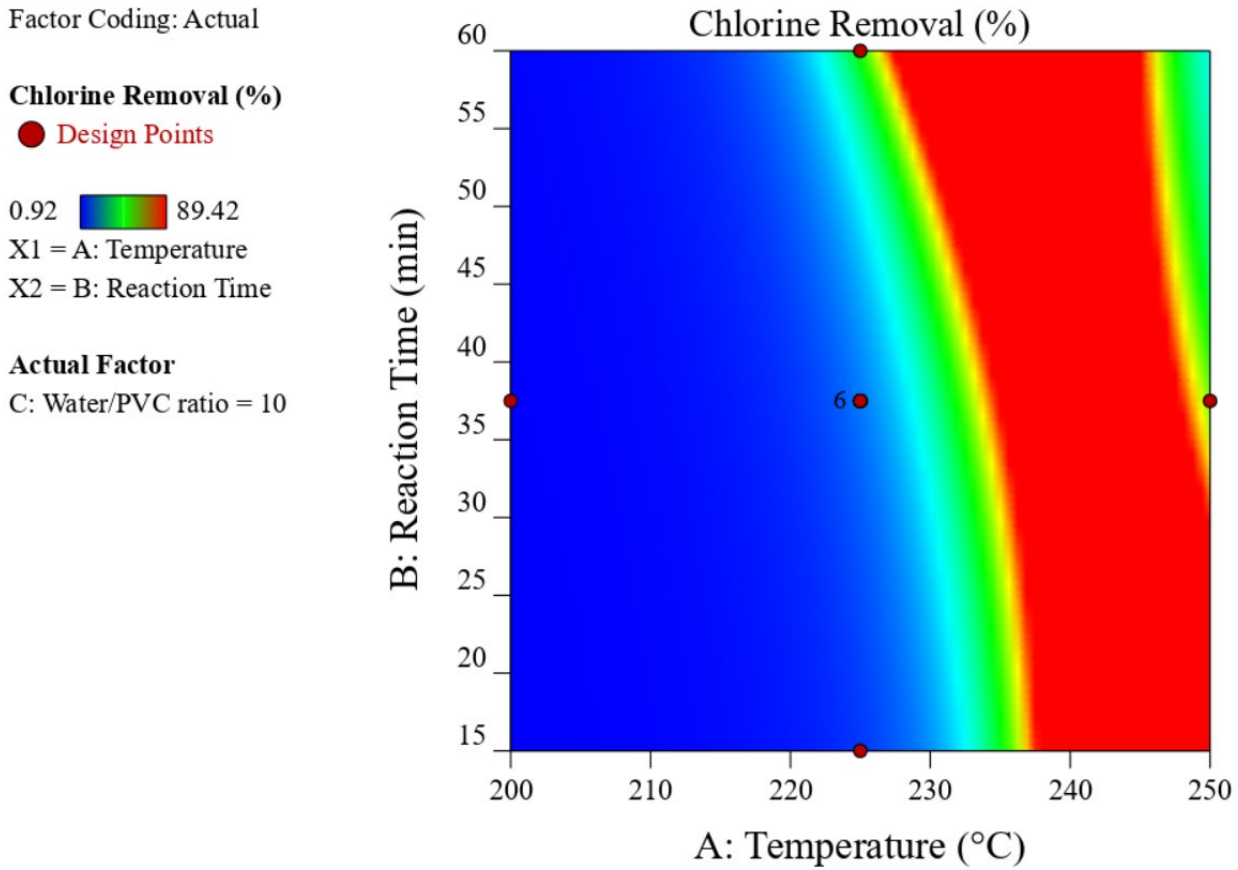
Challenges

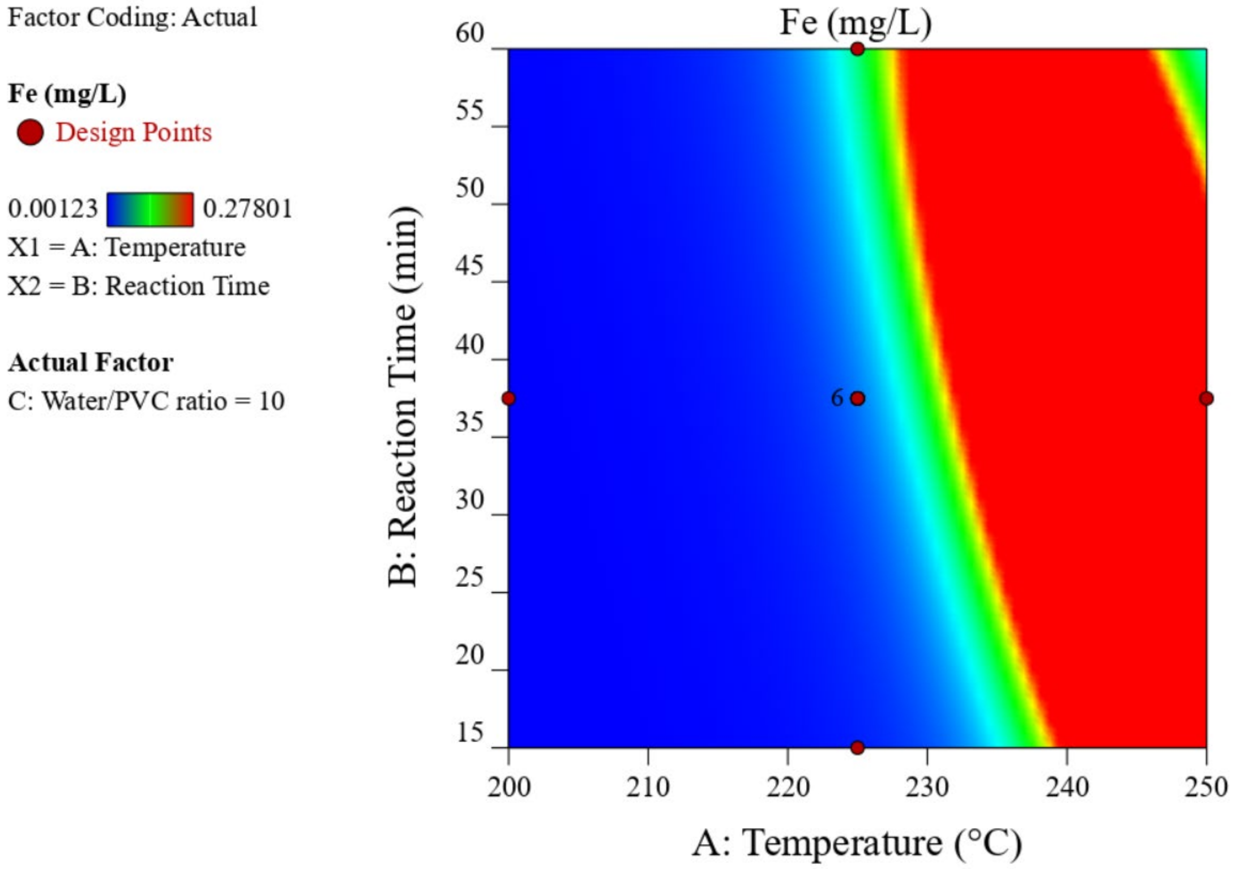
1. Medium contamination
2. Challenges in controlling external perturbation
3. Reactor integrity compromised
4. Metal surface &reactant interaction unavoidable

Effect of Temperature vs. RT on Cl removal from PVC and Fe corrosion

Exp. No	Reaction Data			Fe (mg)	Chlorine Removal (%)
	Water/PVC	T (°C)	RT (min)		
1	10	250	37.5	278.01	89.42
2	13	210	24.0	1.23	1.26
3	13	240	51.0	244.93	79.1
4	10	225	37.5	20.2	8.64
5	7	210	24.0	2.5	1.53
6	7	210	51.0	3.46	2.38
7	7	240	24.0	229.53	82.87
8	10	225	15.0	9.74	5.47
9	10	225	37.5	51.15	11.76
10	7	240	51.0	222.11	78.2
11	10	225	37.5	28.21	12.63
12	5	225	37.5	43.54	9.31
13	10	200	37.5	1.28	0.92
14	10	225	37.5	27.41	13.21
15	10	225	60.0	185.14	54.97
16	15	225	37.5	15.89	9.01
17	13	210	51.0	3.45	2.17
18	10	225	37.5	17.48	9.78
19	10	225	37.5	26.28	11.71
20	13	240	24.0	191.83	69.95

Effect of Temperature vs. RT on Cl removal from PVC and Fe corrosion



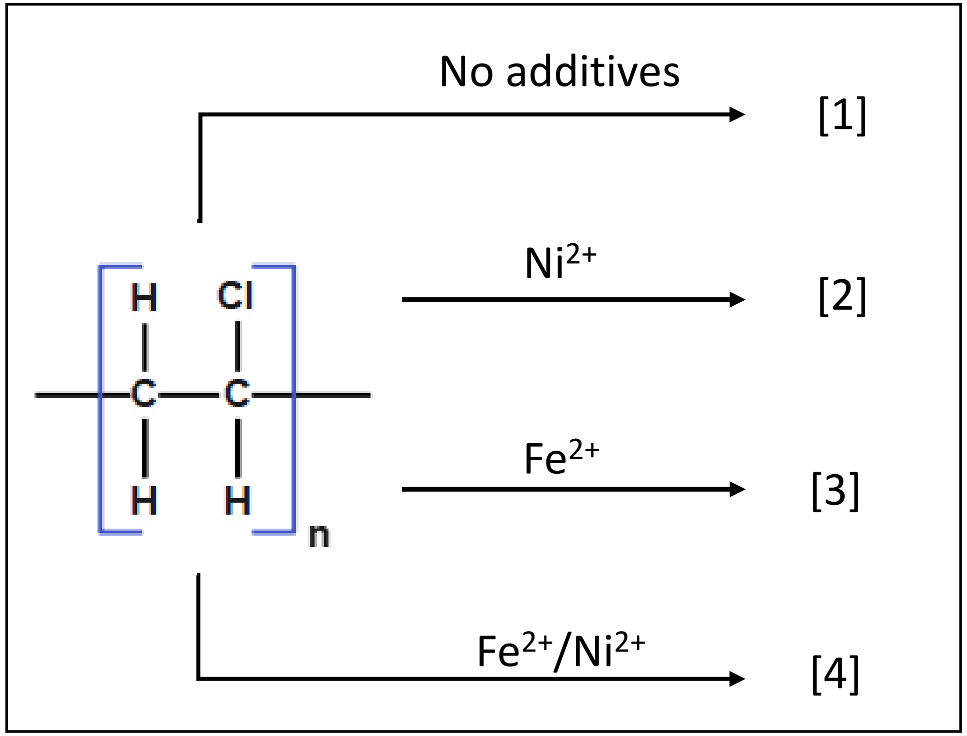


Research Questions

1. What is the effect of Ni^{2+} and Fe^{2+} on dechlorination behavior
2. Is there synergistic interaction between these cations
3. Which conditions promote deviation from the norm

Methodology

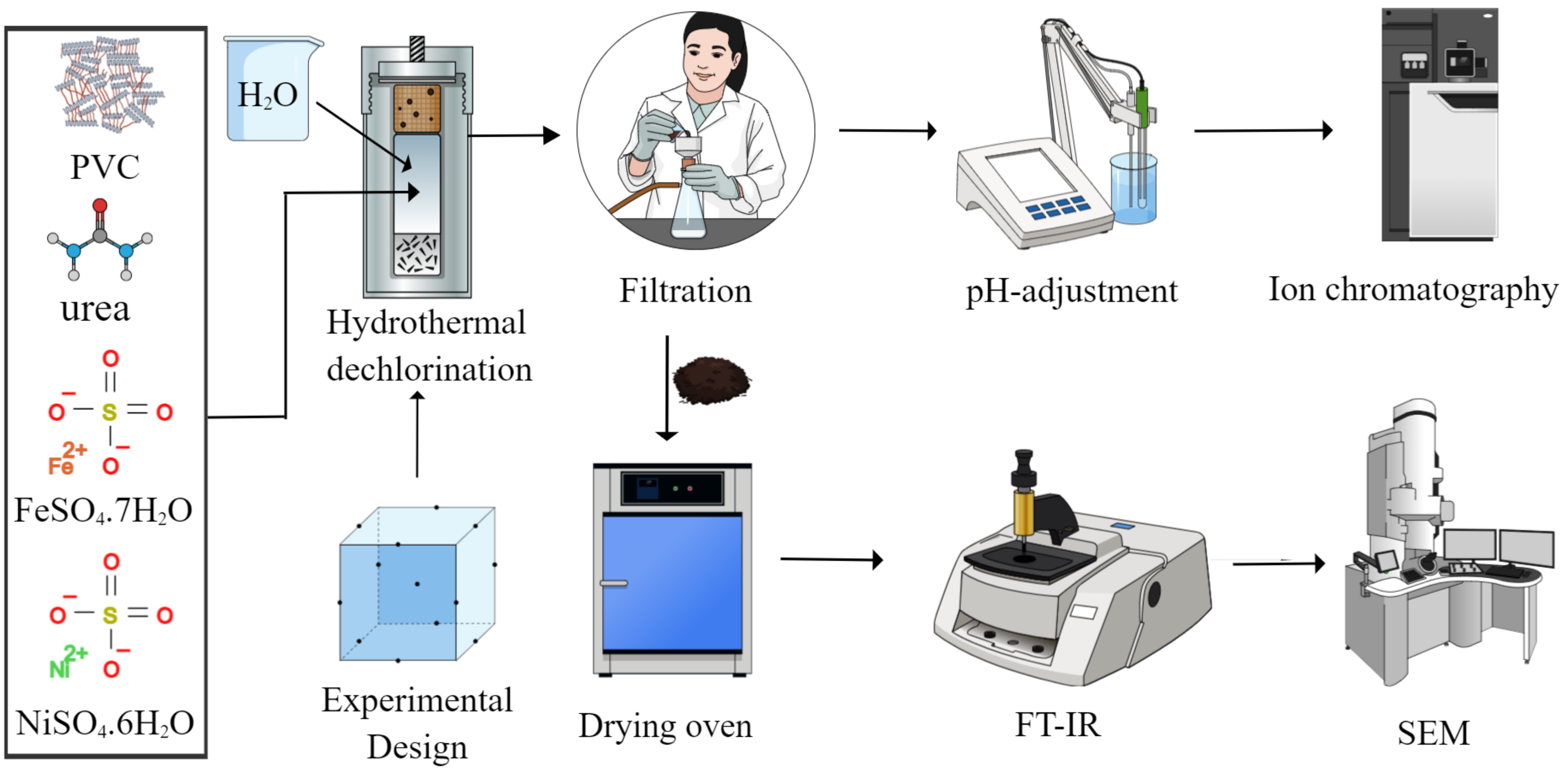
1M Urea (210°C)



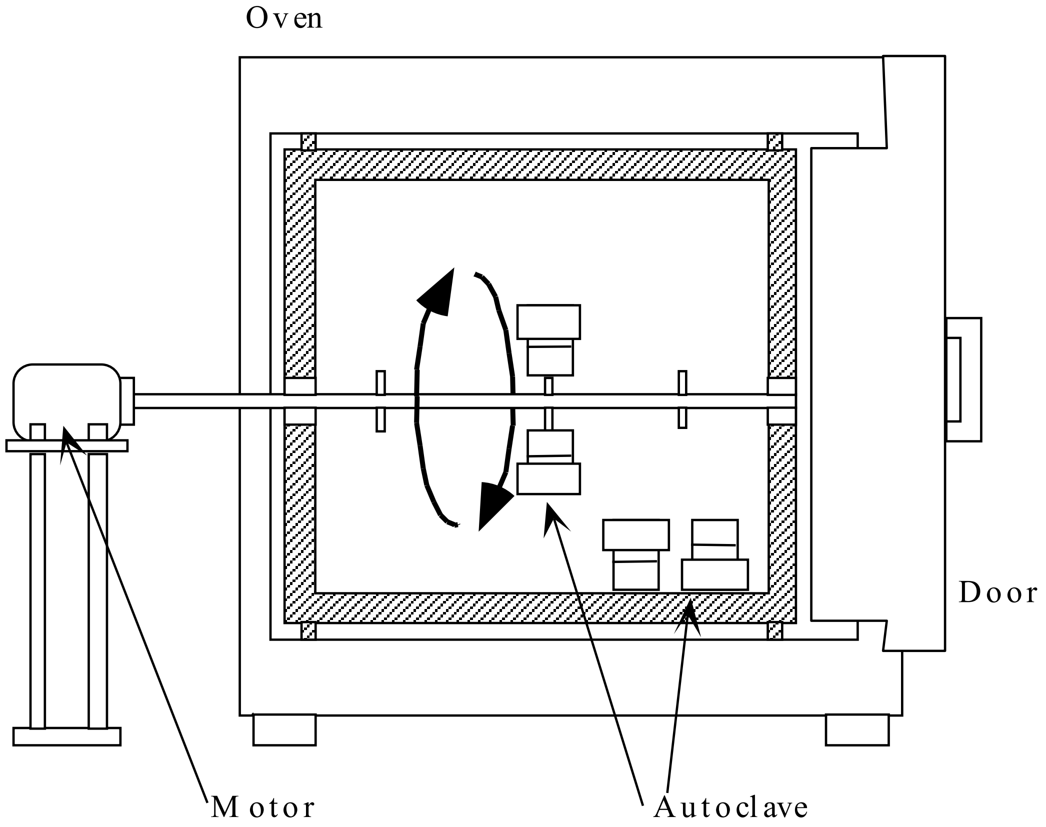
1M Urea Central Composite Design

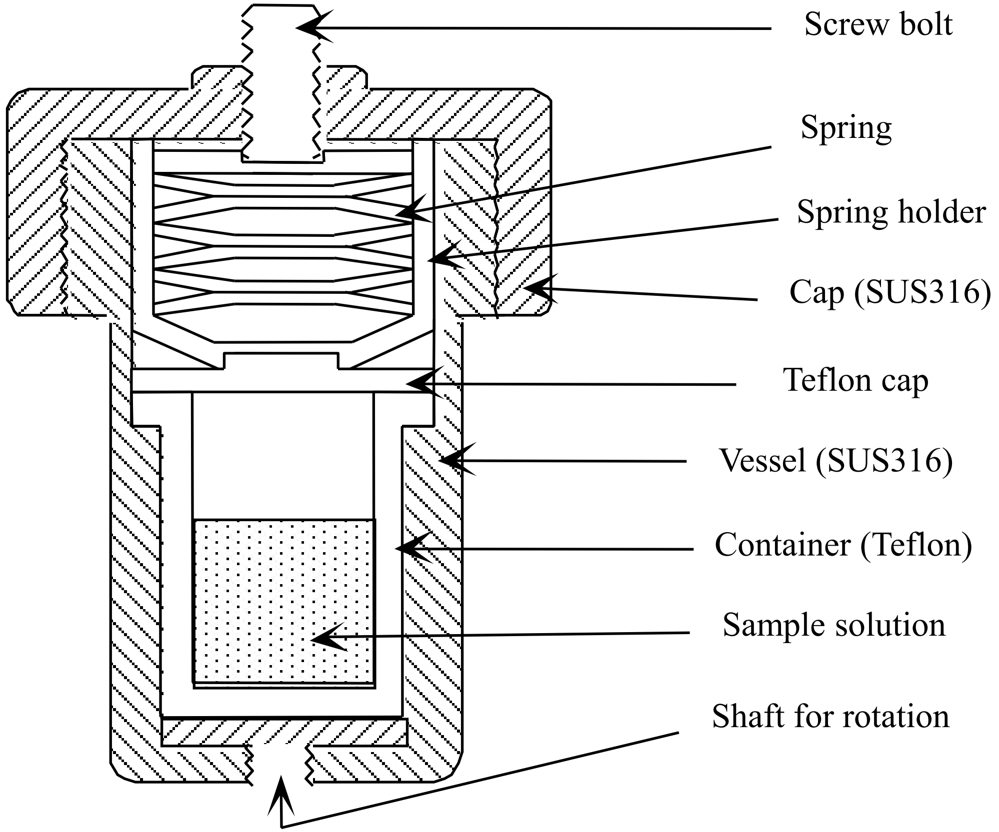
Independent variable	Symbol	Coded levels				
		α	-1	0	1	α
Temperature (°C)	A	203	210	220	230	237
Fe (mmol/L)	B	0.83	1.00	1.25	1.50	1.67
Ni (mmol/L)	C	0.08	0.15	0.25	0.35	0.42

Methodology

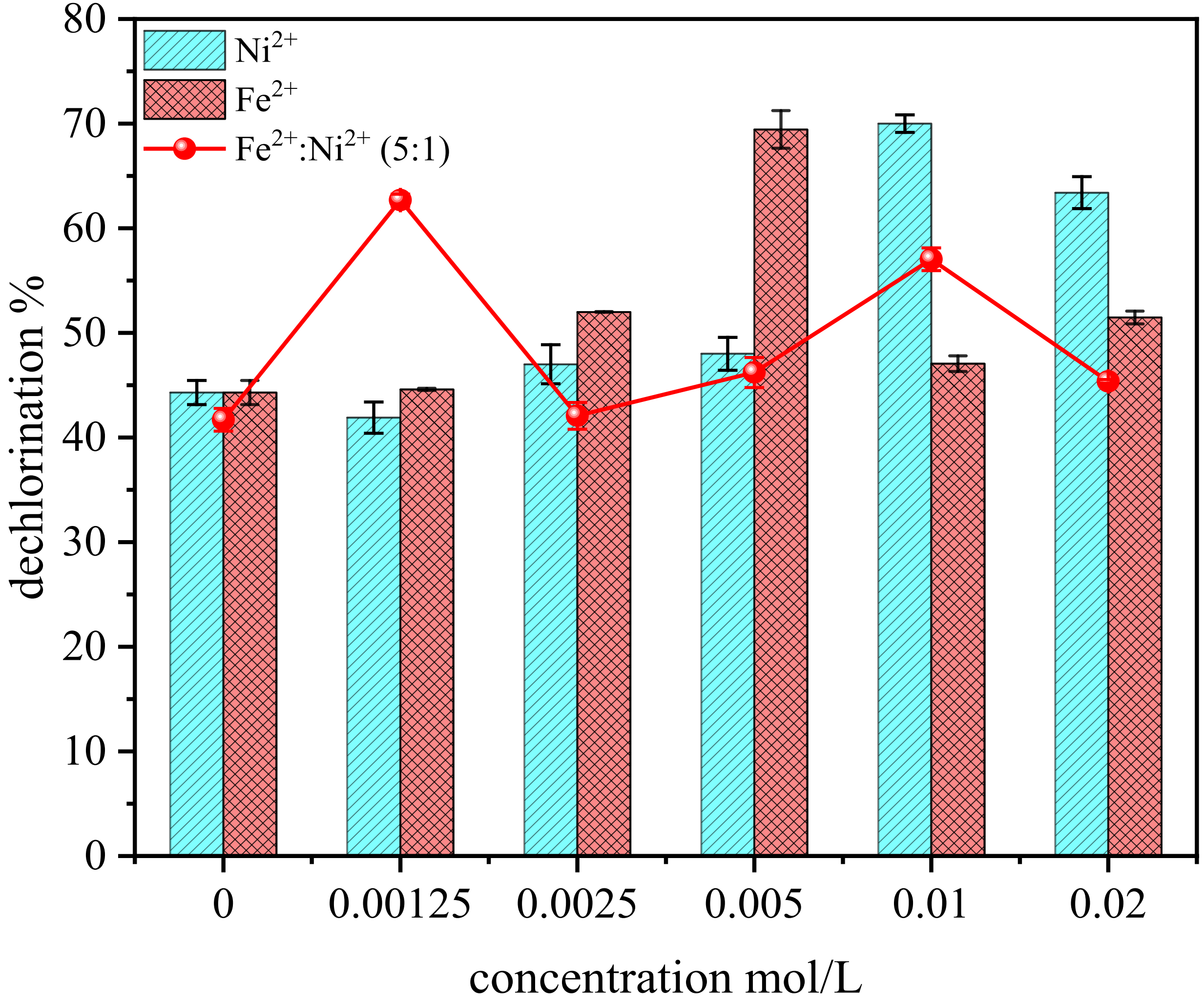


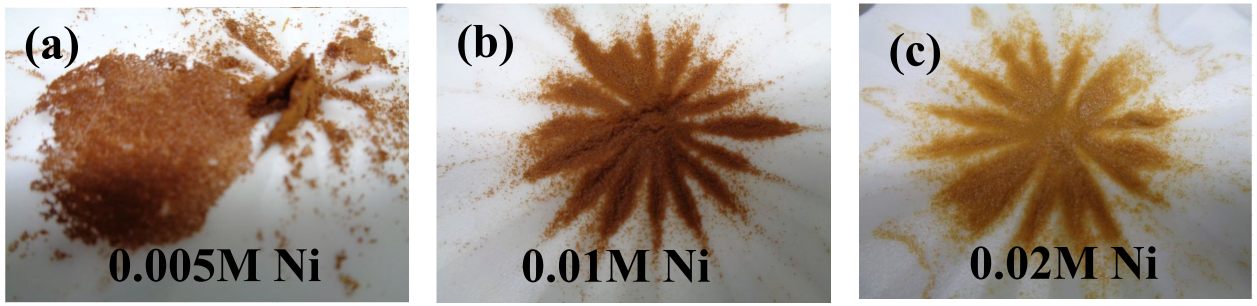
Reactor Design





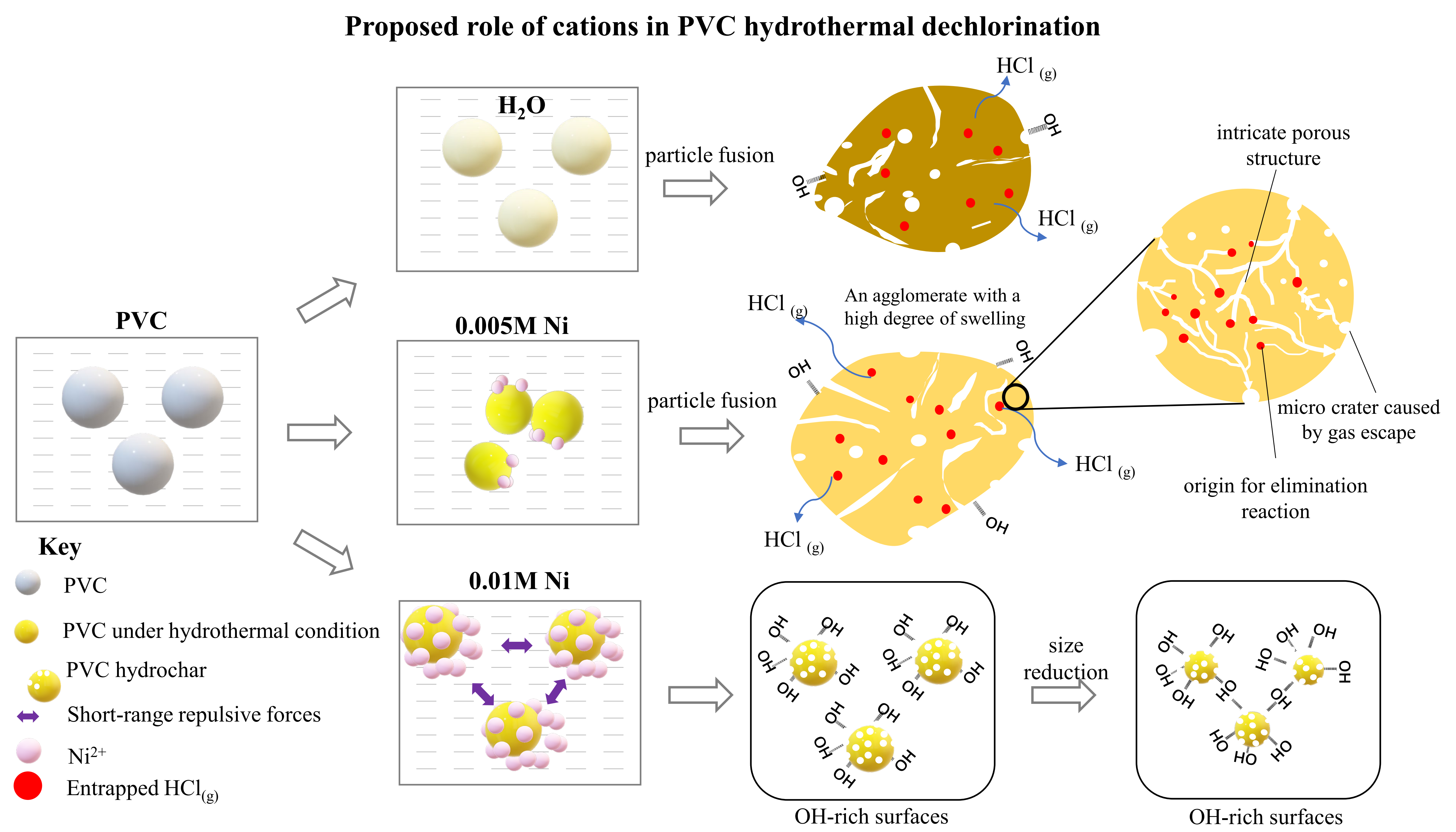
Effect of Ni/Fe on dechlorination in 1M Urea (210°C & 1 hr.)



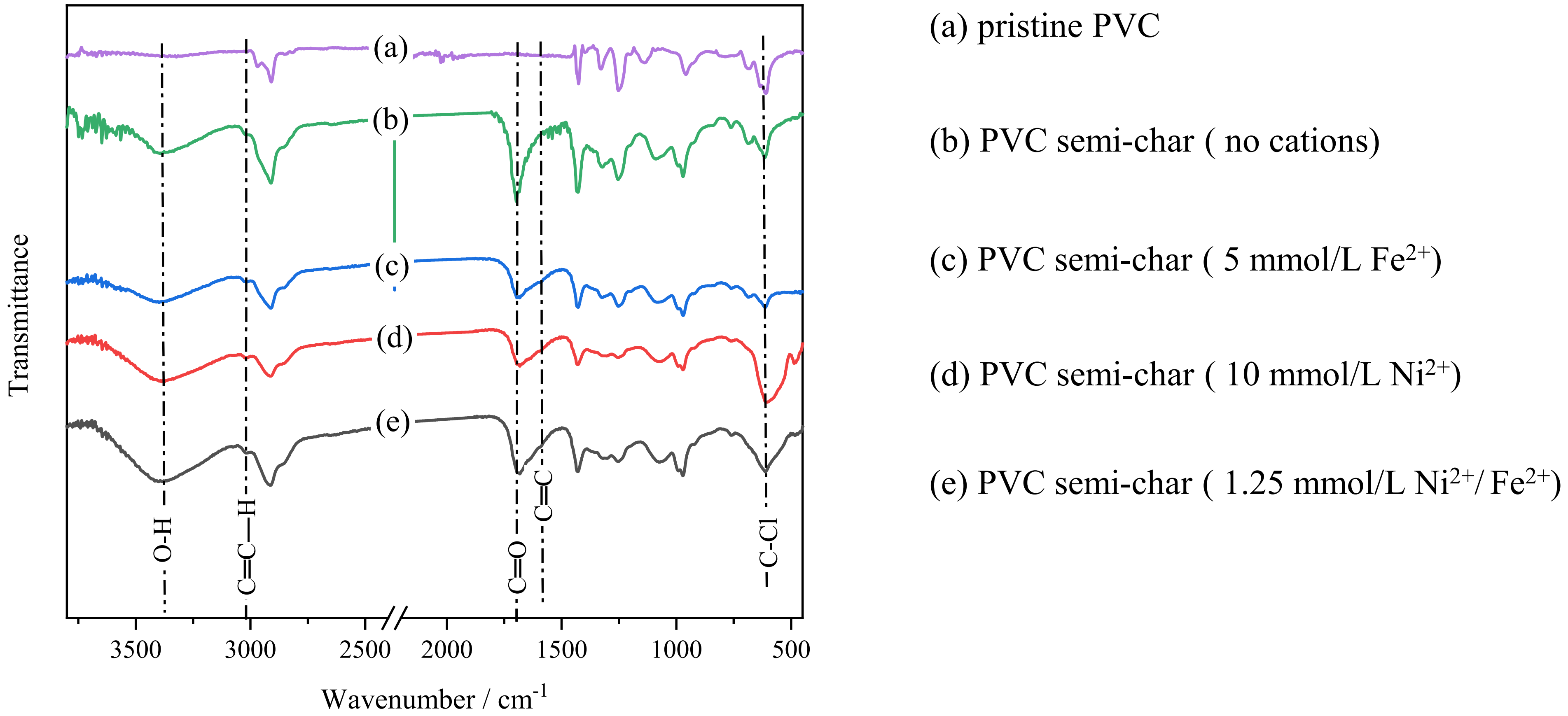


- 10 mmol/L Ni^{2+} improved dechlorination from 44% to 70%
- 5 mmol/L Fe^{2+} exhibits the same catalytic performance
- 1.25 mmol/L of Fe^{2+} and Ni^{2+} mixed at a ratio of 5:1 had similar catalytic effect

There is a synergistic interaction between Fe^{2+} and Ni^{2+} at a combined concentration of 1.25 mmol/L


Proposed role of cations in PVC hydrothermal dechlorination
PVC
H$_2$O
0.005M Ni
0.01M Ni
particle fusion
particle fusion
size reduction
HCl$_{(g)}$
OH
intricate porous structure
An agglomerate with a high degree of swelling
micro crater caused by gas escape
origin for elimination reaction
OH-rich surfaces
OH-rich surfaces
Key
PVC
PVC under hydrothermal condition
PVC hydrochar
Short-range repulsive forces
Ni^{2+}
Entrapped HCl$_{(g)}$

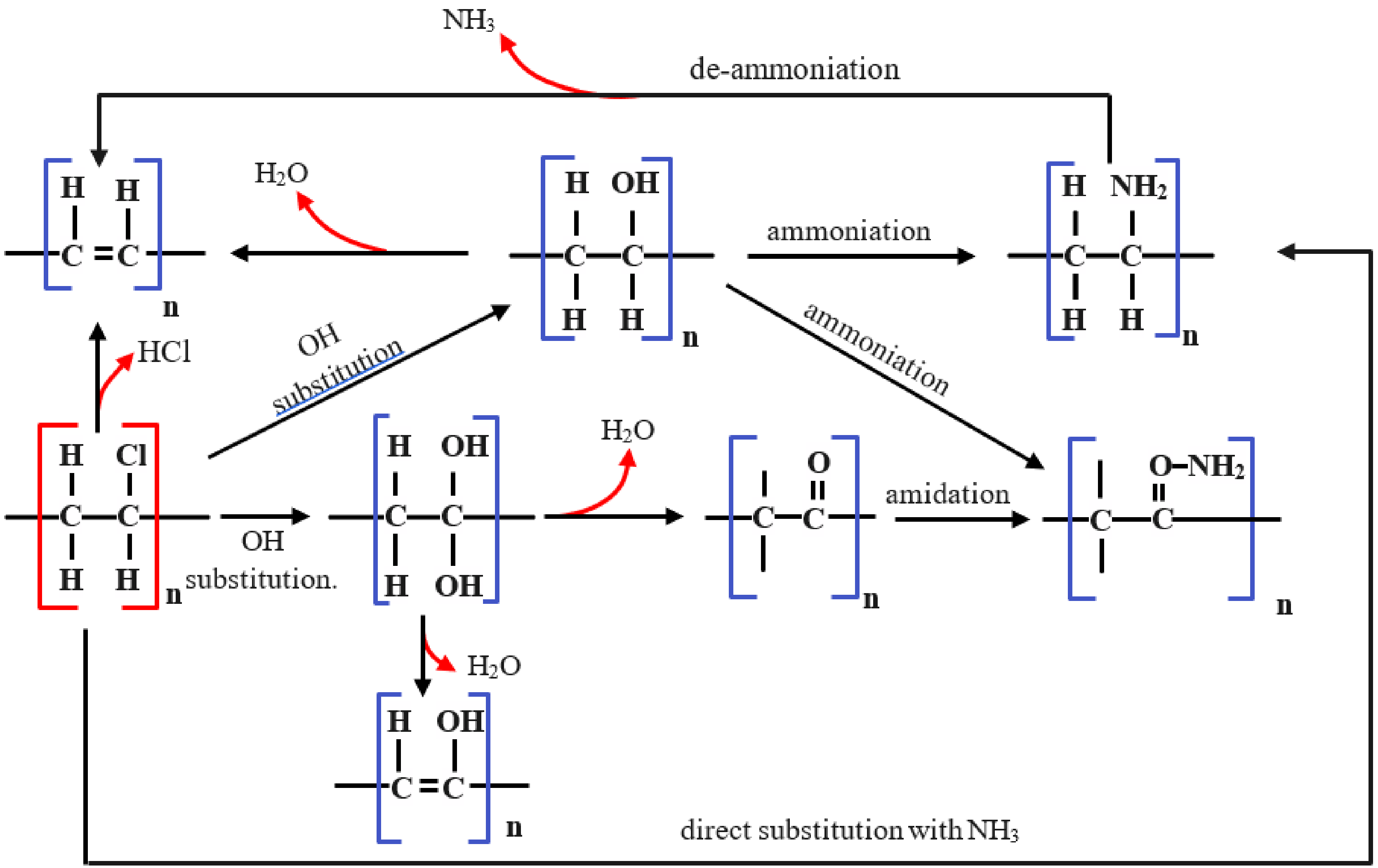
Effect of Ni/Fe on dechlorination in 1M Urea (210°C & 1 hr.)



Elemental analysis of semi-hydrochar

Cations	C %	H %	N%	O%	Cl%
(b) -	50.77	5.44	1.19	8.08	34.52
(c) 0.005 mol/ L Fe^{2+}	55.28	6.16	2.13	11.59	24.84
(d) 0.01 mol/ L Ni^{2+}	55.18	6.34	2.03	8.47	27.98
(e) 0.00125 mol/LFe^{2+}/Ni^{2+}	54.24	5.88	1.72	9.04	29.12

Proposed mechanism for PVC dechlorination in 1M Urea



Effect of Ni/Fe on dechlorination using CCD

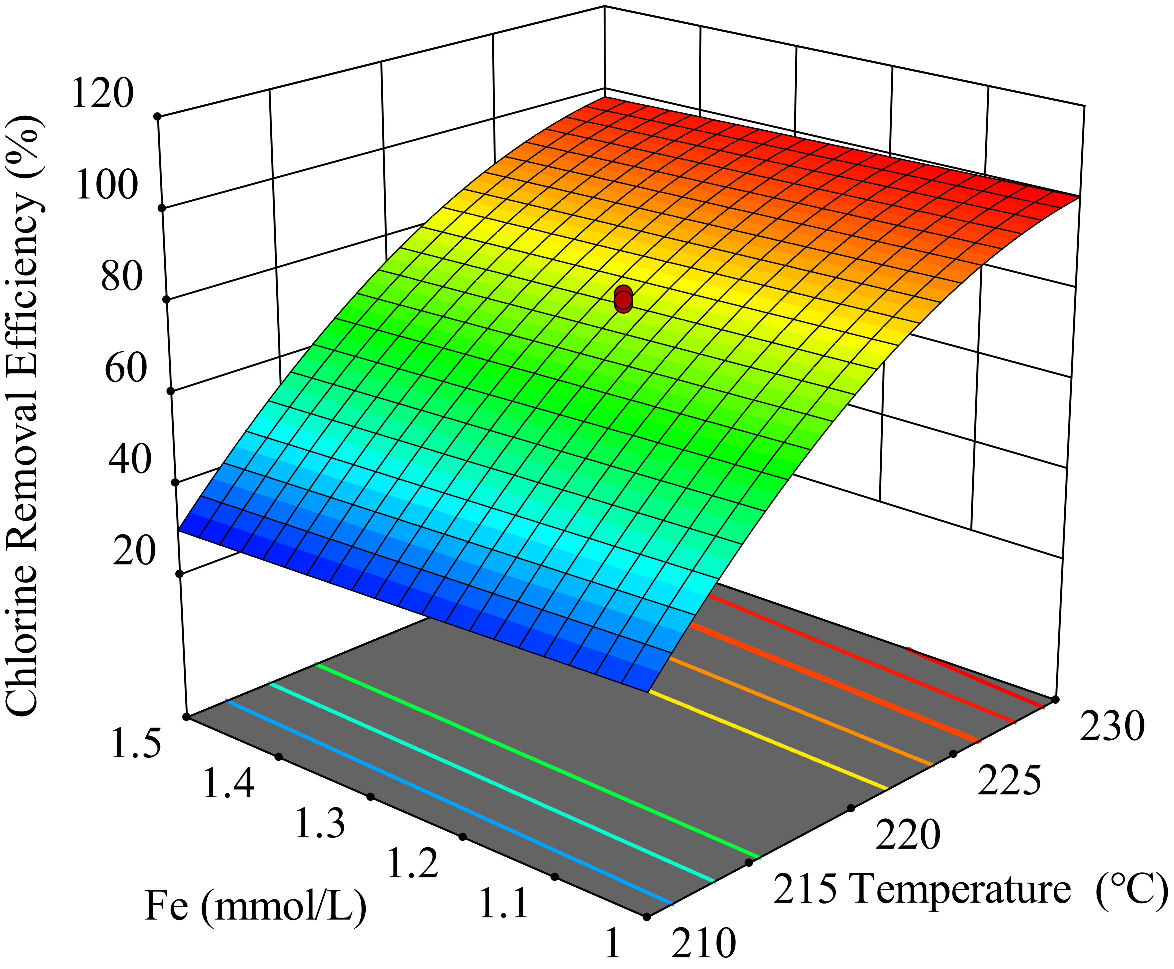
	Independent variables			Response Values	
Run	Temperature °C	Fe^{2+} mmol/L	Ni^{2+} mmol/L	[a]CRE %	[b]DEE %
1	220	1.25	0.25	78.1	26.1
2	210	1.50	0.35	29.5	4.5
3	230	1.00	0.15	99.5	11.5
4	210	1.50	0.15	28.7	3.7
5	230	1.00	0.35	99.8	11.7
6	220	1.25	0.25	77.4	25.4
7	220	1.25	0.25	79.6	27.6
8	220	1.25	0.42	75.0	23.0
9	220	1.25	0.25	77.4	25.4
10	230	1.50	0.15	99.4	11.4
11	220	1.67	0.25	78.2	26.2
12	220	1.25	0.08	76.9	24.9
13	220	0.83	0.25	75.7	23.7
14	220	1.25	0.25	78.7	26.7
15	237	1.25	0.25	100.0	0.0
16	210	1.00	0.35	34.0	9.0
17	230	1.50	0.35	95.8	7.8
18	203	1.25	0.25	25.0	1.0
19	210	1.00	0.15	31.4	6.4
20	220	1.25	0.25	80.9	28.9

(a) CRE – chlorine removal efficiency

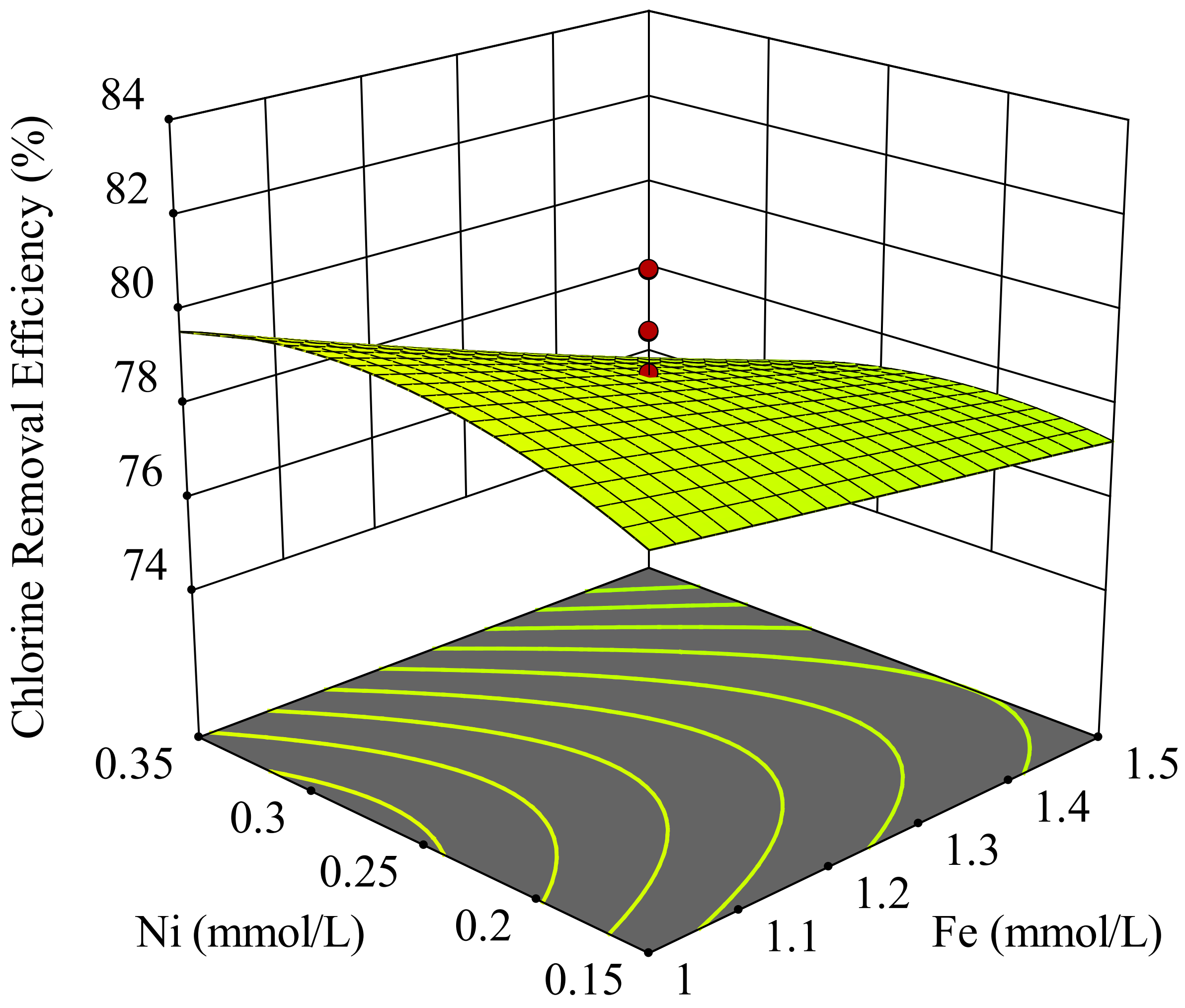
(b) DEE = dechlorination enhancement [dechlorination with cations minus dechlorination without]

Conditions = 1M Urea, 50 mins, Agitation

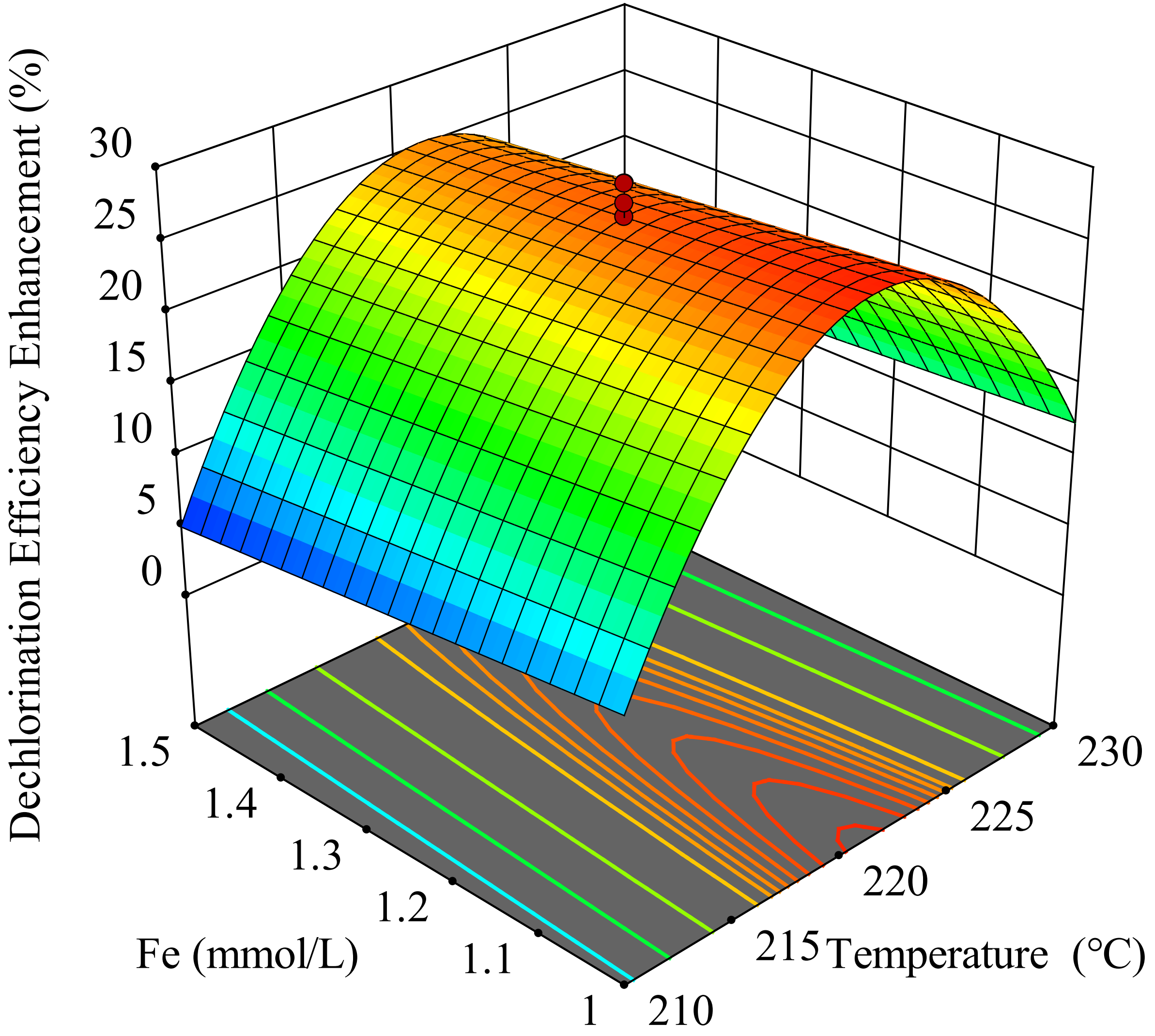
Synergistic interaction of Fe/Ni during hydrothermal dechlorination of PVC



Synergistic interaction of Fe/Ni during hydrothermal dechlorination of PVC



The effect of cations on deviation from the norm



DEE = dechlorination enhancement
[dechlorination with cations minus
dechlorination without]

Conclusions

1. Ni^{2+} and Fe^{2+} can significantly alter dechlorination behavior
2. Synergistic interaction between cations was confirmed
3. Cation activity is temperature dependent and maximizes around 220°C
4. Total cation concentration of as low as 1.08 mmol/L has a pronounced effect
5. It may not be prudent to use steel reactors for intrinsic chemistry determination

Future work

- ❑ Interactive effects of Ni/Fe/Cr and influence of anions (anoxic conditions)
- ❑ Uncover the mechanism of cationic synergy
- ❑ Comprehensive characterization of hydrochar
- ❑ Controlling the reaction mechanism for tailored product composition (production of low-thermal stability dechlorinated PVC)