# Electrochemical Remediation of Industrial Effluents – Few Examples

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# Agenda

1. Introduction
2. Processes developed at CSIR-CECRI
   A. Treatment of dye bath effluents
   B. Treatment of plating effluents
   C. Treatment of PCB effluents
3. Conclusions

# Introduction - Electrochemistry

Electrochemistry is concerned with study of mutual conversion of chemical and electrical forms of energy

Galvanic cell
Electrolytic cell

Basic components of an electrochemical cell

Ionized substances (electrolyte)
Two metal electrodes
External circuit

Faraday's first law of electrolysis

The amount of reacted substance is directly proportional to the quantity of electricity passed through the cell

$$\Delta mass \propto I * t$$

Advantage of electrochemical reaction is the direct control of (apparent) reaction rate

$$Reaction\ rate \propto f(cell\ current)$$

# Treatment of Effluents from Dyeing Industries

# Treatment of Dye Bath Effluents

The textile industry is one of the oldest and largest industrial sectors in India.

Approximately, in India we have about 2500 textile industries. Tamil Nadu, Gujarat, Punjab and Maharashtra account for more than 80 % of total industries

Contributes 4% to the GDP

Water consumption for chemical processing 50-300 L/kg of fibre.

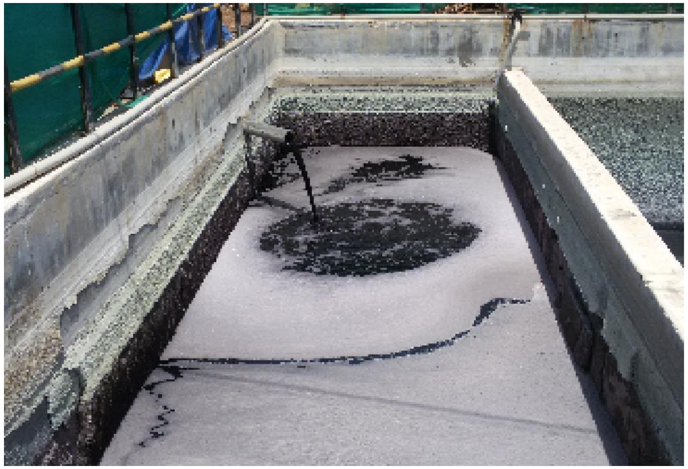
Electrochemical oxidation is considered to be a very powerful process for breaking up even the most resistant organic compounds.

Anodic oxidation of organic compounds can be performed in direct or indirect oxidation.

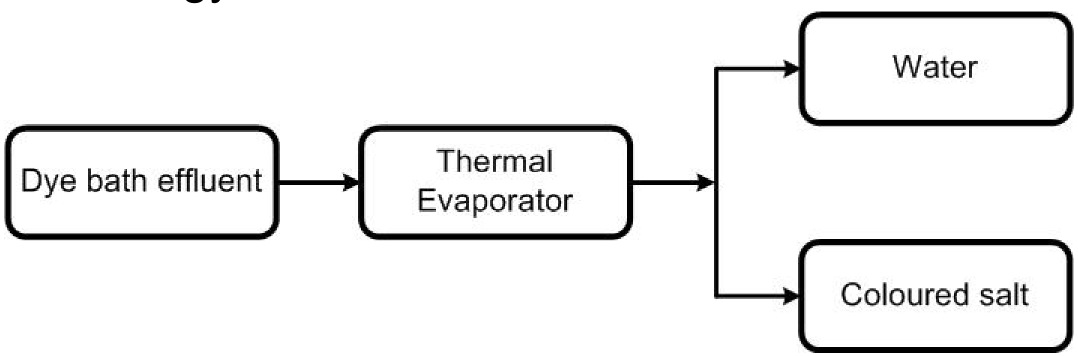
Direct oxidation happens at the surface of the anode.

Indirect oxidation happens at the bulk solution due to generation of oxygen or other radicals viz. $OH^-$, $Cl^-$, $OCl^-$ radicals at the anode surface

# Treatment of Dye Bath Effluents



## Conventional Technology




## Electrochemical process

# Dye Bath Decolourization - Results


Recirculation Process Capacity: 5 L/day

Continuous Process Capacity: 30 L/day

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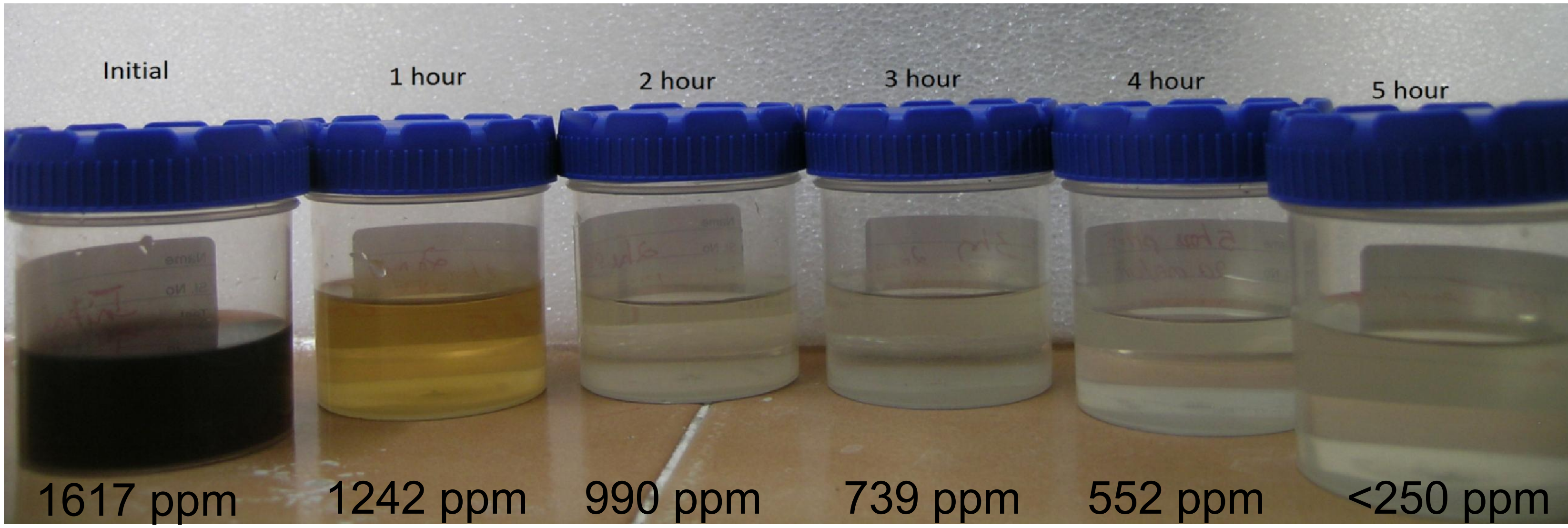
# Dye Bath Decolourization - Results






# Dye Bath Decolourization - Results

**Recovered salt without treatment** | **Recovered salt after treatment**

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# Treatment of Effluents from Chrome Plating Industries

Platinum Jubilee 1942-2016

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# Treatment of Plating Effluents

Hexavalent chromium bearing wastes are produced in chromium electroplating, chromium conversion coatings and in metal finishing operations carried out on chromium as a basis material

Hexavalent chromium is carcinogenic and mutagenic

The discharge limit of Cr (VI) for the surface water is less than 0.1 ppm while the total limit of chromium is below 2 ppm including Cr(III), Cr (VI) and its other forms.

Typical hexavalent concentration in the effluent is 10-2000 ppm.

$Cr^{6+}$ compounds are highly soluble. It has to be converted to $Cr^{3+}$ before it can be precipitated out. Typical reducing agents used: Ferrous sulphate and sodium meta bisulphate.

In the conventional ferrous sulphate chromium reduction process, one kg of Cr theoretically requires 16.03 kg of ferrous sulphate

In the electrochemical process, theoretical iron requirement for the reduction of one kg of Cr is 1.06 kg

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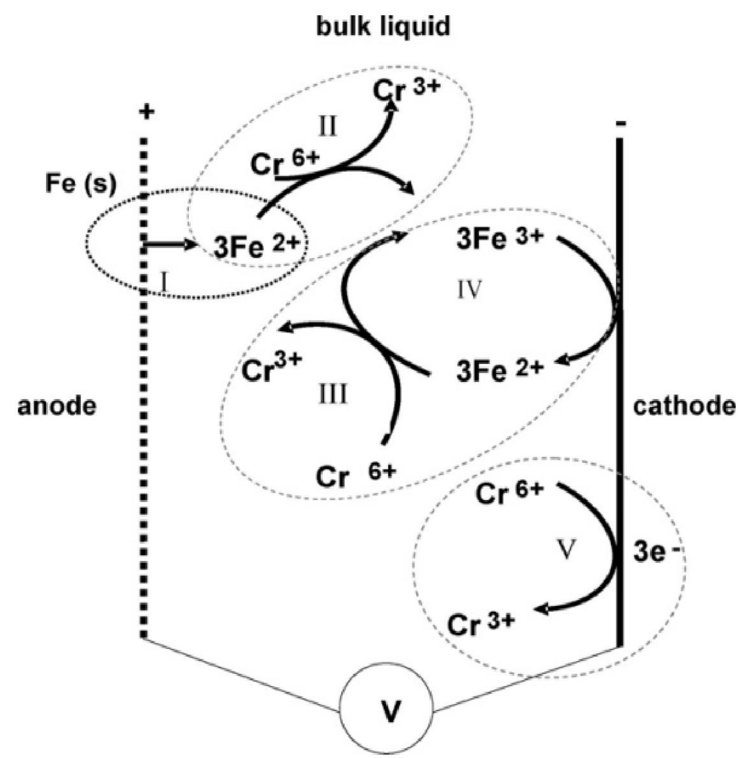
# Treatment of Plating Effluents

**Step I** Iron dissolution at anode

**Step II** Dissolved iron reduces Cr (VI) to Cr (III) in bulk

**Step III** Reduction of Cr (VI) to Cr (III) by regenerated Fe (II) at cathode (Step IV)

**Step V** Direct reduction of Cr (VI) to Cr (III) at cathode




Rodriguez et al. (2009). Journal of Hazardous Materials, 163, 1221-1229

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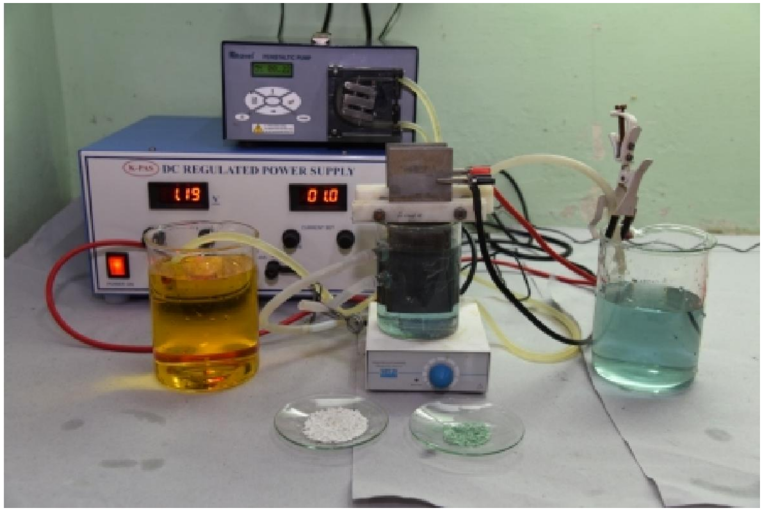
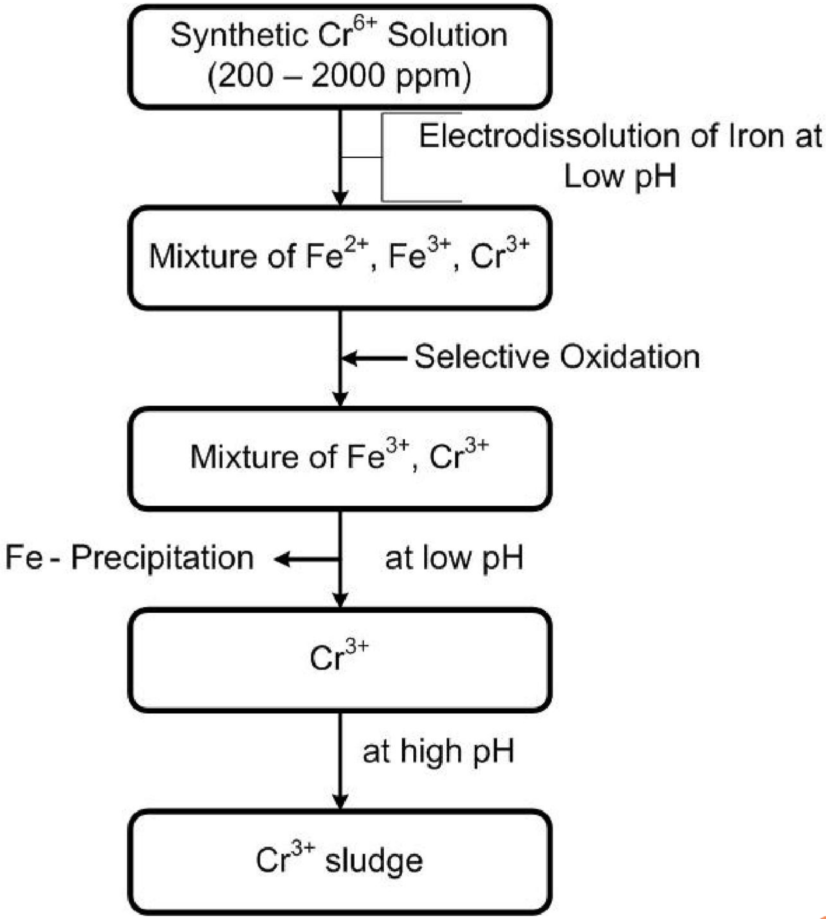
# Chromium Reduction - Results

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# Chromium Reduction - Results

| | |
|---|---|
| Electrodes | : Iron |
| Inlet $Cr^{6+}$ conc. | : 200 - 2000 ppm |
| Outlet $Cr^{6+}$ conc | : < 0.1 ppm |
| Capacity | : 5 g of $Cr^{6+}$/h |
| Flow rate | : 50 – 500 L/day |
| Fe/Cr ratio | : 2 |

To enhance the mass transport, rotating electrode reactor is designed

One kg of $Cr^{6+}$ produces a sludge of six kg of mixed $Cr(OH)_3 + Fe(OH)_3$

Scale-up of the reactor and the economic analysis of the process in progress

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# Treatment of Effluents from PCB Manufacturing Industries

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# Treatment of PCB effluents

Printed circuit boards (PCB) serve as the fundamental components for all kinds of electronic and electrical devices

Based on their functions and utilities, PCBs can be termed as the neural system of any electronic device

The Indian electronics market is one of the fastest growing in the world and is anticipated to reach US$ 400 billion in 2022

Etching process is a critical step in PCB manufacturing. Etching process is carried out to remove unwanted copper from copper laminated boards to get the desired design using chemical etchants. The production of PCBs per square meter generates an average of 1.5 - 3.5 L of spent etchant

# Treatment of PCB effluents

In recent times, the cupric chloride etching solutions are the most popular one

During the etching process,

$$Cu^0 + Cu^{2+} \rightarrow Cu^+ + Cu^+$$

In order to maintain constant etching rate, the excess copper has to be removed and reduced etchant must be regenerated

Regeneration technologies:

1. Chemical regeneration
2. Electrolytic method

Chemical regeneration

$$Cu^+ + Cu^+ + H_2O_2 \rightarrow Cu^{2+} + Cu^{2+}$$

Disadvantage:

Increases the level of copper in the etchant – inhibits the etching

# Treatment of PCB effluents - Acidic

Electrolytic process achieves dual purpose of regeneration of spent etchant (on the anode) and recovery of copper (on the cathode)

At the anode,

$$Cu^{+} + Cu^{+} \rightarrow Cu^{2+} + Cu^{2+} + 2e^{-}$$

At the cathode

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0}$$

Advantages of electrolytic regeneration

1. Elimination of off-site shipments of excess etchant
2. Reducing purchases of fresh etchant
3. Recovering copper

Prevents not only pollution problems but also prevents loss of metal resources

# Conclusions

Electrochemical remediation seems to be the last resort for effluent treatment

- ➢Lack of popularity
- ➢Expensive (perception !!)

Electrochemical processes should not be judged only on electricity cost

Rather should be assessed based on

- ✓zero sludge generation
- ✓elimination sludge storage
- ✓elimination of shipment for off-site reclamation
- ✓reduction in chemicals procurement
- ✓recovery of metal at its purest form

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# Thank you for listening

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