Separations Based on Electrical Field Phenomena

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NAS Study “A Research Agenda for a New Era in Separations Science”
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Advanced Separations in Chemical & Biochemical Industries

Chemical process purification

Metal-Recovery & Resource Extraction

Bio-separations
Environmental Separations & Water Purification

Water Purification
Environmental Remediation

Rural villages, India
Flint, Michigan

Greenhouse Gases
Toxic Volatile Compounds
Overcoming Challenges in Separations Science

Energy Consumption

- Distillation
- Multi-stage flash desalination

Chemical Footprint & Sustainability

Separations step ~80% of production cost
30-40% losses in Extraction & Adsorption
x $10^3$ more excess chemicals & solvent
Poor Water Usage Ratio (~0.5)
Separations Based on Electrical Field Phenomena

Electric field gradient techniques for molecular separations
- Electrophoresis, dielectrophoresis, electrodialysis, electrodeionization
- Capacitive deionization
- Potential-based chromatography

Particle separations, emulsion breaking
- Induced dipoles, charges reacting to field gradients
- Electrostatic precipitation

Electrochemically modulated separations
- Electrocoagulation, electroflotation
- Redox-mediated electrosorption
- Battery desalination and hybrid deionization methods

Minimization of chemical pollution
- Targeting lower energetic costs
- Scalable technologies
- Fine molecular control
- Reduce chemical consumption
Migration-Based Electro-Separations

Electrophoresis

Electrodialysis

Electrodeionization
Migration-Based Electro-Separations

Electrostatic Precipitation

- Collection plate
- Uncharged particles
- Positively charged particles
- Precipitated (collected) particles
- Ionizer (to charge particles)
- Electrostatic precipitator

Electrocoalescence

- Emulsifying device
- Dilution water
- Water
- Crude low water content high salinity
- Emulsion
- Electric field
- Electrode
- Electro-coalescer
- Settling

Capacitive Deionization

(a) Porous Carbon Electrode
- Current Collector
- Feed Water
- Freshwater
- Voltage $V_{cell}$
- Cations
- Anions

(b) Porous Carbon Electrode
- Current Collector
- Feed Water
- Freshwater
- Cation Exchange Membrane
- Anion Exchange Membrane

(c) Sodium Manganese Oxide
- Treated Water
- Anion Exchange Membrane
- Porous Carbon Electrode
- Cations $\text{Na}^+$
- Anions $\text{Cl}^-$
Reaction-Based Electro-Separations

Electrocoagulation

Electroflotation

Electro-membranes
Battery-Based Desalination

Battery Desalination

Ion intercalation into crystalline materials

Hybrid Method
(Battery Cathode, MCDI Anode)
Electrosorption

Uranium capture

- Repulsion
- Competition
- Unwanted adsorption
- Step I: Electric field, ion migration
- Step II: Electric field, ion migration
- Step III: Electrodeposition
- Step IV: Ion rearrangement
- Step V: Electric field, electrodeposition and growth

- Hydrophobic Interaction
- Uncharged Organic

- Uranium capture
- Uranium capture
Redox Polymer Electrodes for Selective Ion Adsorption

\[ E = E^0 + \frac{RT}{F} \ln \left( \frac{[Fc']}{[Fc]} \right) \]

Charge (C/g)

Potential (V)

SEM Carbon fibers
200 μm PVF-CNT Film

HRSEM PVF-CNT Film
400 nm
Selective Electro-Swing Adsorption Operations

Stoichiometric for RCOO⁻.
Fine Chemical Separations

Hammett Series Investigation

Practical Purification in Organic Synthesis: Fluorine Substitutions

Enhanced Separation Factors!
Fine Chemical Separations and Micropollutant Capture

Quinchlorac (Pesticide)

Ibuprofen (endocrine disruptor analogue)

Sodium-dodecyl sulfonate, SDBS (Environmentally persistent detergent)
Electrochemically Mediated Adsorption of Nonionic Organics

$E = E^o + \frac{R' A}{F} \ln \left( \frac{[Fe^2+]}{[Fe^3+]} \right)$

$Q_e (mg/g)$ vs $C_e (mg/L)$

$E^o$

Potential (V)

Charge (C/g)

$0.0 \ V$
$0.1 \ V$
$0.2 \ V$
$0.3 \ V$
$0.4 \ V$
$0.5 \ V$
$0.6 \ V$

$10 \ \mu m$
$2 \ \mu m$
$100 \ nm$

Water
ETAS Adsorbent
Organics
Carbon Fiber
Fluid Stream Concentration Changes

Feed Solution

Reduced - Adsorption

Oxidized - Desorption

Multiple Stages

Feeding Solution

Graphs showing concentration changes over stages for different voltages:

- Feed Solution
  - Concentration $C_f$ (mg/L) vs Stage Number
  - Voltages: 0.0 V → 0.6 V, 0.2 V → 0.3 V

- Receiving Solution
  - Concentration $C_r$ (mg/L) vs Stage Number
  - Voltages: 0.2 V → 0.4 V, 0.0 V → 0.6 V
### Other Contaminants Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
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</thead>
<tbody>
<tr>
<td>2,4-Dichlorophenol</td>
<td><img src="image1" alt="2,4-Dichlorophenol" /></td>
</tr>
<tr>
<td>2-Naphthol</td>
<td><img src="image2" alt="2-Naphthol" /></td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td><img src="image3" alt="1-Naphthylamine" /></td>
</tr>
<tr>
<td>Bisphenol S</td>
<td><img src="image4" alt="Bisphenol S" /></td>
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<tr>
<td>Metolachlor</td>
<td><img src="image5" alt="Metolachlor" /></td>
</tr>
<tr>
<td>Ethinyl Estradiol</td>
<td><img src="image6" alt="Ethinyl Estradiol" /></td>
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<tr>
<td>Bisphenol A</td>
<td><img src="image7" alt="Bisphenol A" /></td>
</tr>
<tr>
<td>Methyl Orange</td>
<td><img src="image8" alt="Methyl Orange" /></td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="image9" alt="Rhodamine B" /></td>
</tr>
<tr>
<td>Propranolol hydrochloride</td>
<td><img src="image10" alt="Propranolol hydrochloride" /></td>
</tr>
</tbody>
</table>

#### Desorption Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>0.0 V</th>
<th>0.3 V</th>
<th>0.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol S</td>
<td><img src="image4" alt="Bisphenol S" /></td>
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</table>
Heavy Metal Oxyanions (HMOAs)

(c) Adsorption Uptake (mg Cr/g adsorbent) vs Potential (V vs Ag/AgCl)

(d) Adsorption Cr (mg/g) vs Equilibrium Conc. (mg/L)

(a) pH vs E (V vs SHE)

(e) Adsorption Uptake (mg Cr/g adsorbent) vs Time (min)

(f) Released Capacity (mg Cr/g adsorbent) vs Time (min)
Redox Counter-Electrode

Charge Matching

Anode

Cathode

$N[A \rightarrow A^+ + e^-]

n[C + e^- \rightarrow C^-]

(N-n)[H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-]

Pt counter 8 A/cm$^2$

8 A/cm$^2$ reduced

8 A/cm$^2$

PMAECOp2$^+$-CNT

PMAECOp2$^+$-CNT

0.6 V cell voltage

PVF-CNT [Anode]

PMAECOp2$^+$-CNT [Cathode]

Potential (V) vs Ag/AgCl

Time (s)

Charge (mC) towards OH$^-$ production

Time (s)
Separation Performance for Micropollutants

- Micropollutant: μM concentration, with 300-fold competing ions
- EPA regulated compounds
- PVF-CNT//Counter-electrode (CNT or PMAECOCP)

**Quinchlorac**: toxic herbicide

**2,4,5-T**: highly toxic pesticide

**DBS**: chemical detergent

**Ibuprofen**: endocrine disruptor

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**Diagram**

- Quinchlorac
- 2,4,5-T
- DBS
- Ibuprofen

**Red**: Conventional
**Blue**: Asymmetric

**Graph**

- Y-axis: Recovery Fraction
- X-axis: pH

**Results**

- pH values: 4, 6, 8, 10
- Start and End values for each compound

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Tandem selective separation

Tandem removal of cationic & anionic pollutant (μM amount)

Asymmetric Deionization

- Overcoming limitations of traditional CDI (operating @ 5-30 mM)
- Targeting 1 mM concentrations of dilute salts
- Voltage windows 0.8 – 1.2 V

![Graph showing concentration of NaCl over time for different materials](image)

- CNT//CNT
- PVF//CNT
- PVF//PCoCpCb
- PVF//PTCAQ

![Bar graph showing adsorption capacity](image)

- Our results: 1 mM NaCl + 1.5 V, 20 min
- Literature: Comparison with other materials:
  - Cn/Cp
  - CNT/CNT
  - PVF//CNT
  - PVF//PCoCpCb
  - PVF//PTCAQ
  - Farmer (Carbon Aerogel)
  - Li (Graphene)
  - Li (Graphene Oxide)
  - Peng (CNT-mesoporous)
Electro-Swing CO$_2$ Capture
Electrochemically-Mediated vs Thermal Amine Regeneration

- **Electrochemical Process**
  - At **Cathode** (T < 60°C)
  - CO₂ + Amine → Amine/CO₂ Complex
  - At **Anode** (T < 60°C)
  - CO₂ + Metal → CO₂ + Metal Complex
  - Metal + M⁺ → Metal Cathode

- **Thermal Process**
  - At **Desorber** (T > 110°C)
  - CO₂ + MEA + CO₂ → MEA + CO₂
  - MEA + CO₂ + Steam → CO₂ + MEA

- **Diagram**
  - Lean Gas
  - Heavy Gas
  - CO₂
  - MEA
  - MEA + CO₂
  - MEA + CO₂ + Steam
  - CO₂ + MEA
  - MEA + CO₂ + Steam
  - CO₂

- **Equation**
  - CO₂ + Amine → Amine/CO₂ Complex
  - CO₂ + Metal → CO₂ + Metal Complex
  - Metal + M⁺ → Metal Cathode
  - CO₂ + MEA + CO₂ → MEA + CO₂
  - MEA + CO₂ + Steam → CO₂ + MEA
  - CO₂ + MEA + CO₂ + Steam → CO₂ + MEA
  - CO₂ + MEA + CO₂ + Steam → CO₂ + MEA
EMAR CO₂ Capture

Graph showing CO₂ Loading, Φ against Copper Loading, η for EDA, TETA, and AEEA.

Graph showing CO₂ Output (sccm), Applied Potential (Volts), and Time (hours).

Graph showing CO₂ Output (sccm) over time with Applied Current (Amps) and Time (Minutes).

Graph showing Theoretical Max and Experiment lines for CO₂ Absorbed (mL/min) vs. Current (A).
Summary and Future Directions

**Fundamental Advances on Materials Chemistry**
- Discovery of novel redox-materials
- Evaluation of chemical interactions
- Find design rules for selectivity
- Combination of experimental and theoretical tools for understanding

**Engineering Practical Electrochemical Systems**
- Coupling with Renewable Resources
- On-site Implementation & Validation
- Optimize Mode of Operation
- Energy recovery & integration
- Techno-economic Analyses

**Electrode Fabrication & Manufacturing**
- Electronic and ionic currents, high surface adsorption areas, adsorption capacities
- Optimize Electrode film coating & morphology: Long term-stability
- Control of overpotential and overcoming current efficiency limitations

Selective electrochemical separations are promising for energy-efficient operations
- Environmental, biological and fine chemical applications
- Mitigation of pollution of water and atmospheric resources
- Resource recovery and waste valorization

**FUTURE NEEDS**