Water treatment containing organic compounds by coupling adsorption and electrochemical degradation at BDD anode: Sawdust adsorption performance for the treatment of dilute phenol solutions

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Phenolic compounds

Origin: pharmaceutical, pesticides, oil, textiles, painting, dyes, plastic, detergent industries ...

Dangers:
- Highly toxic,
- highly oxygen demanding,
- Carcinogenic, mutagenic, and can cause a severe health hazard to human beings.
Phenolic compounds are generally non-biodegradable.

- Main reagent: the electron
- Complete oxidation (Mineralization): possible
- Transformation of organic pollutants into biodegradable products: possible

Cost, secondary waste ...
Degradation of organic compounds (R)

First Step: \( H_2O \rightarrow OH^+ + H^+ + e^- \)

Second Step: \( R \rightarrow \) Biodegradable compounds + \( CO_2 \)

Anode material
Choice of the anode material: high oxygen overpotential

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Pt</th>
<th>PbO(_2)</th>
<th>SnO(_2)</th>
<th>BDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overpotential (V)</td>
<td>0,27</td>
<td>0,50</td>
<td>0,67</td>
<td>1,27</td>
</tr>
</tbody>
</table>
Electrochemical methods

Low current efficiency for the treatment of dilute solutions

Mass transfer limitations → Not economically viable

Coupling of electrochemical processes with a pre-concentration step is needed

How?
Adsorption-electrochemical oxidation coupling

Objective of the work
Commercial activated carbon

Origin: wood
Particles size: 0.4 mm
Specific area: 980 m²/g
\( \text{PH}_{PZC} = 8.9 \)

Red wood sawdust

Origin: Coniferous trees
(by-product of furniture industry)
Specific area: 0.4 m²/g
Particles size: 0.5-1.12 mm
Phenol

Model compound

$\text{OH}$

\begin{center}
\includegraphics[width=0.5\textwidth]{phenol_image.png}
\end{center}
Batch adsorption

Column adsorption

Electrochemical degradation

Conditions:
- Anode: boron doped diamond (BDD)
- Cathode: cylindrical mesh of platinum
- Electrolyte: Na₂SO₄
**Analytical techniques**

- **High Performance Liquid Chromatography (HPLC)**
- Phenol and its oxidation intermediates

**Characterization of adsorbents**

- Automated gas sorption system
- BET surface
- Cyclic voltammetry
- Electrochemical behavior of the activated carbon paste
**General approach**

- **Adsorption**
  - Kinetics study
  - Adsorption isotherms
  - Saturation of adsorbents

- **Desorption**
  - Study of the pollutants desorption without polarization

- **Electrolysis**
  - Electro-oxidation of pollutants
  - Study of the pollutants desorption under polarization
  - Electrochemical regeneration of adsorbent
Desorption studies
Quantify the long term desorption without polarization.

Simple desorption

![Diagram showing desorption process]

Desorption equilibrium

Desorption kinetic of phenol adsorbed

Dosage of desorbed pollutant

Volume of the solution for each step = 1/4 of the simple desorption volume

In the case of sawdust: Solution used: \( \text{Na}_2\text{SO}_4 \) (neutral pH)

In the case of activated:

The process was repeated 4 times

Materials and Setups

Results and Discussion
Electrochemical degradation of phenol

**Desorption equilibrium**

Desorption kinetic of the pollutant

Electrolysis conditions:
- Anode: BDD
- Cathode: cylindrical mesh of platinum
- Electrolyte: Na₂SO₄ (0.1M) of desired pH
Adsorption kinetics of phenol onto activated carbon and sawdust

The phenol adsorption follows a pseudo-second order kinetic for both adsorbents.

Activated carbon: equilibrium time = 3 days
Sawdust: equilibrium time = 20 min

Activated carbon: \[ q = \frac{1}{(1 + \frac{t}{K})} \]
Sawdust: \[ q = \frac{1}{(1 + \frac{t}{K})} \]

The internal transport of phenol in the pores of activated carbon reduces the pollutant scavenging rate on the activated carbon adsorption sites.

\[ q = \frac{1}{(1 + \frac{t}{K})} \]
**Adsorption isotherms of phenol at 30°C**

Equilibrium data are well represented by the Langmuir isotherm equation.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

- \(C_e\): equilibrium concentration of the adsorbate (mg/L)
- \(q_e\): adsorption capacity (mg g\(^{-1}\))
- \(q_m\): maximum adsorption capacity (mg g\(^{-1}\))
- \(K_L\): Langmuir isotherm constant (L mg\(^{-1}\)).
# Adsorption isotherms of phenol at 30°C

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir constants</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
<td>$q_m/S$ (mg/m$^2$)</td>
<td></td>
</tr>
<tr>
<td>Sawdust</td>
<td>18,2</td>
<td>0,003</td>
<td>45,5</td>
<td></td>
</tr>
<tr>
<td>$S= 0.4$ m$^2$/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>333,3</td>
<td>0,02</td>
<td>0,3</td>
<td></td>
</tr>
<tr>
<td>$S= 980$ m$^2$/g</td>
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</table>

$q_m$ of the activated carbon is the highest

Activated carbon has the highest specific surface

The sawdust is capable to adsorb a higher phenol weight per surface unit
**Phenol desorption**

Desorption kinetics of phenol

**Sawdust**
- pH of the solution: neutral
- 15 min

**Activated carbon**
- pH of the solution: 13
- 5 min

The desorption kinetics of the phenol is very fast.

In the case of activated carbon: maximum desorption rate = 50%

The phenol retained by the activated carbon comes in two states: strongly adsorbed (chemisorption) and weakly adsorbed (physisorption).

Hypothesis: an important part of phenol retained on sawdust is rather weakly adsorbed.
**Phenol desorption**

### Multiple desorption

The % of the desorbed phenol does not exceed 60%.

A part of the phenol adsorption is rather chemical and irreversible.

### Re-adsorption of phenol on activated carbon obtained after multiple desorption

Regeneration efficiency: \( E = 73\% \)

Changes in the properties of activated carbon after contact with NaOH during the desorption steps.

- Adsorptive capacity of the activated carbon after multiple desorption steps is higher than expected (60%) initial adsorption capacity of the fresh activated carbon.

- Fragmentation of the activated carbon particles by stirring.

\[
E(\%) = \left( \frac{E_{\text{obtained}} - E_{\text{expected}}}{E_{\text{expected}}} \right) \times 100
\]

\( E_{\text{expected}} = 60\% \)
**Electrochemical degradation of phenol**

Oxydation of phenol on BDD anode at \(i=0.215\ A/cm^2\)

The experiments of degradation of phenol was carried out in two steps: Simple desorption then Electrolyses with the presence of the adsorbent under galvanostatic conditions.

The total disappearance of the phenol was achieved in the presence of adsorbent.

An part of the initially adsorbed phenol was desorbed during electrolysis.
Electrochemical degradation of phenol

Modeling of phenol degradation in the presence of sawdust

\[ C = C^0 \exp \left\{ \left( k_{des} - \frac{k * S}{V} \right) t \right\} \]

\[ k = 0.0252 \text{ m.min}^{-1} \]

\[ k_{des} = 0.0516 \text{ min}^{-1} \]
Adsorption/electrochemical regeneration cycles

Regeneration efficiency (Re) = (1) Initial adsorption + (2) Electrochemical degradation + (3) Re-adsorption

Adsorption/Regeneration Cycles

Repetition: (2) Electrochemical degradation + (3) Re-adsorption

Electrolysis conditions: i=0.215 A/cm², electrolysis time=5 hours

Phenol/sawdust couple

Regeneration efficiency > 95% after four cycles

Sawdust is more easily regenerated because of its surface properties unlike activated carbon.

Possible electrochemical polymerization of the phenol at the boundary of the activated carbon.
Electrochemical behavior study of activated carbon by cyclic voltammetry

Oxidation of phenol solution on a virgin activated carbon paste

CV of phenol in Na$_2$SO$_4$ (0.5M)

The oxidation peak of phenol disappears completely from the second cycle

Electro-polymerization of phenol on the surface of activated carbon
Electrochemical behavior study of activated carbon by cyclic voltammetry

Electrolyte oxidation on an activated carbon (obtained after multiple desorption) paste electrode

Hypothesis confirmed: the electropolymerization of the strongly adsorbed phenol can explain the deterioration in performance of activated carbon by the obstruction of its pores during the electrolysis.

The Search of other nonconductive adsorbents

Sawdust
Conclusion

**Adsorption study:**

*Both adsorbents (activated carbon and sawdust) follow a Langmuir adsorption isotherm.*

*The maximum adsorption capacity of the activated carbon is 18 times greater than the one obtained with sawdust.*

**Desorption study:**

*An important part of phenol retained on the activated carbon is rather irreversible.*

*An important part of phenol retained on the sawdust is rather weakly adsorbed.*
Conclusion

**Electrochemical regeneration study:**

- The regeneration efficiency of the activated carbon is only 59% after 1 cycle of adsorption and regeneration:
  - Low reversibility of the adsorption.

- Electropolymerization of the phenol on the surface of the activated carbon during anodic electrolysis

- The regeneration efficiency of sawdust is more than 100% at the end of the fourth adsorption-regeneration cycle:
  - Sawdust is easily regenerated because of its surface properties.

- Electrochemical treatment seems to activate sawdust by changing its physiochemical properties.


**Perspectives**

- Understanding the mechanism of sawdust activation.

- The application of this method on other types of organic pollutants.

- Studying the competition of several organic compounds which may be present in a real effluent on their abilities to be adsorbed, desorbed and oxidized.

- Development of a reactor (adsorption+regeneration):
Publications


Thank you