Conducting Polymer /TiO$_2$ Photocatalytic Nanocomposite for Wastewater Treatment

Zlata Hrnjak-Murgić, Vanja Gilja, Zvonimir Katančić, Ljerka Kratofil Krehula

4th SCIENTIFIC SYMPOSIUM WITH INTERNATIONAL PARTICIPATION
"Environmental resources, sustainable development and food production"
Wastewater treatment

- BIOLOGICAL methods
- PHYSICAL methods
- PHYSICAL-CHEMICAL methods
- CHEMICAL methods
Wastewater treatment

- **Biological methods** - decomposition of organic contaminants by microorganisms
  - Bacteria, Fungi ...
  - decompose organic matter by producing a number of different enzymes for reactions such as: hydrolysis, acetogenesis ...
  - used to remove or neutralize pollutants
  - advantages - cost/efficiency
  - disadvantage - difficult to control the process
Wastewater treatment

- **Physical** methods – separation of contaminants
  - **Sedimentation** - using gravity to remove suspended solids from water
  - **Flotation** - ion flotation, precipitate flotation, adsorbing colloid, dispersed-air, electrolytic and dissolve-air flotation
    - removal and/or recovery of ions: heavy and/or precious metals, anions, residual organic chemicals
  - **Adsorption** – using to remove organic and inorganic pollutants
    - adsorbents: natural adsorbents and synthetic
      - charcoal, clay, zeolites or industrial wastes, sewage sludge and polymeric adsorbents
  - **Barriers** processes - deep bed filters and membranes
Wastewater treatment

- **Physical-chemical** methods – chemically bonding of contaminants and separation
  - **Coagulants** - two general categories: aluminum and iron salts based compounds (sulfate, chloride)
- **Coagulation** - colloids neutralize, attract between themselves and then adsorb to the surface of each other
- **Flocculation** is the process of gathering stabilized or coagulated particles to create larger clusters or flocs
Wastewater treatment

Physical and Physical-chemical methods

- **Advantages** – removal of
  - organic and inorganic contaminants
  - heavily polluted water

- **Disadvantage** –
  - high concentration of pollutants needs to be further disposed as hazardous or non-hazardous waste
  - increase of the treatment process price
Wastewater treatment

- **Chemical methods** - primarily processes of oxidation and reduction of contaminants in the polluted waters

- **Include:**
  - chemical coagulation, chemical precipitation, ion exchange, chemical neutralization and stabilization, chemical oxidation and advanced oxidation

- **Advantages** – removal of any organic compounds that are produced as a byproduct of chemical oxidation.

- **Disadvantage** - difficult to remove high concentration of pollutants
Chemical methods

Activity of Photocatalyst in Water

**TiO₂ Photocatalyst**
- activation by UV light (*only 5 % of sunlight*)
- by doping TiO₂ becomes active in visible - solar light
- dopant – conducting polymer – active by Vis light
  - Polypyrrole
  - PEDOT
Wastewater treatment

Synthesis of Conducting Polymer/TiO$_2$ Photocatalytic Nanocomposite

The Process of Photocatalyst Action in Water
Modification of Fly Ash (FA)

To increase:
- specific surface area (BET)
- total volume

To obtain
- good carrier for TiO₂

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET m²/g</th>
<th>Total volume cm³/g</th>
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</thead>
<tbody>
<tr>
<td>FA-0</td>
<td>3,9310</td>
<td>6,312 x 10⁻³</td>
</tr>
<tr>
<td>FA3,5-2</td>
<td>4,7412</td>
<td>14,819 x 10⁻³</td>
</tr>
<tr>
<td>FA3,5-4</td>
<td>3,7481</td>
<td>10,102 x 10⁻³</td>
</tr>
<tr>
<td>FA2-3</td>
<td>2,4110</td>
<td>4,422 x 10⁻³</td>
</tr>
<tr>
<td>FA/T-3</td>
<td>3,4598</td>
<td>7,015 x 10⁻³</td>
</tr>
<tr>
<td>FA/T-3/P</td>
<td>9,8748</td>
<td>13,595 x 10⁻³</td>
</tr>
</tbody>
</table>

To increase:
- 3,5 M HCl
- 0,1 M H₂SO₄ + TEOS
- 0,1 M H₂SO₄ + PEG
SEM micrographs of FA sample:
- FA0: unmodified
- FA3,5-1: modified with HCl – 1 day
- FA3,5-2: modified with HCl – 2 days

Cenospheres covered by carbonate
X-ray diffractograms of FA samples

Quartz (SiO$_2$)
Mullite($\text{Al}_6\text{Si}_2\text{O}_{13}$)
Calcite (CaCO$_3$)

UV photocatalytic activity of FA samples – RR45 dye
Synthesis of FA-TiO₂ photocatalyst

<table>
<thead>
<tr>
<th>Samples - TiB</th>
<th>FA4</th>
</tr>
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<tbody>
<tr>
<td>FA4/16-TiB</td>
<td>16</td>
</tr>
<tr>
<td>FA4/20-TiB</td>
<td>20</td>
</tr>
<tr>
<td>FA4/20-TiB-1</td>
<td>19.8</td>
</tr>
<tr>
<td>FA4/20-TiB-3</td>
<td>19.4</td>
</tr>
</tbody>
</table>

**Photocatalytic activity of FA-TiO₂ samples**

- M - mullite (Al₆Si₂O₁₃)
- Q - quartz (SiO₂)
- A - anatase TiO₂

**X-ray diffractograms of FA-TiO₂ samples**
Synthesis of TiO$_2$-PEDOT

Conditions of the synthesis: time, temperature and oxidant

<table>
<thead>
<tr>
<th>Composite TiO$_2$-PEDOT</th>
<th>Oxidant</th>
<th>Time of polymerization</th>
<th>PEDOT Mass %</th>
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</thead>
<tbody>
<tr>
<td>PEDOT-Ti1</td>
<td>FeCl$_3$</td>
<td>24 h (25 °C)</td>
<td>10</td>
</tr>
<tr>
<td>PEDOT-Ti2</td>
<td>APS</td>
<td>24 h (25 °C)</td>
<td>10</td>
</tr>
<tr>
<td>PEDOT-Ti1 (3d)</td>
<td>FeCl$_3$</td>
<td>72 h (65 °C)</td>
<td>13</td>
</tr>
<tr>
<td>PEDOT-Ti2 (3d)</td>
<td>APS</td>
<td>72 h (65 °C)</td>
<td>15</td>
</tr>
</tbody>
</table>

APS (Ammonium peroxydisulfate)

TG thermograms of TiO$_2$ and PEDOT-Ti1 and PEDOT-Ti2 nanocomposites
FTIR spectra of TiO$_2$ and PEDOT nanocomposites with FeCl$_3$ (PEDOT-Ti1) and APS (PEDOT-Ti2) oxidant

poly(3,4-ethylenedioxythiophene)
X-ray diffractograms of PEDOT

**X-ray diffractograms of TiO2-PEDOT**

SEM images of neat PEDOT with a) FeCl₃ and b) APS
Photocatalytic activity of TiO$_2$–PEDOT catalyst during decomposition of RR45 dye

Under UV radiation

Photocatalytic activity of TiO$_2$–PEDOT catalyst during decomposition of RR45 dye

Under solar radiation

Photocatalytic activity of TiO$_2$–PEDOT catalyst during decomposition of RR45 dye
Photocatalytic activity and TOC of TiO$_2$–PEDOT catalyst during decomposition of RR45 under UV radiation and solar radiation

<table>
<thead>
<tr>
<th>Uzorak</th>
<th>struktura</th>
<th>UV-A fotokataliza</th>
<th>Solar fotokataliza</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>vrijeme obezbojenja</td>
<td>TOC uklanjanje</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>X</td>
<td>60 min</td>
<td>60 %</td>
</tr>
<tr>
<td>PEDOT-Ti1</td>
<td>kristalna</td>
<td>30 min</td>
<td>60 %</td>
</tr>
<tr>
<td>PEDOT-Ti2</td>
<td>amorfna</td>
<td>45 min</td>
<td>59 %</td>
</tr>
<tr>
<td>PEDOT-Ti1 (3d)</td>
<td>kristalna</td>
<td>&gt; 90 min</td>
<td>7 %</td>
</tr>
<tr>
<td>PEDOT-Ti2 (3d)</td>
<td>amorfna</td>
<td>&gt; 90 min</td>
<td>5 %</td>
</tr>
</tbody>
</table>
RESEARCH GROUP

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