Carbon Nanotube-Titanium Nanohybrid Material for Photocatalytic Removal of Organic Pollutants in Water with Mild Salinity Levels

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Outlines

Acknowledgements
Motivation
Method Used
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Conclusions
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Acknowledgements

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The occurrence of pathogenic bacteria in some ships' ballast water incoming from various marine regions to the Sea of Marmara, Turkey

The composition and frequency of antibiotic resistance of pathogenic bacteria, the abundance of heterotrophic aerobic bacteria (HPC) and possible in-situ use of chromogenic agar were investigated in the ships' ballast water coming from different regions of the world to the Sea of Marmara, Turkey for the first time. The samples that were taken from 21 unit ships coming from various marine environments of the Southern China Sea, the Atlantic Ocean, the Mediterranean and the Black Sea to the Sea of Marmara, Turkey in 2009 and 2010 were tested. 38 bacteria species, 27 of them pathogenic bacteria belonging to 17 familia, were detected. *Vibrio cholera* was not detected in the samples. However, the presence of a high number of HPC, including a cocktail of pathogenic bacteria showed that the ships carry a potential risk for the Sea of Marmara.

- Butyltin in Ballast water; *Ocean Engineering*

**Ecological, Environmental, and Public Health Impacts by biological and chemical contaminants in Ballast Water need further investigation**
Ecological, Environmental, and Public Health Impacts of Ballast Water

## Motivation

**Ballast Water and other Contaminated Saline Water**

### Table: Capacity in million tonnes

<table>
<thead>
<tr>
<th>Year</th>
<th>Capacity</th>
<th>Oil tankers</th>
<th>Bulk carriers</th>
<th>General cargo ships</th>
<th>Container ships</th>
<th>Other shipping</th>
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<td>2009</td>
<td>418</td>
<td>109</td>
<td>162</td>
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<td>408</td>
<td>105</td>
<td>145</td>
<td>69</td>
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<tr>
<td>2007</td>
<td>383</td>
<td>101</td>
<td>128</td>
<td>63</td>
<td></td>
<td></td>
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<tr>
<td>2006</td>
<td>354</td>
<td>96</td>
<td>111</td>
<td>53</td>
<td></td>
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<tr>
<td>2005</td>
<td>336</td>
<td>92</td>
<td>98</td>
<td>49</td>
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<tr>
<td>2000</td>
<td>282</td>
<td>64</td>
<td>75</td>
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<tr>
<td>1995</td>
<td>268</td>
<td>44</td>
<td>58</td>
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<tr>
<td>1990</td>
<td>246</td>
<td>26</td>
<td>49</td>
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<tr>
<td>1985</td>
<td>261</td>
<td>20</td>
<td>45</td>
<td></td>
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<td></td>
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<tr>
<td>1980</td>
<td>339</td>
<td>11</td>
<td>31</td>
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</table>

*Capacity in million tonnes*
Photocatalytic Mechanism

Photocatalysis mechanism scheme of semiconductor

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Synthesis of TiO$_2$/MWCNT

- Offer great support for materials with photocatalytic properties
- MWCNTs have high mechanical and chemical stability
  - Extraordinary Semiconductor properties

Doping of TiO$_2$ onto CNT improves photocatalytic properties

Vatanpour et al. Volume 90, April 2012 Separation and Purification Technology Science Direct
Sol-Gel Synthesis

- Sol Gel method is one of the best synthetic pathways for creating homogenously coated small particles with less agglomeration potency.
- The high surface area to volume ratio of CNTs combined with photocatalytic titanium nanoparticles increase the life span of generated ROS that facilitates the overall process of pollutant breakdown in the media.

\[
\begin{align*}
&\text{Measured CNT + Ethanol} \\
&\text{Sonicate for minimum 2 hours} \\
&\text{CNT + Ethanol Sol} \\
&\text{Under continuous stirring} \\
&\text{CNT + Ethanol + TTIP Solution} \\
&\text{Under continuous stirring} \\
&\text{Add TTIP} \\
&\text{Drop wise} \\
&\text{Add NH3} \\
&\text{Dry at 70-100° C until gelled} \\
&\text{Hybrid TiO}_2 \text{ CNT} \\
&\text{Calcine at 400° C for 2 hours} \\
&\text{Final product is fine dry powder}
\end{align*}
\]
Characterization TiO$_2$/MWCNT nanocatalyst

SEM Characterization

- x20,000 (Scale 1µm)
- x 100,000 (Scale 100 nm)
- x 100,000 (Scale 100 nm)
- x 200,000 (Scale 100 nm)
- x200,000 (scale 100 nm)
- x 100,000 (scale 100 nm)
Evaluate TiO$_2$/MWCNTs (MB) degradation with Ultra Violet-Visible Light

UV and visible light irradiation both achieved through use of solar simulator (1-sun)

Solar Simulator provides Visible light (1-sun) irradiation for almost complete degradation of MB
Results-I

MB Removal by $\Delta[\text{TiO}_2:\text{CNT Hybrid}]$ over Time $\Delta$ 0-150 min

- (50:1 TiO$_2$:CNT)
- (20:1 TiO$_2$:CNT)
- (10:1 TiO$_2$:CNT)

89 % Methylene Blue Degradation by TiO$_2$:CNT Ratio 10:1 via Sol Gel Method
Results-II

MB Removal by 50:1 TiO$_2$:CNT, TiO$_2$, and CNT over 150 min

![Graph showing MB removal over time for TiO$_2$ alone, CNT alone, and 50:1 TiO$_2$:CNT hybrid.](image)
Results-III
Efficiency of Nano-Hybrid in Fresh Water

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Wavelength (nm)</th>
<th>Absorption (A)</th>
<th>C/Co</th>
<th>1-C/Co</th>
<th>x 100 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>664.36</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>0</td>
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<tr>
<td>0</td>
<td>663.31</td>
<td>0.622</td>
<td>0.778</td>
<td>0.223</td>
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<tr>
<td>30</td>
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<td>0.411</td>
<td>0.514</td>
<td>0.486</td>
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<tr>
<td>60</td>
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<td>0.292</td>
<td>0.365</td>
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<tr>
<td>90</td>
<td>643.40</td>
<td>0.188</td>
<td>0.235</td>
<td>0.765</td>
<td>77</td>
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<tr>
<td>120</td>
<td>643.40</td>
<td>0.188</td>
<td>0.235</td>
<td>0.765</td>
<td>77</td>
</tr>
<tr>
<td>180</td>
<td>611.95</td>
<td>0.044</td>
<td>0.055</td>
<td>0.945</td>
<td>95</td>
</tr>
</tbody>
</table>
Results-IV
Efficiency of Nano-Hybrid in Saline Water/Salt Water (3.5%, 35g/L, 0.600M)

ΔMB Removal (%) by Salt (NaCl) Concentration for 3 Hours

- MB Removal (%)
- Salt Concentration (%)

Graph showing MB Removal (%) vs. Salt Concentration (%). The graph indicates a decrease in MB removal as the salt concentration increases. Key data points are:

- 0% Salt Concentration: MB Removal is 90%
- 0.50% Salt Concentration: MB Removal is 49%
- 1.00% Salt Concentration: MB Removal is 43%
- 1.50% Salt Concentration: MB Removal is 45%
- 2.00% Salt Concentration: MB Removal is 42%
- 2.50% Salt Concentration: MB Removal is 30%

The graph visually represents the relationship between salt concentration and MB removal, highlighting the impact of salt on the efficiency of the Nano-Hybrid process.
The Effects of media pH on dispersion/extent of aggregation of nano titanium NP measured by Zeta Potential

As the absolute value of zeta potential is larger, many colloidal particles show good dispersability as the electrostatic repulsion becomes stronger. However, as the zeta potential registers close to zero, the particles become unstable and are likely to aggregate. 

(http://www.particulatesystems.com/Products/NanoPlus-DLS/Principle-of-Zeta-Potential-Measurement.aspx)
Results-V

The **Effects of media pH on the Sizes of** Nano-Hybrid aggregates in **Saline Water/Salt Water** (pH 7.5-8.5)

<pH 7</p>

<pH 7</p>

> pH 7
The Effects of Increased Sun Light Energy on Removal Efficiency

Removal Percentage (%) vs Exposure Duration (min)

- 0.05%
- 2.00%
Results-VII

pH Influence on the Removal Efficiency at 4-Sun Exposure

Removal Efficiency (%) vs. Exposure Duration (Min)

- pH 5.1
- pH 6.8
- pH 8.2
Conclusions

• Ti-CNT nanohybrid material (50:1) carries a potential for both fresh water and ballast water decontamination

• For an optimal ballast water (or other saline media) remediation, maintaining pH slightly basic conditions may bring better outcomes

• Retrieval process of nanohybrid compounds during or after usage would need further investigation

• Future targets:
  • Testing hybrid material for pathogens (both bacterial and viral) in saline water including ballast/sea water
  • Titanium or titanium ceramic filter for surface bonding with CNT or graphite later for higher flux condition
  • Method development for more securely bonded hybrid material
  • 2-D support (i.e. graphene)