Combination of one-dimensional TiO$_2$ nanowire photocatalytic oxidation with microfiltration for water treatment

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Contamination due to natural organic matter (NOMs) in surface and ground water is one of the serious problem to be faced during drinking water supply.

NOMs can produce undesirable color and taste, serves as food for bacterial growth and can complex with heavy metals in water.

Coagulation and flocculation are used for the removal of NOMs from water.

The incomplete removal of NOMs from water will results in the formation of chlorinated organic by-products or disinfection by-products (DBP) due to the reaction of chlorine used as a disinfectant. Eg. trichloromethanes, chloroacetic acids, chloropicrin, chlorophenol, mutagen X etc.

This DBPs have emerged as a public health issue because they are carcinogenic.
Photocatalysis using TiO$_2$ has been developed as an alternative technology for water purification.

Nanosized TiO$_2$ photocatalysts have been widely used because of their high photocatalytic activity and chemical stability.

Difficulty in separation, recovery and reuse of these nanophotocatalysts are the significant obstacles for practical applications.

Recently, membrane filtration has been applied for the separation of nano TiO$_2$ from treated water.

Serious membrane fouling occurs by nano TiO$_2$ due to the formation of dense cake layer on membrane surface and membrane pore blocking.

Coating nano TiO$_2$ on inorganic membrane has been used to avoid membrane fouling. However, photocatalytic activity of the immobilized TiO$_2$ was much lower than suspended TiO$_2$. 
In this paper,

- Two types of TiO$_2$ nanowires with different diameters were synthesized via hydrothermal method.

- The feasibility of these two materials as photocatalysts were studied in hybrid photocatalysis/membrane process.

- Their photocatalytic activities were evaluated by photocatalytic oxidation of humic acid (HA), typical NOMs in surface and ground water.

- The membrane fouling caused by photocatalyst was investigated.
Experimental Section

**TiO$_2$ nanowire (TNW$_{10}$ and TNW$_{20}$) Preparation**

Commercial TiO$_2$ powder, Degussa P25 (BET surface area, 50m$^2$/g; particle size, 25 nm) were mixed with 10 M KOH/NaOH.

The resulting suspension was transferred into a Teflon-lined autoclave and stored in the electronic oven for 48 h at 180° C.

The resulting white precipitation was recovered and repeatedly washed by 0.1 M HCl and then deionized water with the assistance of ultrasound.

The TiO$_2$ nanowire was gained after calcination of the neutralized product at a temperature of 600° C.
Photocatalysis

5 mg photocatalyst (P25, \(\text{TNW}_{10}, \text{TNW}_{20}\)) was added to 100 ml of 50 mg/l HA and stirred well.

The suspension was left to experience dark absorption for 30 min.

Low pressure Hg lamp (2000 \(\mu\text{W/cm}^2\)) with primary output of 254 nm was placed into the suspension as UV light source.

The concentration of HA left in the aqueous system at different time interval was measured by detecting the absorption at 436 nm on an UV–vis spectrophotometer.

Total organic carbon content was measured using a total organic carbon analyzer.
Membrane filtration

Microfiltration membrane: ADVANTEC MFS Inc., pore size: 0.20 µm, diameter: 45 mm

Transmembrane pressure (TMP): 0.75 MPa was remained during filtration.

The total volume of TiO₂ suspension for filtration was of 700 mL.

Experimental setup for membrane filtration of P25, TNW10 and TNW20 suspensions.
The turbidity of solution before and after filtration was recorded to calculate the rejection rate of photocatalysts during membrane filtration.

The membrane flux was monitored in order to evaluate the membrane fouling.

The resistance-in-series model was applied to evaluate the fouling characteristics

\[ J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_c + R_p)} \]

- \( J \) is the membrane flux (L/hm²)
- \( R_t \) is the total resistance (m⁻¹)
- \( R_m \) is the intrinsic membrane resistance
- \( R_c \) is the cake resistance
- \( R_p \) is the resistance due to pore plugging
- \( \Delta P \) is the transmembrane pressure (Pa)
- \( \mu \) is the viscosity of permeate (Pa s)
Results and discussions

Characterization

a) FESEM and b) TEM images of TNW$_{10}$, c) FESEM and d) TEM images of TNW$_{20}$. 
<table>
<thead>
<tr>
<th></th>
<th>TNW(_{10})</th>
<th>TNW(_{20})</th>
<th>P25</th>
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<tbody>
<tr>
<td>Diameter</td>
<td>10 nm</td>
<td>20–100 nm</td>
<td>25 nm</td>
</tr>
<tr>
<td>Length</td>
<td>100–300 nm</td>
<td>1–10 μm</td>
<td>25 nm</td>
</tr>
<tr>
<td>BET surface area</td>
<td>76.9 m²/g</td>
<td>36.5 m²/g</td>
<td>50 m²/g</td>
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<td>Crystal phase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase–rutile</td>
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HA concentration over P25, TNW_{10} and TNW_{20} photocatalytic oxidation and photolysis.
TOC removal rate at different oxidation time over P25, TNW$_{10}$ and TNW$_{20}$ photocatalytic oxidation and photolysis.
Membrane filtration for recycling of photocatalysts

Membrane flux over filtration of P25, TNW\textsubscript{10} and TNW\textsubscript{20} suspensions.
SEM images of membrane surface and cross-section after filtration of different suspensions, a,b) P25, c,d) TNW$_{10}$ and e,f) TNW$_{20}$. 
Schematic diagram of membrane fouling caused by P25, TNW$_{10}$ and TNW$_{20}$. 
<table>
<thead>
<tr>
<th>Resistance</th>
<th>Value ($\times 10^{11}$ m$^{-1}$)</th>
<th>Percentage (%)</th>
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<tbody>
<tr>
<td>P25</td>
<td></td>
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</tr>
<tr>
<td>$R_m$</td>
<td>6.2</td>
<td>8.1</td>
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<td>$R_c$</td>
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<td>$R_p$</td>
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<td>2.3</td>
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<tr>
<td>$R_t$</td>
<td>77.0</td>
<td>100</td>
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<tr>
<td>TNW$_{10}$</td>
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<td>$R_m$</td>
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<td>10.7</td>
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<tr>
<td>$R_c$</td>
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<tr>
<td>$R_p$</td>
<td>1.1</td>
<td>1.8</td>
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<tr>
<td>$R_t$</td>
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<tr>
<td>TNW$_{20}$</td>
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<tr>
<td>$R_m$</td>
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<td>$R_c$</td>
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<td>74.5</td>
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<tr>
<td>$R_p$</td>
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<td>1.1</td>
</tr>
<tr>
<td>$R_t$</td>
<td>26.7</td>
<td>100</td>
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</table>
Durability test

HA and TOC removal rates over TNW\textsubscript{10} and TNW\textsubscript{20} photocatalytic oxidation in different cycles.
Two types of TiO$_2$ nanowires with different diameters, TNW$_{10}$ and TNW$_{20}$, were fabricated and used in photocatalytic degradation of HA.

The photocatalytic degradation studies revealed that TNW$_{10}$ and TNW$_{20}$ show excellent photocatalytic activity. 99.5% and 94.7% HA removal rates were achieved by TNW$_{10}$ and TNW$_{20}$ after 90 min, respectively.

The TOC removal rate of TNW$_{10}$ and TNW$_{20}$ were 95.3% and 79.1%, respectively, after 150 min.

The durability test showed TNW$_{10}$ and TNW$_{20}$ were stable on photocatalytic activity.

TNW$_{10}$ and TNW$_{20}$ could be totally separated and recovered by microfiltration with less membrane fouling due to the formation of more porous cake and less pore plugging compared to P25.
Thank you
3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, better known by its historical Name 'mutagen X' or MX, is a chlorination disinfection byproduct that forms from the reaction of chlorine and humic acids in raw water.