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Combination of one- dimensional TiO_2 nanowire photocatalytic oxidation with microfiltration for water treatment


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Introduction

- ❖ 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

TiO₂ nanowire (TNW₁₀ and TNW₂₀) Preparation

Commercial TiO₂ powder, Degussa P25 (BET surface area, 50m²/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 TiO₂ nanowire was gained after calcination of the neutralized product at a temperature of 600° C.

Photocatalysis

5 mg photocatalyst (P25, TNW₁₀, TNW₂₀) 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 $\mu\text{W}/\text{cm}^2$) 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

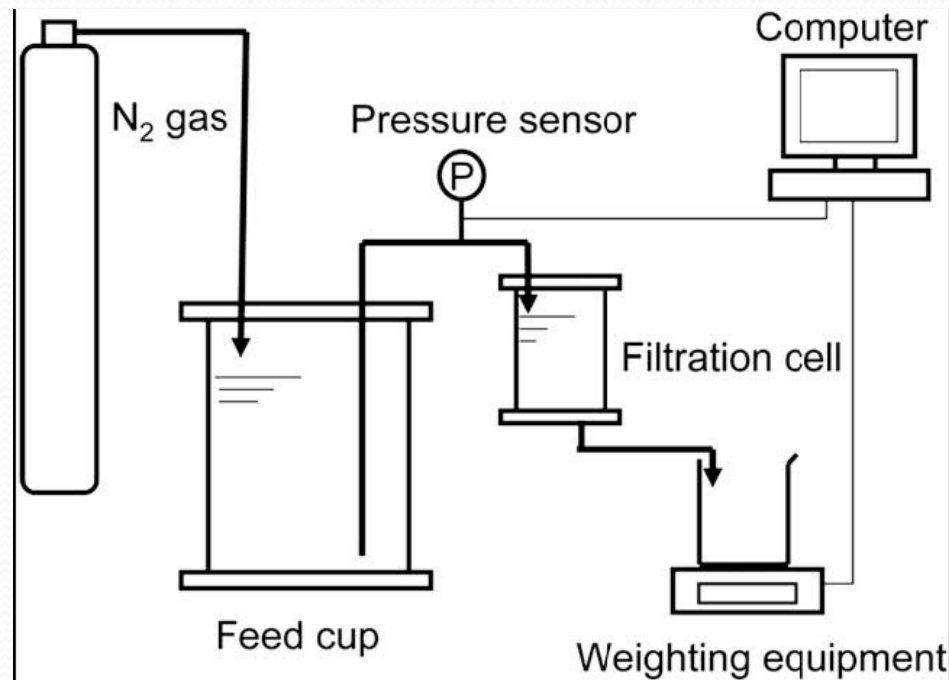
Total organic carbon content was measured using a total organic carbon analyzer

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 TiO_2 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

$$J = \Delta P / \mu R_t = \Delta P / \mu (R_m + R_c + R_p)$$

J is the membrane flux (L/hm²)

R_t is the total resistance (m⁻¹),

ΔP is the transmembrane pressure (Pa)

R_m is the intrinsic membrane resistance

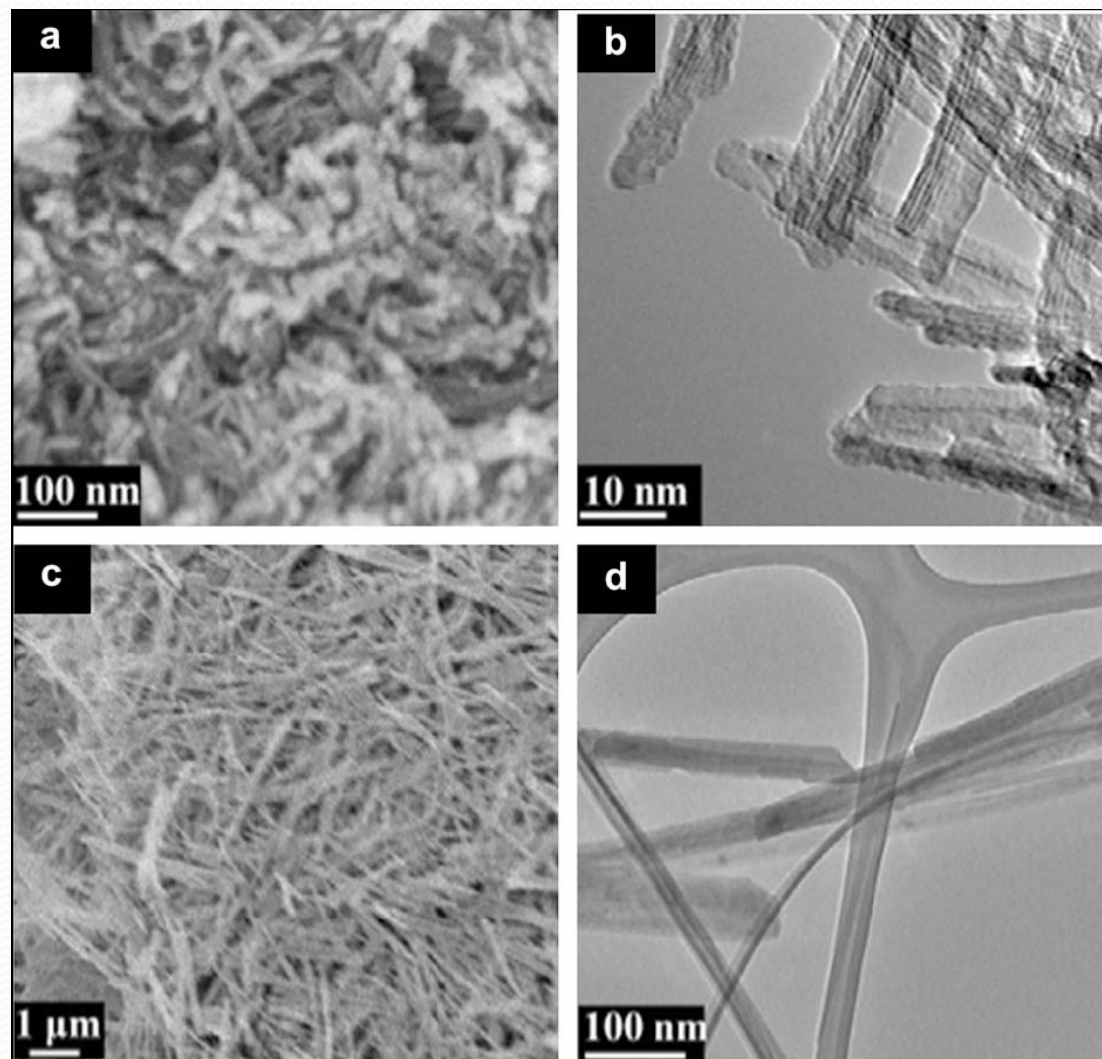
μ is the viscosity of permeate (Pa s)

R_c is the cake resistance

R_p is the resistance due to pore plugging

Results and discussions

Characterization

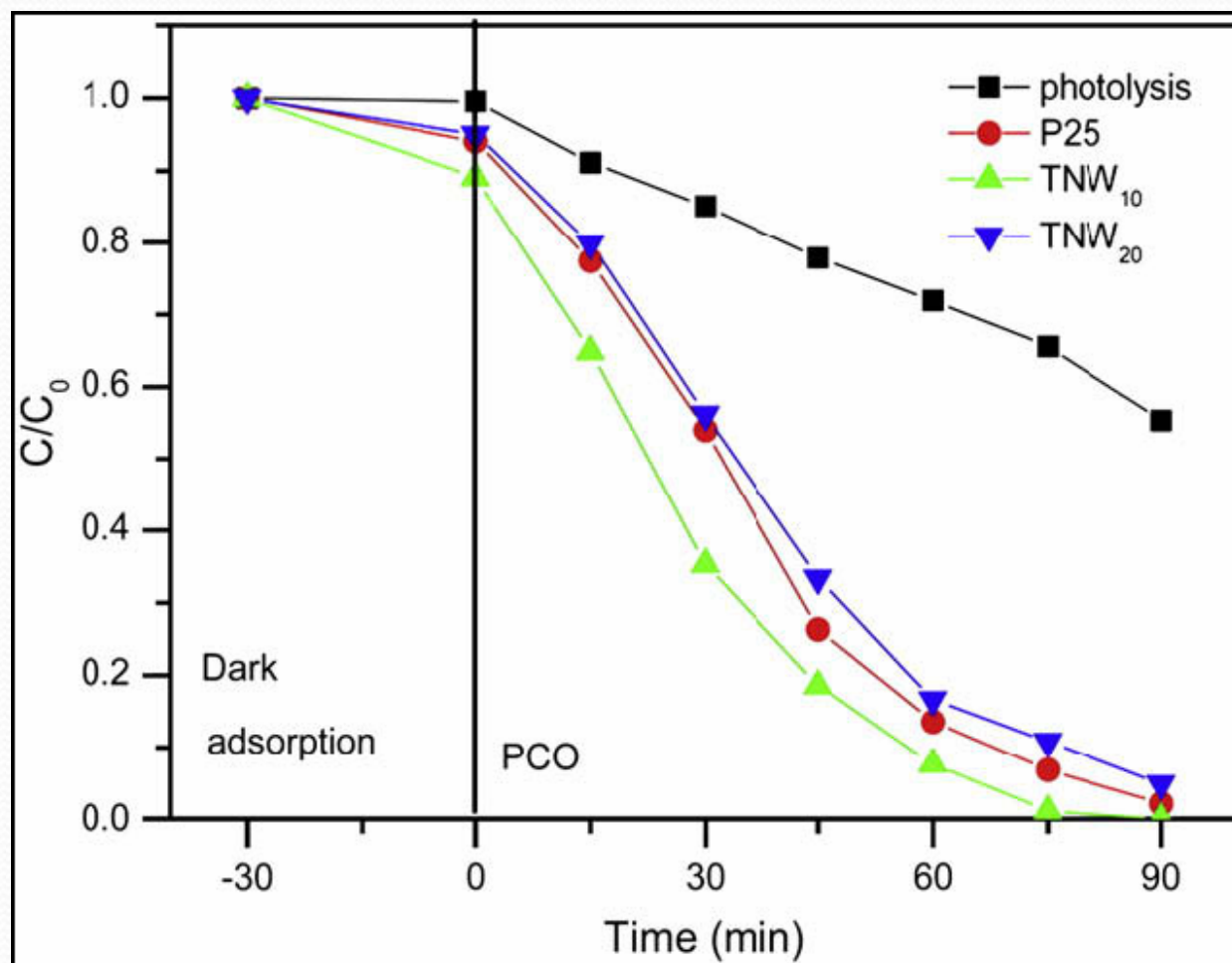


a) FESEM and b) TEM images of TNW₁₀, c) FESEM and d) TEM images of TNW₂₀.

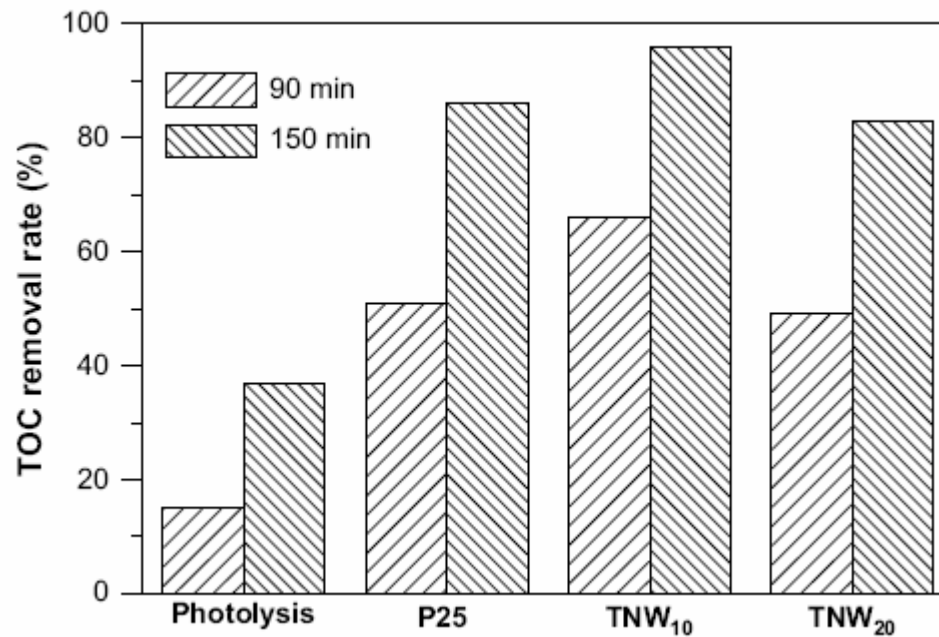
Table 1 – Characteristics of P25 and the two TiO₂ nanowires, TNW₁₀ and TNW₂₀.

	TNW ₁₀	TNW ₂₀	P25
Diameter	10 nm	20–100 nm	25 nm
Length	100–300 nm	1–10 μm	25 nm
BET surface area	76.9 m ² /g	36.5 m ² /g	50 m ² /g
Crystal phase	Anatase	Anatase	Anatase–rutile

Photocatalysis

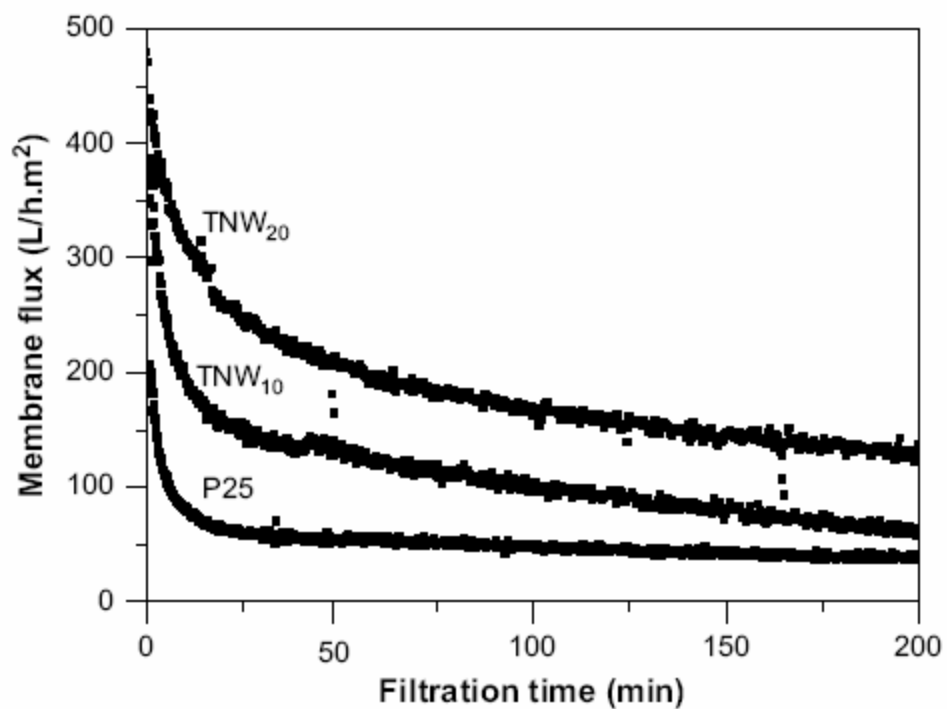


HA concentration over P25, TNW_{10} and TNW_{20} photocatalytic oxidation and photolysis.

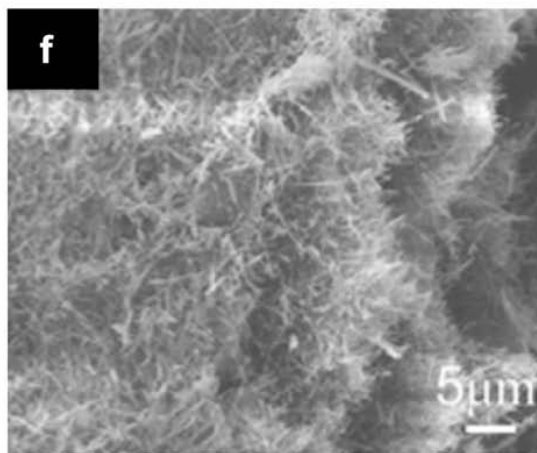
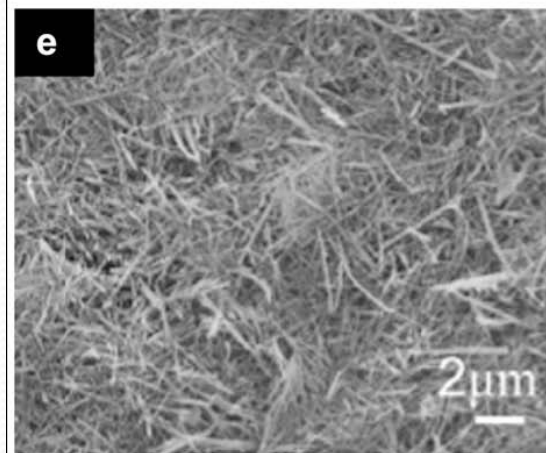
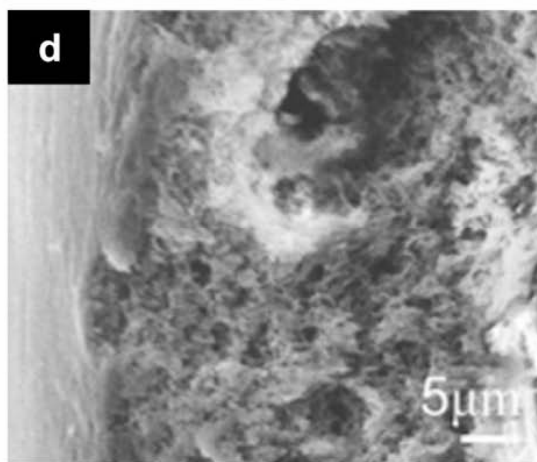
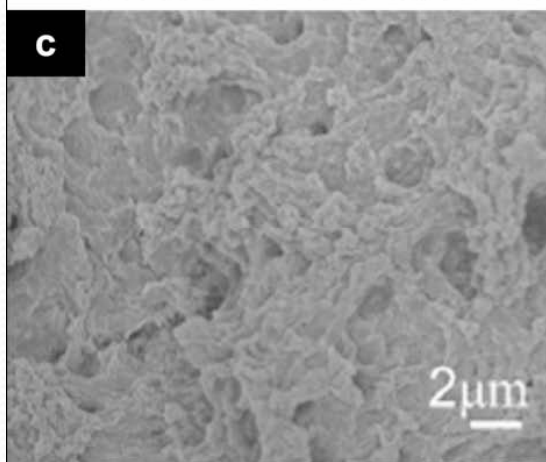
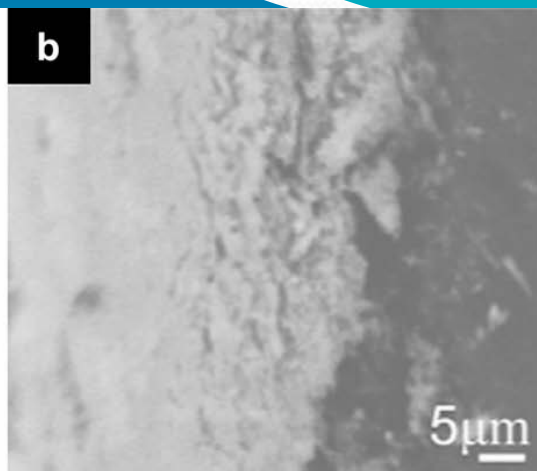
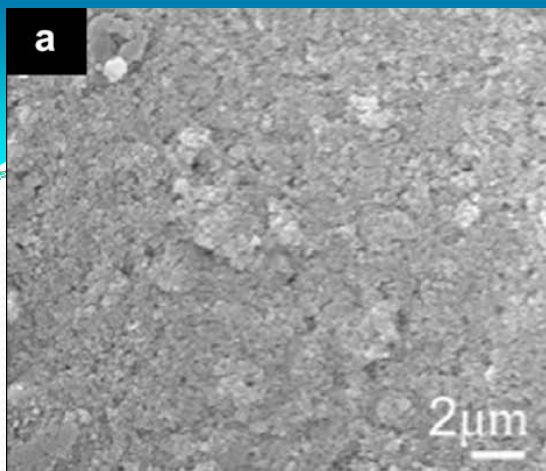


TOC removal rate at different oxidation time over P25, TNW₁₀ and TNW₂₀ photocatalytic oxidation and photolysis.

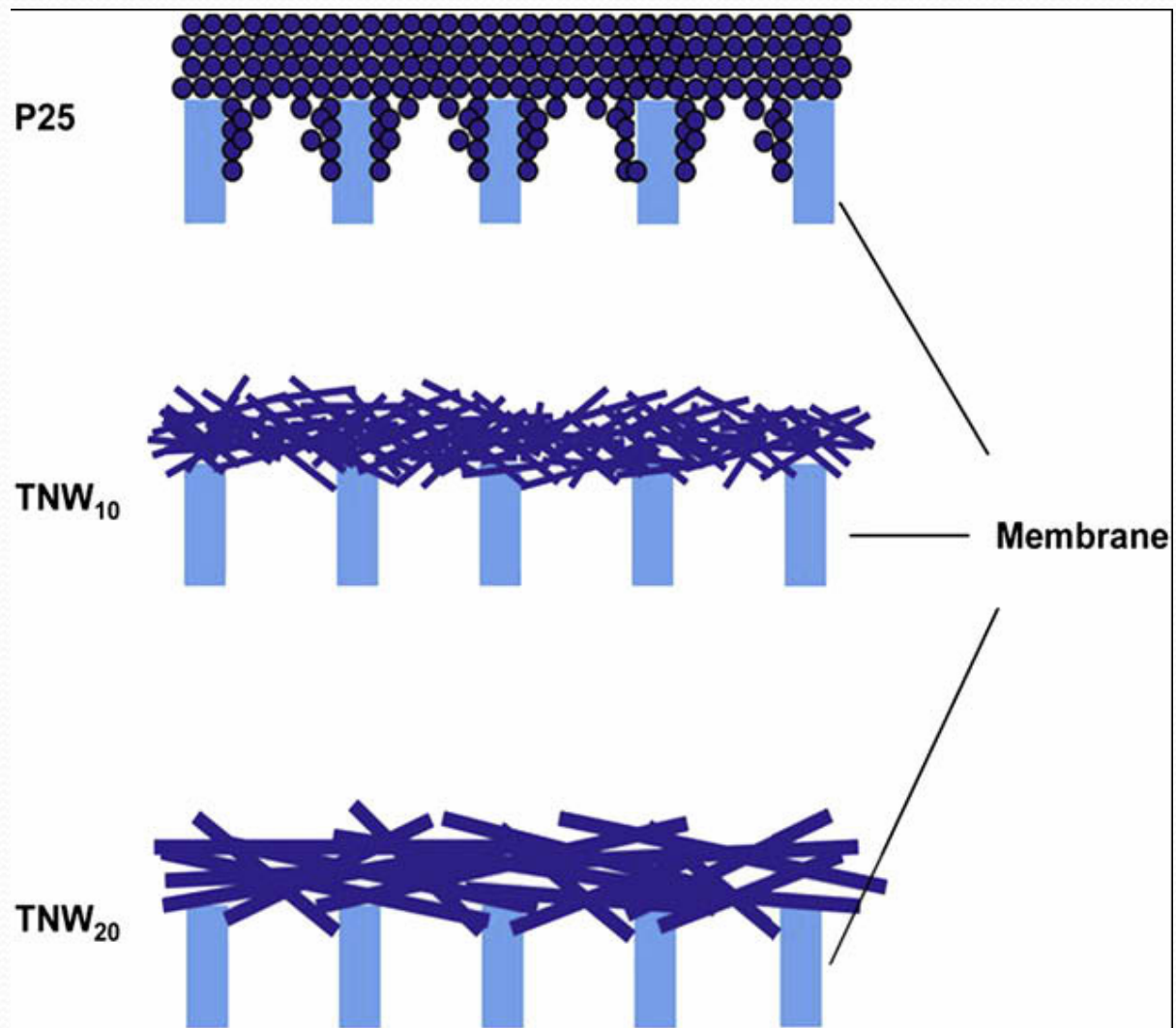
Membrane filtration for recycling of photocatalysts



Membrane flux over filtration of P25, TNW₁₀ and TNW₂₀ suspensions.



SEM images of membrane surface and cross-section after filtration of different suspensions, a,b) P25, c,d) TNW₁₀ and e,f) TNW₂₀.

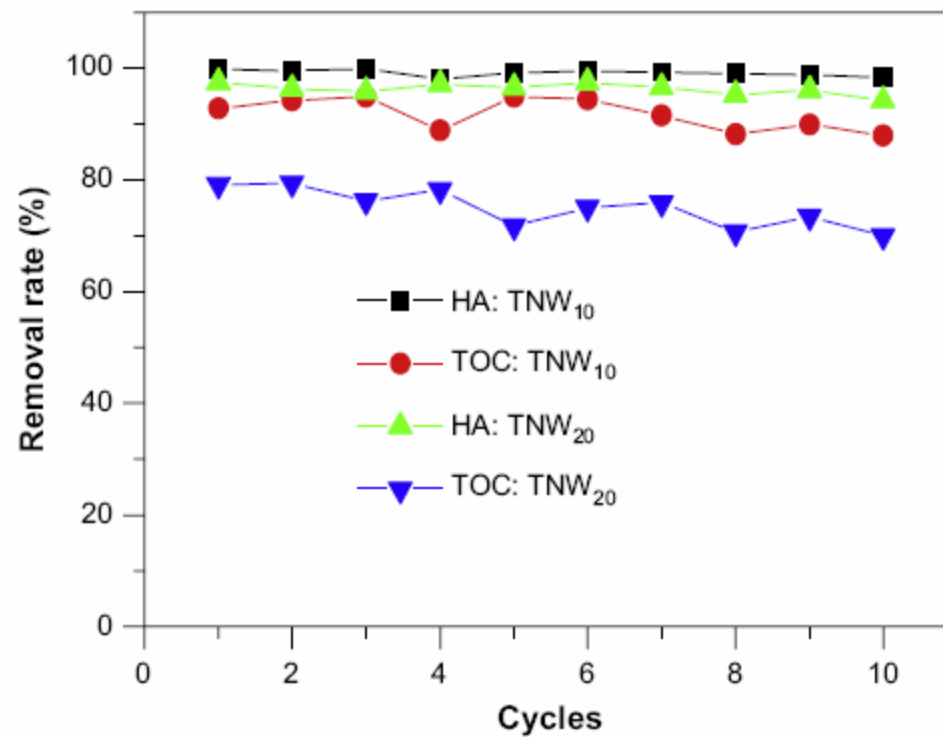


Schematic diagram of membrane fouling caused by P25, TNW₁₀ and TNW₂₀.

Table 2 – Summary of resistances for the MF filtration of P25, TNW₁₀ and TNW₂₀.

Resistance	Value ($\times 10^{11} \text{ m}^{-1}$)	Percentage (%)
P25		
R_m	6.2	8.1
R_c	69.0	89.6
R_p	1.8	2.3
R_t	77.0	100
TNW ₁₀		
R_m	6.4	10.7
R_c	52.3	87.5
R_p	1.1	1.8
R_t	59.8	100
TNW ₂₀		
R_m	6.5	24.4
R_c	19.9	74.5
R_p	0.3	1.1
R_t	26.7	100

Durability test



HA and TOC removal rates over TNW₁₀ and TNW₂₀ photocatalytic oxidation in different cycles.

Conclusion

- ❖ 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(5*H*)-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.

