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Prevention of biofilm formation in water and wastewater installations by application of TiO_2 nano particles coating

Fatemeh Alighaleh Babakhani[a,*], Abdollah Rashidi Mehrabadi[a], Piet N.L. Lens[b], Mohsen Sadatian[a]

[a]*School of Civil Engineering, College of Engineering, University of Abbaspour, Tehran, Iran*
Tel. +989124034773; email: babakhani.fatemeh@gmail.com
[b]*UNESCO–IHE Institute for Water Education, Westvest 7, 2611 AX Delft, The Netherlands*

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ABSTRACT

In this research we tried to prevent formation of a biofilm layer which is the major reason of biological corrosion by using TiO_2 coating. TiO_2 is a photocatalyst material which can produce free hydroxyl radicals and super oxide ions by receiving energy from UV light irradiation. These produced radicals are very strong oxidants which cause oxidation of organic materials, penetration in and deterioration of cellular membranes and cause inhibition of microorganisms and at last prevents the biological layer growth. In this research, TiO_2 thin films with antibacterial activity were prepared on glass slides (width = 2.5 cm, length = 10 cm) by using the sol–gel method. Samples with TiO_2 coating and control samples without TiO_2 coating, placed in the water containing various kinds of microorganism were exposed to UV irradiation. To study the thickness and the amount of biofilm formation the weighting method has been applied. After 30 d monitoring the control samples were covered by biofilm and this layer thickened. After analyzing data, it was shown that the growth of biofilm on the coating samples is less than the control samples. So this study shows that using of TiO_2 coating is an effective way for prevention MIC.

Keywords: Biofilm; Microbial influence corrosion (MIC); TiO_2; Water and wastewater facilities

1. Introduction

All countries around the world are spending a large amount of their national gross income to prevent corrosion or to cope with its effects which often costs about 1–5% of their total national gross product every year. Microbiologically-influenced corrosion (MIC) is one of the corrosion type which includes 40% of corrosion loss. Thus, application of new technologies is necessary in order to reduce the effects of biological corrosion and facing its effects.

Some microorganisms, such as bacteria and algae adhere on the metal surfaces to form a biofilm usually within 3 d. The attached microorganisms excrete extracellular polymeric substances (EPS) which also contributes to the biofilm formation [1]. Biofilm formation creates serious problems of hygiene, odour and taste in cooling water as well as in drinking water systems. The attachment of biofilm on the walls of metal surfaces encourages pitting corrosion of mild steel, copper, etc., and also reduces the heat transfer efficiency of the system [2]. Hence, the microbes should be killed in drinking water or should be removed in water and wastewater system to protect the materials against MIC. MIC occurs as a consequence of heterogeneous biofilm formation [3]. The formation of biofilm can be controlled by addition of biocides viz. sodium thiocyanate, bromine-based compound, ozone or chlorine in water and wastewater system.

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*Corresponding author.

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This treated water will be having toxic components, like chlorination of water leads to the formation of dangerous chlorinated hydrocarbons and ozonization treatment also encourages carcinogenesis. Therefore, alternative technologies are required for water purification for their effective application. Since the biocides are toxic to human beings, cheaper and ecofriendly technology is needed for water and wastewater system. Hence, it is the right time to identify such non-toxic and eco-friendly technology to control MIC in water and wastewater installation. TiO_2 has attracted expensive interest owing to its great advantages in the complete mineralization of organic pollutants in the wastewater. TiO_2 is a popular photocatalyst that has been used widely because of its various metric such as low cost, high photocatalyst activity, chemical stability and non-toxicity [4]. The use of TiO_2 as a biocide was first demonstrated by Matsunaga et al. [5]. Subsequently there have been a number of papers reporting disinfection of bacteria, viruses and other pathogens by photoactive TiO_2. Most of this early work utilized suspensions of TiO_2 to investigate its anti-pathogenic properties [6]. More recently TiO_2 as a thin film has been examined for biocidal activity with the substrate in variably glass [7–10]. When TiO_2 is exposed to ultraviolet light (λ = 365 nm), holes (h_{vb}^+) and excited electron (h_{cb}^-) are generated. The hole is capable of oxidizing water and hydroxide anions into hydroxyl radicals ($OH^\bullet$) [11,12]. $OH^\bullet$ is known to be powerful, indiscriminate oxidizing agent to degrade a wide range of organic pollutants, including aromatics and aliphatic, dye, pesticides and herbicides [4,13,14].

In this research, results are presented concerning the progressive development of a biofilm on a TiO_2 coating in synthetic water in over 30 d.

2. Material and method

2.1. Material

Methyl orange (4-[[(4-dimethylamino) phenyl]-azo] benzenesulfonic acid sodium salt) (MO) was used as soluble organic and its chemical structure is shown in Fig. 1.

Particles of TiO_2 as a photocatalyst were used in the experiment of the photooxidation of organic materials. Average diameter, specific surface area (BET), and density of TiO_2 particles were 20 ± 5 nm, 50 ± 15 m^2/g, and 3.89 g/cm^3 at 20 °C, respectively.

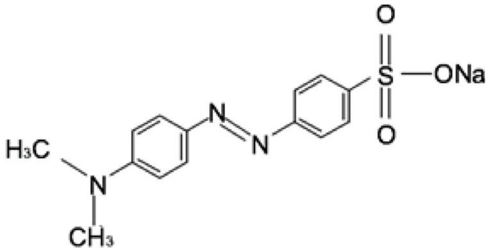


Fig. 1. Chemical structure of MO.

2.2. Preparation of TiO_2 precursor sol

The titanium sol-solution as a binder to enhance the stability of an immobilized TiO_2 particle was prepared by a sol–gel method [15]. Titanium isopropoxide (TTIP, purity over 98%) and ethyl alcohol (purity of 99.9%) were used in the synthesis of titanium sol-solution, respectively. Distilled water and hydrochloric acid (purity of 35%) were used to induce the hydrolysis in the mixture. A 9.47 ml TTIP was dissolved in the mixture containing a 92.14 ml ethyl alcohol and an 8.0 ml HCl, and then 7.5 ml water was added to the mixture. The mixture was stirred for 90 min and then heated up in an autoclave to 200 °C with a rate of 5 °C/min and kept at 200 °C for 1 h, and then the titanium sol-solution was prepared [16].

The titanium sol-solution and TiO_2 particles (P-25) were placed in the mixer and agitated at 1500 rpm. TiO_2 particles as photocatalysts were immobilized onto the glass sample (width = 2.5 cm, length = 10 cm) by using a dip coating method [17], where the coating solution was prepared by mixing TiO_2 particles and the titanium sol-solution at a ratio of 5:95 wt.%. The dip-coater could move the samples into and out of the coating solution by a constant rate of 5 cm/min.

2.3. Deposition of thin films

The TiO_2 film immobilized on the glass sample was dried at room temperature for 30 min and evaporated at 150 °C for 1 h. Finally, it was placed at the calcinations temperature of 500 °C for 1 h, since the adsorption capability was the highest at the calcinations temperature of 500 °C in the preliminary experiment. Then second layer of TiO_2 like previous stages was deposited.

2.4. Photocatalyst decomposition of methyl orange on TiO_2 films

The photocatalytic activity of each sample was evaluated in terms of the degradation of methyl orange. Methyl orange was selected as a model pollutant because it is a common contaminant in industrial wastewater and has a good resistance to light degradation.

The photocatalytic activity of the catalyst under UVA lamp (80 W, 150 cm) was tested using a container with samples under UV-A lamp. The TiO_2 coated glasses were loaded into the container. The solution of methyl orange (40 ml, 5 ppm) was fed into the container and kept at a dark place for 30 min. After 30 min the reactor was irradiated with UV for different time intervals. The samples after irradiation were separated and analyzed with UV–visible spectrophotometery. The differential absorbance at 490 nm for methyl orange (absorption peak of methyl orange) was measured. The change in the concentration of methyl orange of the irradiated sample with time was monitored by UV–visible spectrophotometery and compared with the blank (i.e., glass without catalyst coating was used instead of catalyst coated glass) kept in UV at the same experimental conditions.

2.5. Biofilm formation

Experiments were performed in a photoreactor equipped with a fan to keep a constant temperature of 25 ± 5 °C and a UV-A lamp of 80 W was used as the UV light resource, where its major peak wavelength occurs at 365 nm. The distance between samples and the UV lamp was 30 cm. In the photoreactor there were two channels with 5 l capacities. TiO_2 samples were installed in one of the channels and blank samples were installed in another.

For the formation of biofilm, channels were filled by water without any chlorine. For raising rate of biofilm growth, nutrients were used. The nutrients were added into channels every week. Dilution solution BOD test was used as nutrients source. One ml dilution solution of BOD test was used as nutrients for 1000 ml synthetic water. Amount of BOD_5 for synthetic water was 5 mg/l. This amount was reduced to 2 mg/l by biologic activities at the end of the seventh day. Soil bacteria were used as a source of microorganisms. The turbidity was determined. At first day of the turbidity was 5.5 NTU and it was reduced to 1 at the end of seventh day. For evaluating the biofilm formation on surface of samples, dry weight change was measured according to 2540 G standard method [18]. The weight of samples was measured by a digital balance which has 0.0001 g accuracy.

3. Result and discussion

3.1. Photocatalytic activity

The generally accepted first steps in photocatalytic processes are [2]

$$TiO_2 \rightarrow TiO_2(e^-_{cb} + h^+_{vb}) \quad (1)$$

$$TiO_2(h^+) + H_2O(ads) \rightarrow H^+ + HO^\bullet + TiO_2 \quad (2)$$

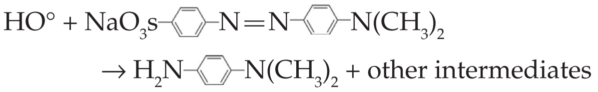
In the presence of adsorbed oxygen, the cathodic process will be the O_2 reduction by conduction band electrons, which can also result in the formation of hydroxyl radicals [2]

$$e^-Cb + O_2 \rightarrow O_2^{-\bullet} \quad (3)$$

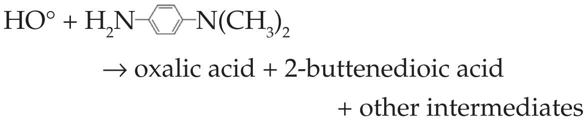
$$O_2^{-\bullet} + 2H^+ + e^- \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 + e^- \rightarrow HO^\bullet + OH^- \quad (5)$$

The main reactions of the photocatalytic degradation of methyl orange have been suggested to be schematically represented by the following scheme [19]



(6)



(7)

$$h^+(HO^\bullet) + \text{oxalic acid} + \text{2-buttenedioic acid} \rightarrow CO_2 + H_2O \quad (8)$$

The photocatalytic degradation of methyl orange under UV irradiation proceeded with the cleavage of the azobond, generating 4-dimethylamino aniline, and then underwent a further opening of the phenyl-rings to form small molecular compounds such as oxalic acid and 2-butenedioic acid, which readily decomposes irreversibly liberating CO_2.

The plot of change in concentration of methyl orange with time of irradiation Fig. 2 shows that by using glass sample without catalyst coating (blank sample) only 1.5% (negligible) methyl orange was decomposed in 28 h but within same time interval the single TiO_2 coated sample decomposed 86.5% of the methyl orange.

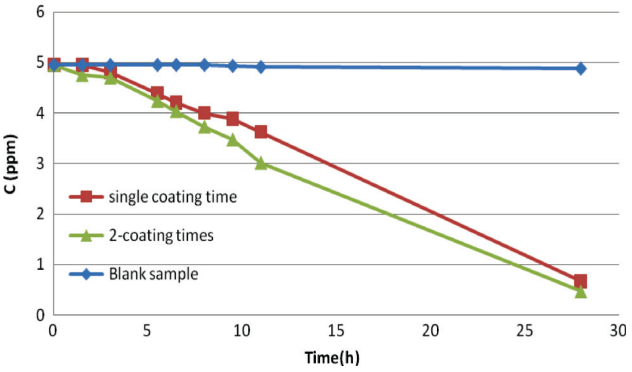


Fig. 2. The change of methyl orange concentration as a function of duration of UV exposure.

Two-coating times TiO_2 sample decomposed 91% methyl orange.

The removal efficiency with two-coating times TiO_2 sample was higher than single coating time TiO_2 sample. Because the TiO_2 concentration on the two-coating times TiO_2 sample is more than the single coating TiO_2 sample. The photocatalytic reaction with respect to the initial concentration can be explained as the reaction rate with an apparent first order [20].

$$r = dC/dt = -KC \tag{9}$$

K is the apparent rate constant. The integral form of the rate equation is

$$In(C/C_0) = -Kt \tag{10}$$

Values of K with number of single and two-coating times were 0.070 and 0.085 h^{-1}. The rate constant (K) of two-coating times is much more than the single coating time, since the real contact area of the OH radical on the photocatalyst increased with increasing TiO_2-film thickness.

Fig. 3 shows the average rate of methyl orange degradation for two-coating times samples at different times, during the experiment. As can be seen in this graph, the degradation rate of methyl orange increased from 0.0001 to 0.0005 mg/h cm^2. It can be explained, due to the decrease in color of methyl orange solution. Reduction in color of solution let the TiO_2 coat to expose easily to the UV. But as the degradation rate is related to the concentration of methyl orange at the end of experiment, the rate of degradation decreased to 0.0003 mg/h cm^2.

3.2. Investigation of biofilm

TiO_2 and blank samples were put in the photoreactor for 30 d. Microorganisms adhered on the glass surfaces to form biofilm in the first days. The results of dry weight tests as dry microbial mass are given in Fig. 4.

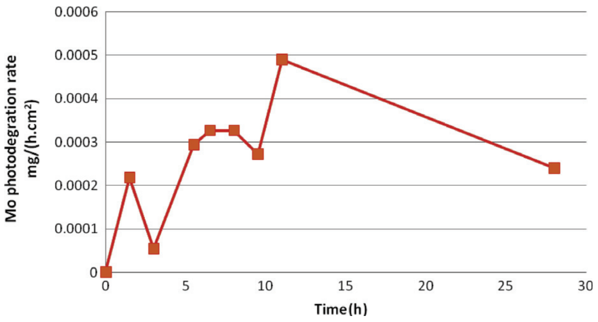


Fig. 3. Methyl orange photo-degradation rate as a function of duration of UV exposure.

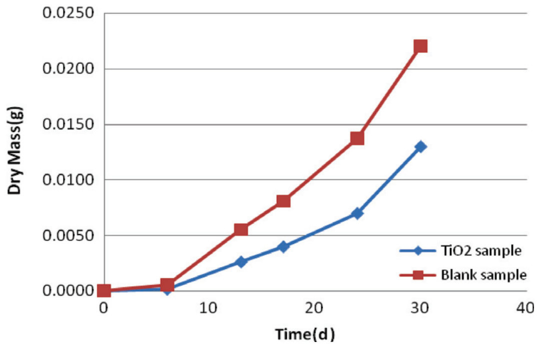


Fig. 4. The change of dry mass weight as a function of duration of UV exposure.

As the results indicate the that amount of microbial mass on blank samples were much more than TiO_2 coated samples.

The hydroxyl radical ($OH^•$) which is generated at the surface of TiO_2 or at the TiO_2/biofilm interface is mainly responsible for the formation of H_2O_2, is expected to destroy the microbes within the biofilm. The hydrogen peroxide produced during the reactions has a short life period, but sufficient to produce significant results in bacterial destruction.

4. Conclusions

Photodegradation of methyl orange and biofilm were done using immobilized TiO_2 particles, where the titanium sol-solution synthesized by a sol-gel method was used as a binder. Numbers of TiO_2 layer on the photodegradation were investigated.

The results are summarized as follows: The apparent rate constants (K) of first order, with the number of single and two-coating times were 0.07, 0.085 h^{-1} for photodegradation of methyl orange. Two-coating times sample under UV lamp can decompose 91% methyl orange and single coating time TiO_2 sample under UV lamp can decompose 86.5% methyl orange.

TiO_2 coating on samples can reduce approximately 50% biofilm on the blank samples. TiO_2 under UV lamp produce hydroxyl radicals and superoxide that are strong oxidant. These materials oxide microbial mass and prevent biofilm formation.

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