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Investigation of water disinfection efficiency using titanium dioxide (TiO_2) in permeable to sunlight tubes

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ABSTRACT

In this study, photocatalytic-solar disinfection using immobilized layer of TiO_2 in the polyethylene tube, which transmits solar UV from itself , is investigated. The aim of this research is surveying the efficiency of these tubes in water disinfection instead of chlorination method supplying drinking water for small communities. Index of coliform was considered as contamination index. This research was based on pilot studies that consist of three tubes. The first one was a polyethylene light-transmitter tube with an interior coating of immobilized TiO_2. Second tube was similar to first tube and had not any TiO_2 coating. Third tube was an ordinary polyethylene tube without light-penetrability coated by TiO_2 layer. At first decomposition of colour solution of methyl orange was investigated. The initial concentration of methyl orange was 4 ppm. Water retention times in tubes were 120, 240 min. For the effect of sunlight intensity, tests were implemented in midday from 11:00 to 15:00. Tests results showed that in the first tube inactivation of the coliforms was 99.01%. The influence of temperature on system's efficiency was obvious. The 4 ppm concentration of methyl orange became less than 0.2 ppm in 12 d.

Keywords: Photocatalytic disinfection; Polyethylene light-transmitter tube; Coliform; Solar UV; Methyl orange

1. Introduction

Study about generating safe and clean water particularly in rural areas with insufficient facilities and finding more cost-effective methods by using clean energies is a necessity. Nowadays, with regard to energy supply crisis as well as existence a clean and renewable energy source with the name of "Sun", man is increasingly considering using this kind of energy. In this regard, advanced oxidation activities have been used as a substitution of current treatment methods in recent years [1].

The main idea of this study has been derived from existing researches carried out on the useful photocatalysts characteristics and also tubes with capability to transmit solar UV. Titanium dioxide (TiO_2) as a photocatalyst is a material with disinfection capability. It produces superoxide and hydroxide by absorbing UV released from the Sun. These hydroxyl radicals have oxidation and disinfection characteristic and therefore are capable to remove pathogenic micro-organisms.

To initiate this process, one TiO_2 layer is fixed on the inner surface of polyethylene tubes which can transmit UV radiation of the Sun. By flowing water inside these tubes contacting TiO_2 layer and UV radiation, existing micro-organisms in the water (water pollution indicator) will be disinfected.

Capability of these kinds of tubes in decomposition of colored methyl orange solution and also in

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disinfection process has been studied in this research. The main objectives of this study are as follow:

- Determining optimized contact time to the surface of TiO_2 to disinfection.
- Study about impacts of environmental parameters such as temperature and solar radiation on disinfection capability of the tubes.
- Study about tube efficiency in decomposing methyl orange color molecules.

To achieve the objectives, retention time variation, seasonal changes, temperature variation and radiation rate were determined.

Titanium dioxide (TiO_2) is one of the most widely used semiconductors for heterogeneous photocatalysis. This is mainly due to its activity, photostability, non-toxicity and commercial availability. It is found in nature and can exist in three crystal modifications: rutile, anatase and brookite. Its composition is temperature dependent: at calcination temperatures above 900 K, anatase modification is transformed into rutile. It has a high surface activity and corrosion stability. The commercial production of this white pigment has been known since the early 1900 s [2].

The photocatalytic activity of TiO_2 is strongly affected by its crystallinity and particle size. Interestingly, only the anatase is sufficiently active in photocatalysis having a band gap energy of 3.2 eV. But rutile can absorb the wavelength near to the visible light. So TiO_2 is active in a part of the wavelength of solar UV-A and all wavelength of the UV-B [2].

When light is absorbed by titanium oxide, two carriers-electrons (e^-) and positive holes (h^+)—are formed. In ordinary substances, electrons and positive holes recombine quickly; however, in titanium oxide photocatalyst they recombine more slowly. One of the notable features of titanium oxide is the strong oxidative decomposing power of positive holes, which is greater than the reducing power of electrons excited to the conduction band [3].

The surface of a photocatalyst contains water, which is referred to as "absorbed water". When this water is oxidized by positive holes, hydroxy radicals (•OH), which have strong oxidative decomposing power, are formed. Then, the hydroxy radicals react with organic matter. If oxygen is present when this process takes place, the intermediate radicals in the organic compounds and oxygen molecules can undergo radical chain reactions and consume oxygen in some cases. In such a case, the organic matter eventually decomposes, ultimately becoming carbon dioxide and water. Meanwhile, the reduction of oxygen contained in the air occurs as a pairing reaction. The reduction of oxygen results in the generation of superoxide anions (•O^{2-}). Superoxide anions attach to the intermediate product in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water [3].

The majority of investigations have been performed using Degussa P-25 TiO_2. This material consists of about 80% anatase and 20% rutile and has a BET specific surface area of 55 m^2/g. The diameter of its particles usually lies between 25 nm and 35 nm. A key technique for simple applications seems to be the preparation of immobilized TiO_2 coatings on different substrates (glass sheets, tiles, etc.) without loss of photocatalytic activity [2].

2. Methods and materials

2.1. Pilot test

This study is based on pilot test. At the first stage, methyl orange solution with 4 ppm concentration is made in the main tank and then injected into the tubes. Then, the injected solution is sampled daily in order to determine absorbsion rate of UV spectrum and its variations. At the second stage, raw water (without any organic substances) is spilled into the main tank. Sodium thiosulfate for chlorine neutralizing and colifrom bacteria add to the tank by dozing pump and microbial stock tank, respectively. After that, contaminated water injected to the tubes. Samples are captured from sampling valves during retention times (Fig. 1).

2.1.1. Raw water tank

Raw water tank is the main water source with the required quality which is injected into the tubes. Volume and type of the tank is 300 l and polyethylene. Water inside the tank is supplied from potable water which was contaminated artificially. Turbidity of the water was determined because effectiveness of TiO_2 is affected by turbidity. An electromechanical mixer is an attachment of the tank which is used to keep it in complete mixing state.

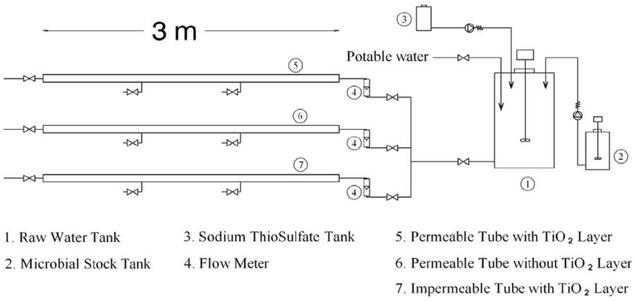

Fig. 1. Schematic layout of pilot test.

2.1.2. Microbial stock tank

To have artificial contamination, polluted water is produced in this tank and then injected into the main tank. Stock tank contains 30 l and is made of polyethylene. Microbial stock consists of colifrom bacteria (water pollution indicator). Fecal colifrom bacteria will be counted in the output results.

2.1.3. Sodium thiosulfate ($Na_2S_2O_3$) tank

This tank with 10 l volume and polyethylene type is used to chlorine neutralization of the water. Amount of added $Na_2S_2O_3$ solution determined according to the Standard Methods for the Examination of Water and Wastewater. A dozing pump is an attachment of this tank which is used for transferring the solution into the main tank.

2.1.4. Tubes

Tubes used in this study are made of three-layered polyethylene manufactured in BasparSan'at Pajooh Company by in-situ co-extrogen mechanism.

As shown in Table 1 , to form a good connection to inner layer of the tubes have been grafted to mineral nano-particles of TiO_2. This compound is about 50% permeable against UV radiation. Layering the inner surface of tube with TiO_2 has been done by fluidized-bed method.

Manufacturing technology and type of fixed TiO_2 layer belong to BaspaSan'at Company. Three tubes were considered to use in the tests, one as the main and two as blank tubes with 3 m length.

2.1.4.1. Permeable tube to solar radiation with TiO_2 layer: It is the main tube used in the test with 3 in. (7.62 cm) in diameter. This tube is permeable to solar radiation and transmits UV light. As said earlier, a TiO_2 layer is fixed inside the tube by fluidized-bed method by manufacturing company. Contaminated water (with colifrom bacteria) of the main tank flows inside the tube and will be disinfected by compounding TiO_2 and solar radiation. Rate of bacteria removal indicates efficiency of this process.

2.1.4.2. Permeable tube to solar radiation without TiO_2 layer: This tube is permeable to solar radiation. But, there is not any TiO_2 layer inside. Bacteria removal occurs because of UV radiation (photolysis) and temperature increasing.

Table 1
Specifications of the tubes used in pilot test

	1	2	3
Layer Substance	Outer HDPE (natural)	Middle MDPE (natural)	Inner HDPE (grafted with natural color)

2.1.4.3. Impermeable tube to solar radiation with TiO_2 layer: This tube layered with TiO_2 but not affected by solar radiation. As said earlier, TiO_2 is a photocatalyst. Actually, TiO_2 activity rate is determined in the absence of solar radiation.

2.1.4.4. Other equipments:

- Flow meter which is used to control flow velocity.
- Sampling valves.
- Inflow and outflow control valves.

2.1.5. Microbial stock

To produce microbial stock, raw wastewater of Shahid Abbaspour University was used. To do this, 1 l fecal wastewater mixed with 100 l raw water. Then, 10 ml of this stock is injected into the main tank.

2.2. Parameters and variables

2.2.1. Exposure time

To compute optimized disinfection time, appropriate exposure times with TiO_2 layer have been determined. The times are 120 and 240 min, respectively. To compute the times, inflows to the tubes regulated as samples would be taken from sampling valves in certain times.

2.2.2. Solar radiation rate

Since tests were directly affected by solar radiation, they carried out under highest intensity of sun radiation between 10:30 and 15:00.

2.2.3. Counting of bacteria

Carried out tests by multi-tube method were done according to the Section 9221 of standard methods. The tests carried out with nine tubes in water and wastewater microbiological laboratory of Shahid Abbaspour University. Total colifrom and fecal colifrom level, were determined in these tests. Collecting samples also carried out according to Section 9060 of standard methods and Section 4208 of Iran Industrial Research and Standard Institute.

2.2.4. Determining Cl_2 level in potable water

To determine the amount of injected sodium thiosulfate, the Cl_2 of the water sample was measured by HACH Pocket colorimeters. To determine the amount of remained Cl_2, we poured DPD pill to the water sample and then measured variation of color of water sample. The amount of remained Cl_2 was 0.4 mg/l. Required sodium thiosulfate rate for injection determined according to the Section 9060 A of standard methods.

2.2.5. Methyl orange decomposition rate by photocatalyst

To determine absorbsion rate of UV in methyl orange solution, a SHIMADZU/UV mini 1240 spectrophotometer from water and wastewater laboratory of Sh. Abbaspour University was used.

3. Results

3.1. Capability of layered tube to decompose methyl orange solution

To study about capability of manufactured tubes, some tests carried out by methyl orange color indicator. Methyl orange is an anionic color containing two aryl groups with 327.33 g/mol molecular weight and $C_{14}H_{14}N_3SO_3Na$ formula and melting point in 300 °C temperature. It is one of the major pigments because of good stability and therefore used in many textile and printing industries [4]. This test has been done in August with intensive sun light and clear sky.

3.1.1. Computing longest wavelength

Appropriate wavelength to determine methyl orange concentration was computed 460 nm by estimating absorbsion rate within UV spectrum. Then, calibration curve had been drawn for various methyl orange concentrations.

3.1.2. Variation in methyl orange concentration

To carry out this test, 100 l of methyl orange solution was generated with 4 mg/l concentration and then, transferred to three test tubes. The tubes were exposed to solar radiation. Each tube contained about 10 l of the solution. Sampling was done from each tube every day. Absorbsion rate was recorded at wavelength of 460 nm by spectrophotometer.

As seen in Fig. 2, variations recorded within 12 d. Different functions of the tubes were obviously clear. Permeable tube with TiO_2 layer was capable to decompose methyl orange solution completely while impermeable tube with TiO_2 layer and permeable tube without TiO_2 layer were not, namely TiO_2 is not activate in the absence of light.

However, it should be noticed that reactivity of permeable tube with TiO_2 layer also should be improved with regard to the volume of decomposed solution (10 l), TiO_2 amount inside the tube and solar radiation rate (August).

DIV—factor in Fig. 3 defines by following equation:

$$DIV = (C_0 - C)/C_0 \quad (1)$$

where C_0, concentration of initial sample of methyl orange solution; C, concentration of methyl orange solution captured in different days.

The activity of permeable tube with TiO_2 layer has been specified by this graph in different days. As seen in Fig. 3, decomposition rate was faster within first four days as well as slope of the graph. This slope has been declined gradually.

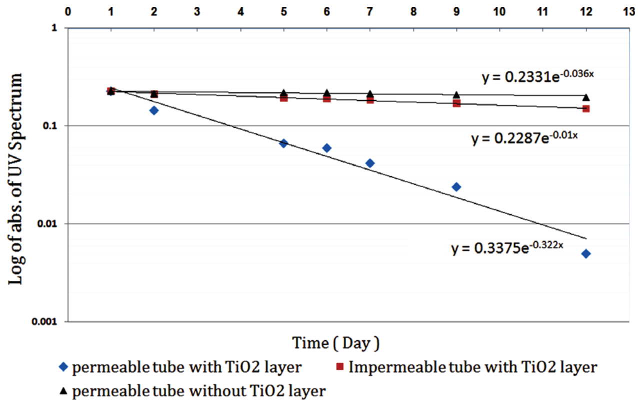

Fig. 2. Comparison of absorbsion rate in each tube.

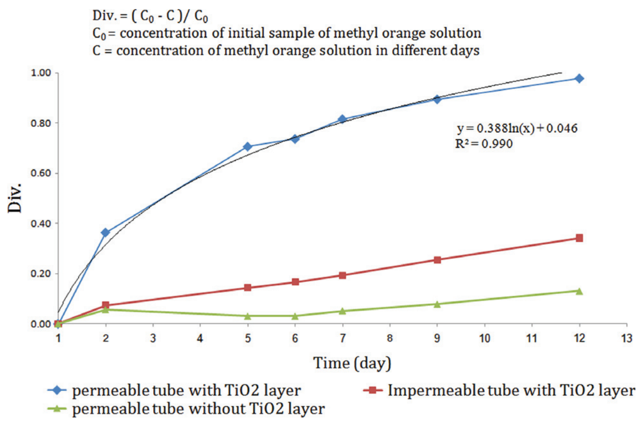

Fig. 3. Variation in concentration of methyl orange solution.

This was probably because of long contacting time of the solution and TiO_2 which caused consequently reduction of contacting surface due to not solution mixing. This was also because of decreasing methyl orange pigments inside the solution. Therefore, variation of absorbsion rate will not be recognizable.

3.2. Capability of tube with TiO_2 layer in water disinfection

Capability of tube with TiO_2 layer in water disinfection had been studied as the main objective at the second stage. To do this, about 100 l water contaminated with colifrom bacteria and then injected into the tubes. Test was carried out between 10:30 and 14:30 when there was intensive solar radiation. The weather was totally clear. Tests were iterated for five times during late August to late September. Variables related to two different times (120 and 240 min). Turbidity was 1 NTU in all tests. Only, temperature changed into 10 °C colder by changing season.

In Fig. 4 N_0 is the number of counted bacteria entering into the tubes, N is the number of counted bacteria in taken samples in different times.

Sampling has been done in two 120 and 240 min times for this test. This graph has been drawn according to the average of recorded data in the test.

As shown in Fig. 4, reactivity of permeable tube with TiO_2 layer is higher than two other tubes. Theoretically, microbial killing characteristic of two other tubes should be much less than this level. But, reactivity of impermeable tube with TiO_2 layer and permeable tube without TiO_2 layer is because of high temperature of the water inside these tubes. The temperature reaches over 40 °C. On the other hand, retention time is 4 h. This caused bacteria removal.

With regard to above-mentioned explanations, there seemed some uncertainty in studying about the main tube (permeable tube with TiO_2 layer) reactivity condition. However, this tube was more active than the two other tubes. At last, it could be said that TiO_2 is not as capable as it must be and therefore, there should be some technique taken in order to have a better efficiency.

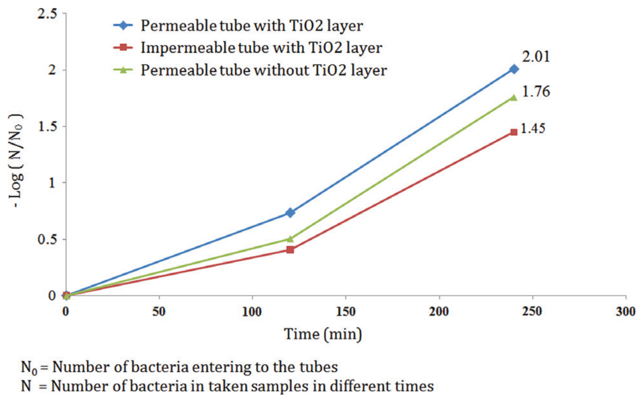

Fig. 4. Bacteria variation logarithm.

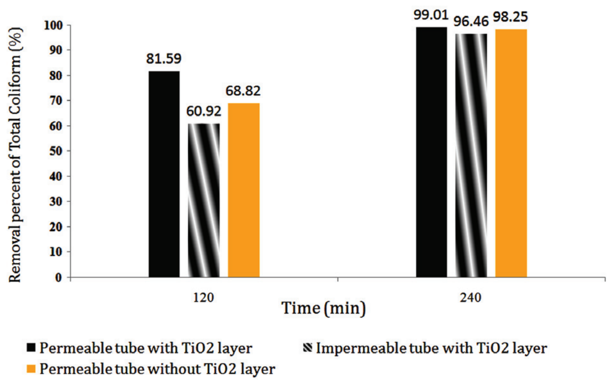

Fig. 5. Bacteria removal percentage.

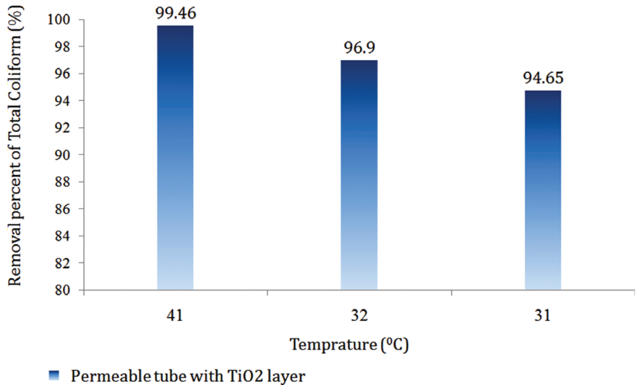

Fig. 6. Bacteria removal according to the temperature.

Difference level between tubes operation in different times are shown in Fig. 5. In these tests, temperature of the sample was averagely 31 °C and 37 °C in 120 and 240 min, respectively. Difference in bacteria removal percentage in permeable tube with TiO_2 layer and other two tubes in 120 min in comparison with 240 min was appeared because of temperature variations. According to the graph, 99.01% percentage bacteria removal in permeable tube with TiO_2 layer in 240 min indicates high capability of disinfection but not desired.

To define effect of temperature on disinfection process in tubes with TiO_2 layer, reactivity of the permeable tube with TiO_2 layer was compared in different temperature (Fig. 6). Temperature effect in bacteria removal process is clearly specified. Temperature has a synergic effect in bacteria removal. It should be noticed that, the temperature variation is occurred because of seasonal change and consequently solar radiation rate (it reduced).

4. Conclusion

- According to the results, tubes with TiO2 layer has photocatalytic reactivity to degrade pigments and to disinfect water. By comparing this study to other carried out studies, effectiveness of the tubes should be seemingly improved. However, tests in all previous studies had been done only about photocatalytic reactivity of TiO2, but in this study, the objective is to produce tube with photocatalytic treatment capability. Glass reactors had been used in all previous researches while polyethylene tubes were used in this study with reasonable efficiency. Therefore, it could be concluded that an application method is being presented in photocatalytic disinfection of the water by this study.

- Impact of environmental parameters on reactivity of disinfection of the tube is clearly seen. Parameters such as temperature and solar radiation rate which increase disinfection capability of the tube. Temperature increasing induced higher and better effectiveness.
- There are tubes which are capable to transmit solar UV. But by using photocatalytic reactivity of TiO_2 layers, a new method in disinfection of water has been invented. This method is a beginning of new ways in using solar energy in water and wastewater treatment and consequently saving energy by reducing consuming energy and chemical substances as well as generating lower value of byproducts of disinfection. This method can be applied widely in water and wastewater treatment in the future if the weak points are defined and improved.

Acknowledgements

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