TESTING THE PHOTOCATALYTIC ACTIVITY OF TiO₂ NANOPARTICLES WITH POTASSIUM PERMANGANATE SOLUTION

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Abstract

Heterogeneous photocatalysis is a new promising alternative method of removing of organic compounds especially from water by using an irradiated dispersion of titanium dioxide. This field is in the foreground of an increasing interest of basic as well as applied research. This paper is focused on testing photocatalytic activity with a manganometric titration.

Keywords: titanium dioxide, potassium permanganate, hydrogen peroxide, photocatalytic activity

1. INTRODUCTION

1.1 Photocatalysis

Photo-catalysis is photochemical reaction. The acceleration of this reaction is escorted by present the catalyser. Photochemical reaction is inviting absorption of lights by materials, which molecules absorbed energy are broken up to radicals, ions or atoms.

In actual time is a photo activity of nano particle TiO₂ in front of scientific interests, on the score of hers general using in the area of innovate environment. Titanium dioxide belongs to mostly used photo-catalysers. Photo-catalytically an effect of TiO₂ by the instrumentality of UV radiation at the normal temperature makes it possible to oxidative decomposing of organic structures and also bacillus. [1] The result of these effects is broken of all organic materials to elemental inorganic components. The superhydrophily induced by photo-catalytically way is the next important property of TiO₂. It offers a lot of possibilities of practical application.

Photo-catalytically reactions are exploited on cleaning of waters, air act. This technology is able to prevent contaminate of outside wall of buildings and also to compared way tunnels, to prevent misting of frontal glass and driving mirror at the cars and next undesirable effects with grow black glass covering of lamps in moto. [2]

Fig. 1 Schematic diagram of the mechanism for the photocatalytic action of nano-structured TiO₂ [3]
When a semiconductor, such as TiO\textsubscript{2} absorbs a photon of energy that is equal to or greater than its band gap width, an electron (e\textsuperscript{−}) may be promoted from the valence band (VB) to the conduction band (CB) thus generating an electron vacancy – “hole” (h\textsuperscript{+}). The electron and the hole can migrate to the catalyst surface where they participate in redox reactions with different species adsorbed on catalyst surface. Holes can react with surface-bond H\textsubscript{2}O or OH\textsuperscript{−} to produce the hydroxyl radical OH\textsuperscript{−} whereas electrons during reaction with oxygen can generate superoxide radical anion O\textsubscript{2}\textsuperscript{−}. The hydroxyl radicals (OH\textsuperscript{−}) and superoxide radical anions (O\textsubscript{2}\textsuperscript{−}) are supposed to be the primary oxidizing species in the photocatalytic oxidation processes.[4]

### 1.2 Principle of manganometric method

An electron is generated when an acidic solution is irradiated in the presence of titanium dioxide. This electron reacts with molecular oxygen and forms superperoxide ion which transforms into hyperperoxide ion and then forms hydrogen peroxide which is decomposed by the present electron. [5]

\[ e^- + O_2 \rightarrow O_2^- \]  \hspace{1cm} (6)

A process with a similar principle to the one used in a manganometric determination of hydrogen peroxide concentration where H\textsubscript{2}O\textsubscript{2} reacts with KMnO\textsubscript{4} at room temperature in a solution acidified by H\textsubscript{2}SO\textsubscript{4} and forms a manganate salt was designed based on this theory. The O\textsubscript{2} molecule is released during this reaction and the autocatalysis by manganate ions occurs.

\[ O_2^- + H^+ \rightarrow HOO\rightarrow H_2O_2 \]  \hspace{1cm} (7)

\[ e^- + H_2O_2 \rightarrow (H_2O_2)^- \cdot \rightarrow HO^- + OH^- \]  \hspace{1cm} (8)

Hydrogen peroxide forms as a bi-product of a radical reaction during the irradiation of the acidic solution of potassium permanganate with the addition of photoactive titanium dioxide and immediately reacts with the present KMnO\textsubscript{4}. The decrease of permanganate is then determined by titration by hydrogen peroxide and the percentage of degradation of KMnO\textsubscript{4} is calculated from the volume of hydrogen peroxide used during the titration. The effect of permanganate concentration as well as the amount of TiO\textsubscript{2} was observed in this research.

### 2. EXPERIMENT

#### 2.1 Materials

Titanium dioxide photocatalyst (P25, 80% anatase, 20% rutile, specific surface area of 50m\textsuperscript{2}g\textsuperscript{−1}) was supplied Degusa Co. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), potassium permanganate p.a. (KMnO\textsubscript{4}), sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) were purchased from Lach - Ner, s.r.o. (Czech Republic). Deionized water was used throughout.

For filtration was used glass filter (por size 0.2 – 2 μm).

#### 2.2 Light source

Light source was used a lamp from Bandelin Co. D – 69168 Wieslich, type N – 36 K. It gives radiation with wavelengths 254nm with performance 4x6 W.
2.3 Procedures

Testing was conducted on a Petri dish. The Petri dish was added 10 ml potassium permanganate solution, 10ml of sulfuric acid and a few drops manganese sulphate (catalyst) and a defined amount of titanium dioxide. At certain time intervals was tested by loss of potassium permanganate titration of hydrogen peroxide.

The results were evaluated by percentage of degradation.

\[
PD_{KMnO_4} = \frac{V_0 - V_1}{V_0} \cdot 100
\]

\[V_0 \text{ volume of hydrogen peroxide before UV irradiation}
\]
\[V_1 \text{ volume of hydrogen peroxide after UV irradiation}
\]

Also, an experiment was performed with potassium permanganate (0, 1 g.l\(^{-1}\)), when a solution was filtrated after UV irradiation. This test was a reference test. After the filtration solution of permanganate, absorption was measured.

\[
PD_{KMnO_4} = \frac{A_0 - A_1}{A_0} \cdot 100
\]

\[A_0 \text{ absorption of potassium permanganate before UV irradiation}
\]
\[A_1 \text{ absorption of potassium permanganate after UV irradiation}
\]

3. RESULTS

3.1 Effect of concentration KMnO\(_4\)

Particles of TiO\(_2\) were dispersed in ultrasonic homogenizer (Bandelin, Sonopuls HD 3200). TiO\(_2\) (0,1g) was added to a solution of potassium permanganate (0,1 g/l; 0,5g/l; 1g/l). Degradation of KMnO\(_4\) was observed by a titration of hydrogen peroxide. Amount test substances were 10ml KMnO\(_4\) and 10ml H\(_2\)SO\(_4\). Irradiation time was 0, 5, 10, 20 and 40 min.

Lowest concentration of TiO\(_2\) degrades half KMnO\(_4\) after 1,5 min, concentration 0,5 g.l\(^{-1}\) after 10min and concentration 1 g.l\(^{-1}\) after 10min.

3.2 Effect of concentration TiO\(_2\)

Different amount of TiO\(_2\) (0,1g; 0, 01; 0,001g) was tested on the solution potassium permanganate with a concentration 0, 1 g.l\(^{-1}\).

Radiation was transformed by the biggest weight TiO\(_2\) largely on hydrogen peroxide and a rate of decomposition KMnO\(_4\) is maximal for the intensity. Curves don’t show large deviations.
It can come to reduction of formation of hydrogen peroxide by the weight 0.001g TiO$_2$. Energy will be used for degradation of dirt and it will be not absorption. It is obvious that the use of the incident radiation would be enough on the weighed 0.01 grams of TiO$_2$.

**Fig. 4** Graph of different concentration TiO$_2$ after the irradiation UV

### 3.3 Titration versus filtration

We can see in graph comparison two real curves. During the filtration may change action of incident light. This may affect the result.

**Fig. 5** Curves for two different methods of measure photocatalytic activity

### 3.4 Decomposition of potassium permanganate by UV radiation

It was tested the influence of potassium permanganate solution without the addition of titanium dioxide. The test was used for two solutions of potassium permanganate at concentrations 0; 1; 0, 5; 1 g/l. Potassium permanganate decays without TiO$_2$. Therefore it was performed a correction.

It can be assumed that both production of H$_2$O$_2$ and decomposition KMnO$_4$ are in parallel.

**Fig. 6** Decomposition of potassium permanganate by UV radiation without TiO$_2$
Therefore model of kinetic was proposed. The kinetic of the degradation rate is described by first order reactions. Reactions are characterized then the rate is directly proportional by concentration only one of the reactants. The concentration of reactants is decreasing exponentially with time. [6-8]

The reaction rate constant is \( k = (k_1 + k_2) \).

\[
\frac{dc}{dt} = k \cdot c \quad \Rightarrow \quad c = c_0 \cdot e^{-kt}
\]

- \( k_1 \) the reaction rate constant of KMnO\(_4\)
- \( k_2 \) the reaction rate constant of H\(_2\)O\(_2\) and the disintegration of KMnO\(_4\)
- \( k \) the reaction rate constant of the experiment

To correct were used the calculated constants \( k_2 \), which were substituted back into equations of lines of concentration. Decomposition of potassium permanganate is not a linear function of time, but has an exponential course.

![Fig. 7 Decomposition of potassium permanganate by UV radiation without TiO\(_2\) after a correction](image)

4. CONCLUSIONS

This method has several advantages compared to other methods. The evaluation of photocatalysis is faster using this method, then by using methods based on decolorisation of dyes. It is not necessary to separate TiO\(_2\) particles since their presence doesn’t affect the titration.

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LITERATURE