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Synergetic water purification modulus for the methylene degradation in the water-methylene mixtures

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Abstract: A simple and compact module has been designed and tested for the implementation of a synergetic process of water purification using the example of methylene impurity in a methylene-water mixture under the simultaneous action of ozonation, ultraviolet radiation, ultrasound, and nanomaterials based on the TiO_2 photocatalyst. It has been shown that adding TiO_2 nanopowder to the mixture dramatically accelerates the process of methylene degradation, with the simultaneous action of the other three factors of the synergetic process. Internal surfaces of iron modulus were covered using electroless technology by Ni-TiO_2 layer, which proved to be a good photocatalyst and having good cohesion and abrasion resisting properties. By selecting the composition of the used photocatalyst and combining different water purification mechanisms, it is possible to obtain an environmentally friendly technology to purify drinking and technical water. The use of modulus ensures the continuity of the water disinfection procedure since cleaning of the elements located in the chamber from various types of dirt is completed during the operation of the device and does not require interruption of the technological process. The outlet removes the dirt and other particles from the sterilization chamber.

Keywords: *Electroless, Photocatalysis, Synergy modulus, Titanium dioxide, Water purification.*

1. Introduction

The rapid growth of the global population and industrialization have led to a concomitant increase in environmental pollution. It becomes crucial to find ways to mitigate pollution, provide a clean and safe environment for humans, and supply renewable, sustainable, and ecologically valid energy sources.

The disposal of dye-contaminated wastewater is a major concern around the world for which a variety of techniques are used for its treatment.

The production and application of photocatalytic nanopowders are considered the most promising direction for resolving the mentioned problems [1, 2]. This is predetermined by their properties: low cost, environmentally friendly process, and lack of secondary contamination. The photodegradation of dyes is regarded as a promising technology for industrial wastewater treatment. This technology demonstrates the light-enhanced generation of charge carriers and reactive radicals that non-selectively degrade various organic dyes into water.

Photocatalytic nano powders, from light absorption, acquire oxidizing properties, which makes them able to decompose water into hydrogen and oxygen [3] and subsequent redox reactions with adsorbed species on the catalyst perform the destruction of bacteria and viruses.

Nowadays a topical problem is the increase of efficiency of the photocatalytic reaction. Titanium dioxide TiO_2 is believed to be the most promising substance as the basis for efficient photocatalysis for this aim [4]. The choice in favor of nanoobjects for photocatalysts is explained by the higher ratio of their surface to the volume and, as a consequence, the larger contact area of the photocatalytic reaction

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compared to larger objects. In particular, nanosized particles (<50 nm) have the greatest photocatalytic activity.

Photocatalysis is initiated by the absorption of a photon by semiconductor oxide TiO_2. The resulting energy is equal to or greater than the band gap of the semiconductor (3.2 eV for TiO_2), which produces electron-hole (e-/h+) pairs, therefore in the catalytic reaction participate only ultra-violet rays that share in the solar radiation spectrum are only about 4 %. The necessary energy for water dissociation is 1.23 eV. The energy of corresponding photons is situated in the visible part of the spectrum. Therefore, to improve the catalytic reaction efficiency it is important to increase the contribution of the visible part of the light spectrum in the photocatalytic process.

Created electron/hole pairs could reach the surface of TiO_2 particles and act as either an electron donor or acceptor for molecules in the surrounding media, Figure 1 [5].

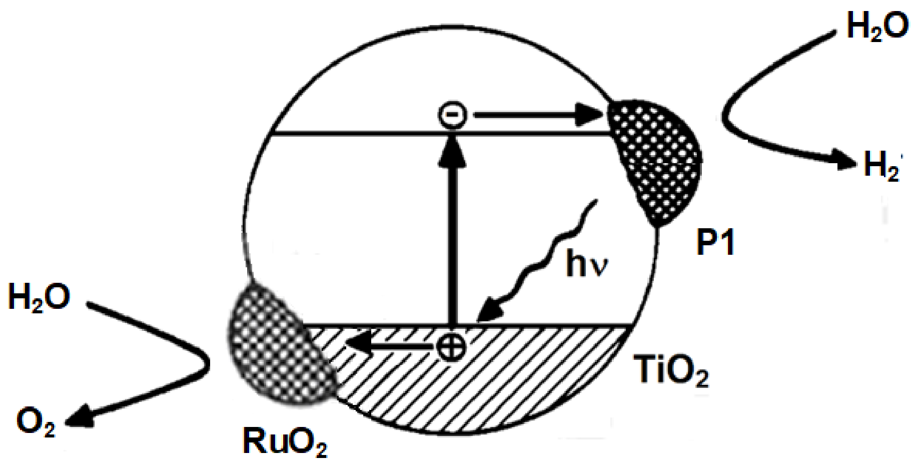

Figure 1.
Electron-hole pair production in cluster-deposited particles of TiO_2 powder under the effect of sunlight quanta and their interaction with surrounding molecules.

However, the photo-induced charge separation in bare TiO_2 particles has a very short lifetime because of charge-fast recombination. The high recombination rate of photogenerated electron

(e^-)-hole (h^+) pairs confines the photo quantum efficiency of TiO_2 thereby reducing its utility. Therefore, it is important to prevent hole-electron recombination before a designated chemical reaction occurs on the TiO_2 surface.

The optimization of charge separation could be reached by adding metal or metal-oxide clusters to the surface of the semiconductor particle, Figure 1 [5, 6].

Therefore, the development of contemporary nanotechnology to improve photocatalytic properties in the direction of better use of the visible range of solar energy and the improvement of the quantum yield of photocatalytic reactions present topical contemporary problems.

Previous investigations were carried out for the synthesis of such photocatalysts [7-11]. To achieve the above objectives, it is necessary to elaborate technology for the coating and doping of TiO_2 nanopowders by even smaller magnetic nanoclusters, which is principal for improving their photocatalytic and magnetic properties.

The main feature of the conducted studies was that ultrafine titanium dioxide nanopowders with a particle size of less than 5 nm were used as the coating material. As studies have shown, these powders are superior in their effectiveness to all other titanium dioxide powders, including the mixture of anatase and rutile, the so-called P25 Degussa, which is considered the best to date.

The following important problem is the study of the absorption spectra of these powders and the study of the dependence of the properties of powders on magnetic nanocluster type and size. TiO_2/Ni nanocomposites are biocompatible and recyclable photocatalysts having outstanding photocatalytic activities for the decomposition of organic pollutants and great biocompatibility [12].

Nickel has been used as a dopant for TiO_2 due to similar ionic radii of Ni with Ti (0.72 Å for Ni and 0.68 Å for Ti), which thus allows Ni to be a substitute in the lattice structure of TiO_2. Doping TiO_2 with Ni creates an impurity energy level on the conduction band of TiO_2 which separates the electron-hole pair and lowers the energy barrier of TiO_2.

The existence of magnetic nickel provides good magnetic properties for composite enabling the photocatalysts to be easily separated and recycle-used. TiO_2/Ni is also a promising low-cost photocatalytic system for solar H_2 production [13].

The Ni-P-TiO_2 coatings were successfully obtained on nickel and iron substrates by electroless plating [14]. It showed their excellent photocatalytic activity. We could conclude that magnetic photocatalytic nanopowders could be used in suspensions and as coatings on metal surfaces of photocatalytic units. Similar considerations could be applied also to such promising magnetic photocatalytic nanopowders as TiO_2/Co and TiO_2/CoO [15, 16].

Despite impressive gains made over the last decade, there are more than 2 billion people who still do not have access to adequate sanitation facilities, and more than 892 million people do not have access to treated sources of drinking water. Globally, diarrhea caused by inadequate drinking water, sanitation, and hand hygiene kills an estimated 842,000 people every year. More than 1/2 of all primary schools in developing countries lack adequate access to water, and nearly 2/3 lack adequate sanitation. By 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, 2/3 of the world's population could be living under water-stressed conditions.

Removing contaminants by traditional purification methods and by filtration has become ineffectual and labor-consuming. Additionally, most water supply systems are outdated and in poor condition, which results in secondary water contamination, aggravating the problem even more.

There are multiple methods for water treatment, to remove unwanted constituents and turn water safe to drink or satisfy specific purposes in industry or medical applications. Usually, methods used are single procedures, rarely two or more, like inverse osmosis, ozonation, ion exchange, sediment filtration, activated carbon towers, ultraviolet (UV) irradiation, disinfection using chemicals, boiling, distillation, and others.

The kinetics for photodegradation reactions is examined based on the dye concentration change by measuring the characteristic absorbance peak at different irradiation times. All the common dyes have their specific characteristic absorptions in the visible range (400–700 nm), herein, the efficiency of photodegradation (also known as the decolorizing ratio) may be simply determined using the following equation:

$$\text{Degradation Efficiency (\%)} = (C_0 - C)/C_0 \times 100,$$

where C_0 and C are the solution concentrations at $t = 0$ and after some irradiation time.

In our water purification modulus, we simultaneously use well-known effective purification methods, which create a strong synergetic effect in purification and can improve the water purification level by several orders of magnitude compared to the action of applying each process separately.

An advanced model of a combined water purification modulus is proposed and tested in this work—one that simultaneously uses several well-known and effective purification features: ozonization (O_3), ultraviolet (UV) irradiation, ultrasound (US), and a new nano-technological coating material Ni-TiO_2, to create a strong synergetic water purification action. Internal surfaces of iron modulus were covered using electroless technology by Ni-TiO_2 layer which, as it was shown in Pang, et al. [12] and Chen, et al. [13] proved to be a good photocatalyst and has good cohesion and ware resisting properties.

The principle of action of ultrasonic purification installation is based on the process of cavitation. As a result of the impact of high-frequency sound on water, strong vibrations are formed, thanks to the change in pressure, the cell membranes of various microorganisms are ruptured, and they die. This method of cleaning has high efficiency, however, the equipment for ultrasonic disinfection is expensive and requires knowledge to set it up.

The system of ultraviolet water purification consists of several lamps that create this radiation. The lamps themselves are immersed in quartz casings, thanks to which they do not cool. Its transparency affects the quality of liquid purification using ultraviolet light. In connection with this, before starting to treat water with radiation, it is necessary to carry out its mechanical filtration, removing turbidity. For the disinfection process to be as effective as possible, it is necessary to stir the liquid.

The ozonator produces active oxygen and doses it into the water in the required amount, destroying bacteria, fungi, and algae in it. Since after cleaning there are no dangerous compounds in the water, and the products of ozone oxidation are ordinary oxides, the water becomes much clearer, the color and turbidity of the water decreases, and the taste of the water improves.

Both methods of water purification — ultraviolet and ultrasonic — are effective and safe versions of equipment for disinfecting water that does not change the taste and accumulates potentially harmful chemical compounds.

It is possible to boldly state that the simultaneous combination of ultrasound and ultraviolet in the process of water disinfection is guaranteed to give a qualitative result.

2. Experimental Results and Their Discussion

A tubular synergistic photocatalytic reactor with a rotating flow was constructed and made, Figure 2.

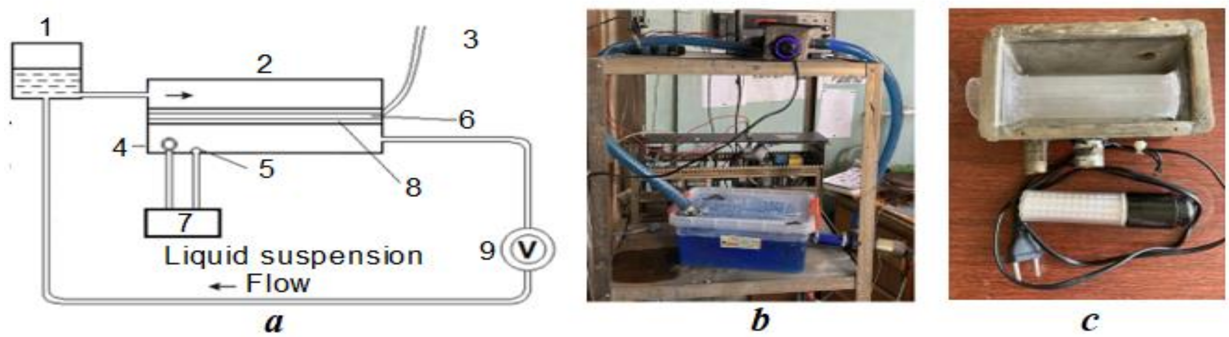

Figure 2.
(*a*) Test tubular synergetic photocatalytic reactor with rotary flow: 1. Reservoir tank with methylene blue and TiO_2 suspension, 2. Photocatalytic reactor, 3. Power supply for UV lamp, 4. Ultrasonic transducer, 5. Ozon inlet disperser, 6. 12 W E27 Socket 254 nm UV-C Light Germicidal LED disinfection lamp,7. US and Ozon (O_3) generators, 8. Quartz tube, 9. Centrifugal pump; (*b*) The modulus photo, and (c) is the photo of its cell

The main components of the modulus are presented in Figure 3.

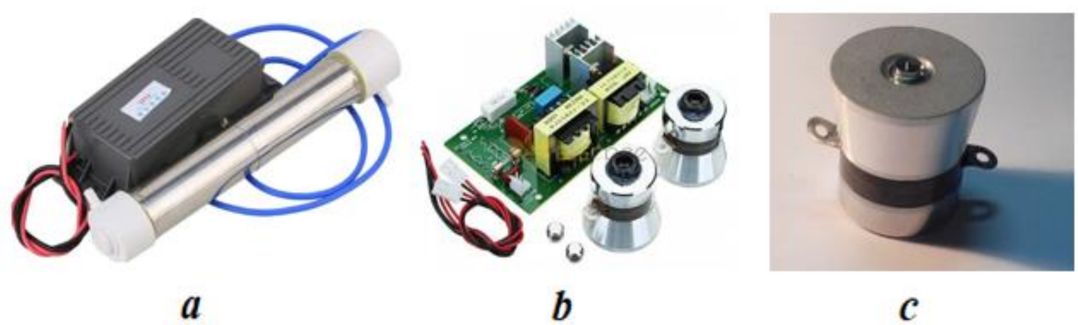

Figure 3.
(*a*) - 2 g quartz ozone tube generator, (*b*)- AC 220-60 W-100 W Ultrasonic Generator with transducers, (*c*)- Ultrasonic transducer.

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The methylene blue dye is harmful to human and aquatic life when flushed into the water and produces a carcinogenic effect as well as disturbs the reproductive system. Even at very low concentrations (below 1 part per million), dyes are visible in water and seriously deteriorate aqueous environments.

Because conventional methods have proven to be ineffective in removing pollution from water, an advanced oxidation process is used to remove them. During the photocatalysis, the source of light and catalysts are used to accelerate the process of the degradation of organic pollutants. According to the source data, photocatalysis can remove 70–80 % of pigments from industrial effluent. Several researchers are working on heterogeneous photocatalysts such as ZnO, TiO_2, and WO_3 for dye degradation.

For studying the influence of that or other cleaning technology on polluted water, they often use the methylene blue as a model. The methylene blue is protein-based pigments which are nondegradable in nature. The methylene blue degradation mechanism is well known [17, 18].

Four liters of methylene blue solution were prepared with a concentration of 5 mg/l. and put it in a polyethylene container. An ultraviolet lamp, as shown in the picture, is placed in a quartz tube and the solution was circulated under conditions of constant light. Probes were taken every 20 minutes. After taking 5 probes, ozonation was added in the process for 20 minutes, then a probe was taken, and ultraviolet light and ultrasound were added along with the ozonation for another 20 minutes, and a sample probe was taken again. At the last stage, ultraviolet light, ozonation, and ultrasound work simultaneously, and we take a final probe.

With the spectrophotometer "SPEKOL 20" the absorption wavelength dependence curves were measured, Figure 4.

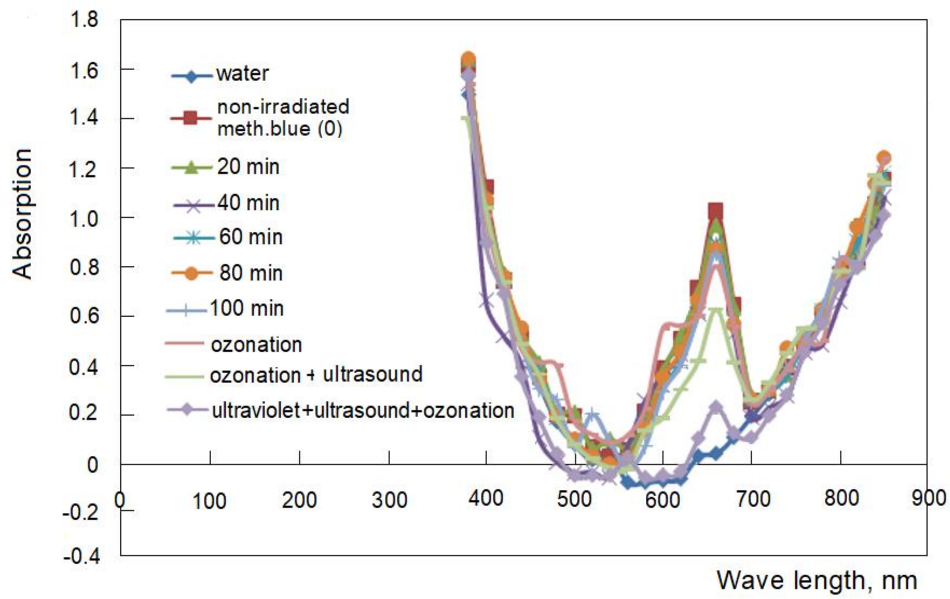

Figure 4.
Absorption wavelength dependence curves.

Using the given figure, we built the curve of dependence of the concentration of methylene blue on time for the wavelength of 660 nm. Figure 5.

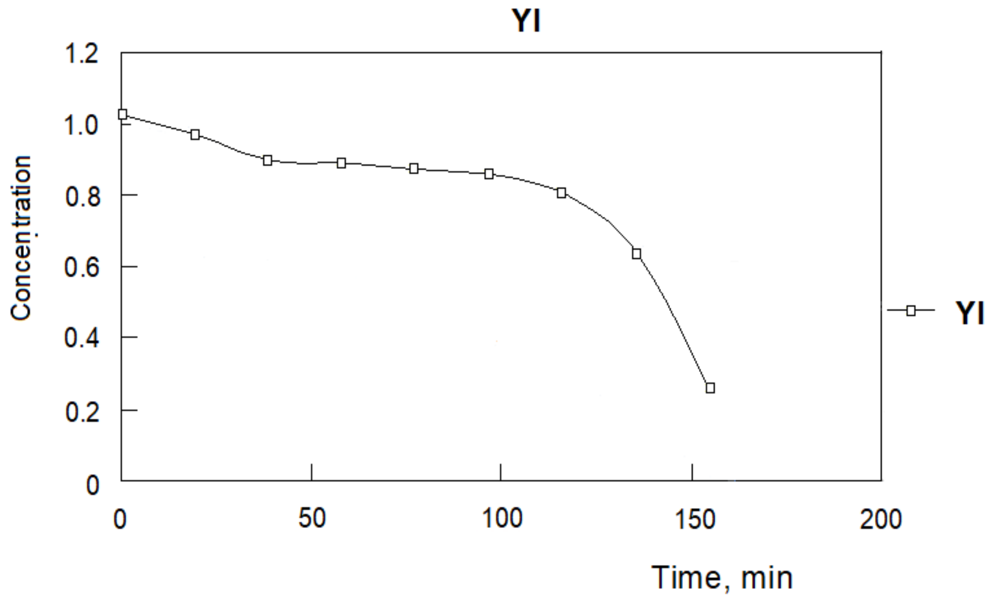

Figure 5.
Methylene blue concentration change (degradation) over time.

We continue the experiment with the addition of TiO_2-anatase, i.e. we put 2 g of anatase (TiO_2 5-10 nm) in the newly prepared 4 l in an aqueous solution of methylene blue (concentration 5 mg/l). Identical to the previous experiment, we start irradiating this suspension with an ultraviolet lamp. We take probes every 20 minutes and draw a parallel with the results of the previous experiment. Let's build the curves of the dependence of the wavelength on the absorption. Figure 6.

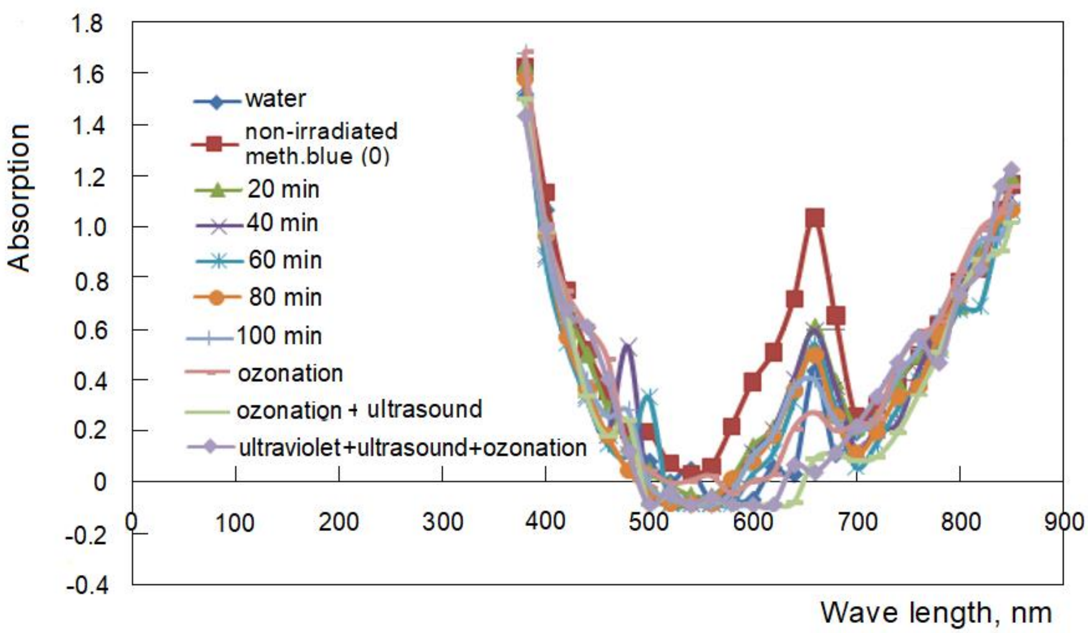

Figure 6.
Absorption wavelength dependence curves.

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Using the given figures, the curve of dependence of the concentration of methylene blue on time for the wavelength of 660 nm was drawn in Figure 7.

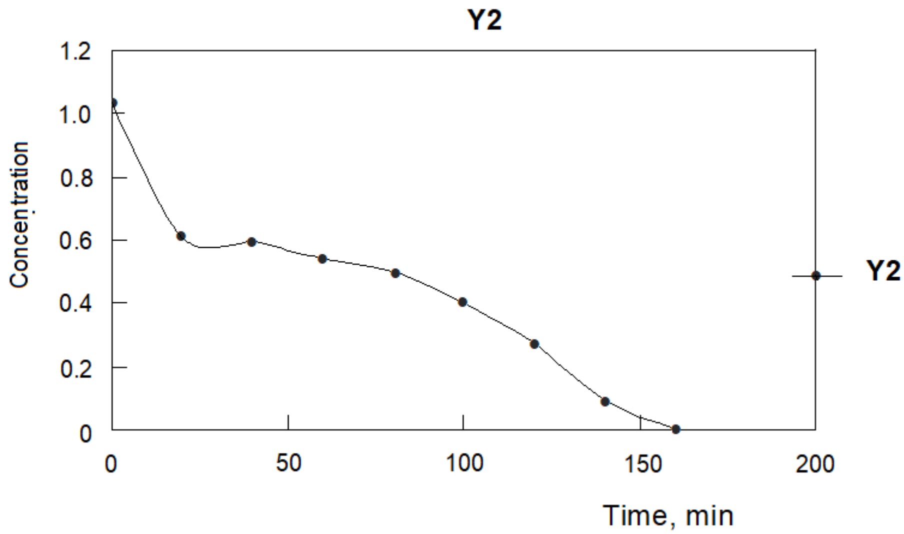

Figure 7.
Methylene blue concentration change (degradation) over time with TiO_2 (Y2).

The comparison of Figure 5 and Figure 7 shows the influence of anatase on the degradation process of methylene blue. Figure 8.

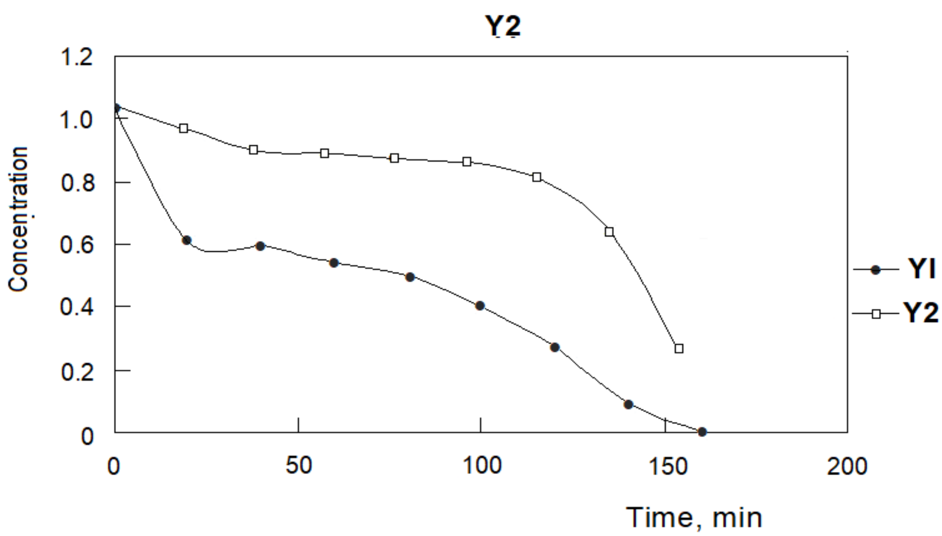

Figure 8.
Methylene blue concentration change (degradation) over time in the presence of TiO_2 (Y2) and without it (Y1).

Before starting the water purification experiment, the modulus inner surfaces were mechanically treated with sandpaper, degreased, activated, and chemically coated in an acid nickel plating solution.

The composition of the used solutions is as follows:

1) Degreasing by CaO-MgO with a mixture of both oxides mixed in equal amounts, e.g. 10g/10g, and then washing inner surfaces thoroughly with warm water.

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2) Chemical degreasing;

NaOH -10 g/l; Na_2CO_3 - 20 g/l; Na_3PO_4–30 g/l; t = 700C; τ = 10 min. (washing with hot and cold water)

3) Etching,

H_2SO_4 - 5% with solution; t = 20-250 C; τ = 20 sec. (wash with running cold water).

4) Chemical nickel plating,

$NiSO_4 \cdot 6H_2O$ -20 g/l; $CH_3COONa \cdot 3H_2O$ -20g/l; $NaH_2PO_2 \cdot H_2O$ -15g/l; pH=4.5-5; t-75-850C.

The chemical coating was carried out during the 2 hours.

Then, in the same nickel-plating solution 2 g/l TiO_2-anatase (5-10 nm) nanopowder was dissolved, and this suspension was introduced into the experimental apparatus, where along with the recovery of nickel, the surface of the apparatus was coated by TiO_2. When we loaded TiO_2-anatase (5-10 nm) into the nickel-plating solution, the nanopowder began to be coated with nickel clusters very quickly, and at the same time, these clusters, together with TiO_2, were deposited on the surface of the device (which is typical of the nickel-plating process). When the surface of the device was completely covered with the photocatalyst, we stopped the nickel-plating process removed the remaining nanopowder from the device, and washed the device with warm running water. The synergetic process of methylene degradation takes place when in the first 15 minutes interval acts UV, in the next 15 minutes interval acts UV+US, then in the next 15 minutes intervals acts UV+US+ O_3 for methylene degradation. In this case, we used a 30 W power UV LED source.

When we loaded TiO_2-anatase (5-10 nm) into the nickel-plating solution, the nanopowder began to be coated with nickel clusters very quickly, and at the same time, these clusters, together with TiO_2, were deposited on the surface of the device (which is typical of the nickel-plating process). When the surface of the device was completely covered with the photocatalyst, we stopped the nickel-plating process removed the remaining nanopowder from the device, and washed the device with warm running water.

Experimental results for synergy effect testing for the Ni-TiO_2 coated modulus cell are shown in Figure 9.

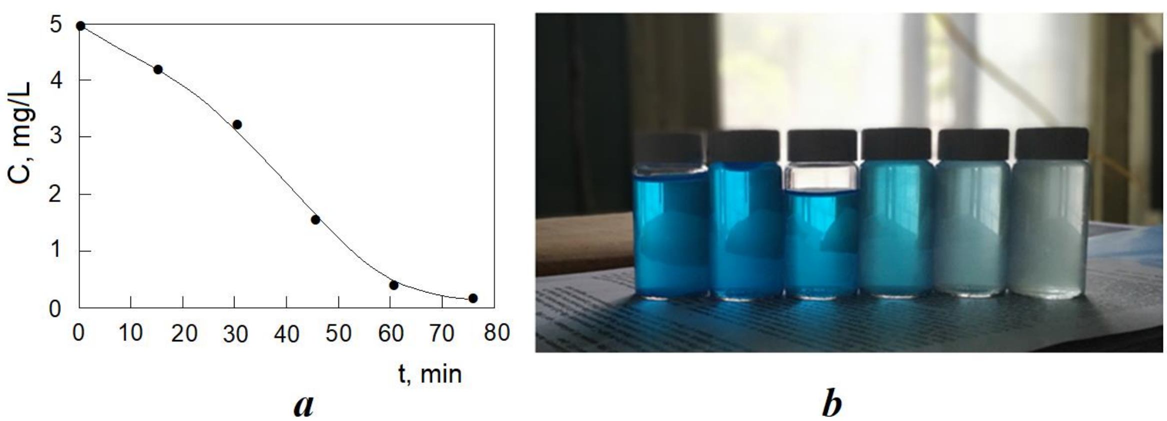

Figure 9.
(*a*) Experimental results for synergy effect testing for the Ni-TiO_2 coated modulus cell. The curve represents the synergetic process of methylene degradation when in the first 15 minutes interval acts UV, in the next 15 minutes interval act UV+US, then in the next 15 minutes intervals act UV+US+ O_3 (*b*) Synergistic water purification process in methylene suspension.

The curve shows a significant synergistic effect in this case too.

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3. Conclusion

A simple and compact synergetic modulus for water purification has been designed and tested using the example of methylene degradation in a methylene-water mixture. A combination of four processes has been studied: ozonation, ultraviolet radiation, ultrasound, and the action of nanomaterials based on the TiO_2 photocatalyst. It has been shown that adding TiO_2 nanopowder to the mixture dramatically accelerates the process of methylene degradation, with the simultaneous action of the other three factors of the synergetic process. The Ni-TiO_2 coatings were successfully obtained on iron substrates by electroless plating. It showed their good photocatalytic activity. We could conclude that magnetic photocatalytic nanopowders could be used in suspensions and as coatings on metal surfaces of photocatalytic units. The synergetic modulus could be potentially used for purification of the domestic and commercial water in industries such as beer, soft drinks, wine and juice production, agriculture, swimming pool water supply, and in many other areas where it is necessary to provide the consumer with safe water.

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Transparency:
The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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