

Electrochemically Synthesized Nano-photocatalysts for Photodegradation of Organic Compounds

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Abstract: Over the last decades, extensive studies have been carried out on nano-photocatalytic materials finding a broad range of applications mainly in solar energy conversion and environmental remediation. This article focuses on synthesizing a novel nano-photocatalyst material for purifying water from chloro-organic pollutants and microbes. It was synthesized in the electrolytic cell with titanium and graphite electrodes. TEM analysis revealed that the obtained nanocarbon-titanium composite has a spherical morphology, the average dimension of nanoparticles is 6 ± 2 nm. The electrochemically synthesized nano-photocatalyst forms OH radicals in the presence of water vapor during daylight hours under sunlight's ultraviolet radiation. As soon as extremely reactive OH radicals are formed, they react with organic pollutants. The results of photodegradation of *E. Coli*, methyl orange, methyl blue, and polychlorinated biphenyls in the ultraviolet spectrum of sunlight have been discussed. The effect of pH value on the decolorization efficiency has been also observed. The obtained photodegradation time of methyl orange (MeO) and methyl blue (MeB) solutions was less than 60 minutes, and the destruction time of polychlorinated biphenyl (PCB) compounds was about 6-8 hours. The practical application of the developed nano-photocatalyst material promises to be an inexpensive, viable alternative or complimentary method for water and wastewater treatment at ambient temperature to degrade various chemical and microbiological pollutants in water.

Keywords: Nano-Photocatalyst, Photocatalysis, Organic Substance, Sunlight

1. Introduction

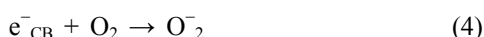
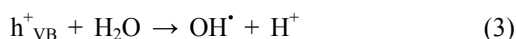
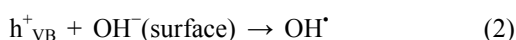
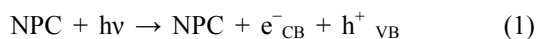
Photocatalysis based on nano-catalysts is a very promising method for the treatment of contaminated water. Both solar photocatalysis and photocatalytic systems equipped with artificial ultraviolet (UV)-light systems can be applied at ambient temperature to degrade various chemical and microbiological pollutants in water and air: organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), inorganic molecules such as nitrous oxides (NO_x) and, in combination with precipitation or filtration, can also remove metals (such as mercury) [1]. There are several potential photocatalysts, but the most widespread substance is nanotitanium dioxide. Nano-sized particles are preferred to

bulk TiO_2 because they are significantly more reactive than larger particles due to their larger surface area. TiO_2 is chemically stable and has a high ability to break molecular bonds leading to degradation. To avoid free nanoparticles in water, nano- TiO_2 particles are usually immobilized on a substrate or integrated into thin-films and other materials [2]. But the lifetime of nanoparticles before their agglomeration can be easily regulated [3]; this allows removing particles from water or air in required time. This method opens an opportunity to increase efficiency of catalysts significantly by using colloidal nano-photocatalysts homogeneously dispersed in water or air to be treated. Moreover it is important to develop new types of nano-photocatalysts with

enhanced catalytic properties. This paper describes a new technology for destruction of bacteria and organic substances which is based on usage colloidal nanocarbon-metal compositions (NMC) as nano-photocatalysts.

2. Principle of the Method

The principle of the method is based on destruction of organic substances and bacteria by nano-photocatalysts (NPC) dispersed on polluted open land or water. These nano-photocatalysts under natural ultraviolet radiation form OH-radicals in presence of water molecules and the radicals destroy decompose organic substances and bacteria. In brief, photocatalytic reactions of aqueous NPC suspension system can be described as follows [4]:



where $h\nu$ is the UV irradiation, h_{VB}^+ is valence-band holes, and e_{CB}^- is the conduction-band electrons. It is known that active oxygen and radical species existing in the presence of oxygen and water take part in the oxidation-reduction reaction and destroy decompose organic molecules and bacteria [5]. The nano-photocatalysts must be harmless; their concentration in water must be lower than permissible level; and nanoparticles must form agglomerates during required time, coagulate and precipitate, i.e., must form safe ordinary particles. Many semiconductive metal compounds are used as the photocatalysts and the most known among them is TiO_2 . Usually photocatalysts are applied on a carrier, have sizes more than 1 μm and cannot be used for dispersion on a large area. That is why it is necessary to develop new type of nano-photocatalyst which can meet all described above requirements. As well known, nanocomposites combine the properties of two or more different materials with the possibility of novel mechanical, physical or chemical behavior arising [6]. Nanocomposites of conjugated materials and metal nanoparticles are prepared from different metals, different types of conjugated polymers and oligomer linkers [7, 8]. Another type of nanoscale materials are nanocomposites of carbon nanoparticles and polymers. Indeed, for example, electrolytically generated nanocarbon colloids (NCC) have functional groups such as carbonyl, hydroxyl and carboxyl groups formed on the surface of carbon nanoparticles [9, 10]. These nanocomposites can be modified by attaching different cations. On the other hand, most of polymers can react with different ions and molecules and also participate in modification of nanocomposites, for example, like nanocarbon-polymer nanocomposites (NCP) prepared via electrolytically generated NCC and polyethylenimine PEI [3]. A similar method can be used to prepare nanocarbon-metal

nanocomposites (NMC) as the nano-photocatalysts to control cyanobacteria.

3. Materials and Equipment

Nanocarbon-metal nanocomposites with titanium as the metal NMC (Ti) were prepared by the electrochemical method. The process was based on the use of two-electrode device [11, 12] in which one electrode was made of a high-density isotropic graphite OEG4 (Russia) and the second electrode was made of titanium plate. The electrodes were immersed in a plastic electrolytic cell filled with 0.025M H_2SO_4 as the electrolyte. The process of device operation involved 2 repeatable consecutive steps: 1) the electrolysis during 2-10 min when Ti-electrode was as an anode, 2) the electrolysis during 2-5 min when carbon electrode was as an anode. The size and the shape of nanoparticles were determined with transmission electron microscopy (TEM) (LEO-912-OMEGA, Carl Zeiss, Germany). Concentration of Ti in solutions was determined by neutron activation analysis by irradiating water samples in the Nuclear Reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). The photocatalytic oxidation of methyl orange (MeO) and methyl blue (MeB) in NMC (Ti) suspension under UV illumination was investigated in order to evaluate the photocatalytic activity of the nanoparticles. A 150 ml of a 3.2×10^{-3} mol/l MeO and MeB solutions were filled into a Petri dish. A 60 W UV lamp (DB-60, Russia) fixed at a distance of 25 cm above the solution surface was used as the UV light source and provided radiation power of 1 W/m^2 in the interval from 220 nm to 320 nm. The absorbance of the MeO and MeB solutions were measured with Cary 50 UV-Vis spectrophotometer (Varian) with Xenon flash Lamp. Experiments with bacteria were conducted with culture *E. Coli* (272) in temperature range 18-36°C. The cultivation, culture enrichment, the testing bacteria were performed following the Standard Methods (USSR, Russia) for Testing Chemical Procedures (Drinking Water, Hygiene requirements and quality control 1982) for the evaluation of disinfection [13]. PCBs from transformer ("transformers oil") were used. The analysis of PCBs was performed by GC/MS (Agilent Technologies 6890 N network gas chromatography system with 5973 inert MSD) operating in SIM mode. The PCBs were separated using a DB-5 (60 m, 0.25 mm, 0.25 μm) chromatographic column.

4. Results and Discussion

Experiments have shown that yield of NMC (Ti) in electrolysis process depends on voltage V between electrodes and pH of solution. Figure 1 shows that the yield dC_{Ti}/dt of Ti in 6 minutes after beginning the electrolysis process, where C_{Ti} is the concentration of Ti in the electrolyte, increase with increasing voltage between electrodes up to 12-13 V but then decrease slowly. This behavior is explained by formation of three - valence titanium on the surface of Ti-electrode, the electrode becomes of blue color. Figure 2 demonstrates

dependence of dC_{Ti}/dt against the concentration of H_2SO_4 in the solution in 6 minutes after beginning the electrolysis process. When pH of the electrolyte closes to neutral value three – valence titanium is formed on the surface of the Ti electrode.

During the first stage of the electrolysis process when Ti-electrode is the anode, electric current between electrodes is about $3-4\text{ mA/cm}^2$. In the second stage after changing the polarity electric current increases up to $180-200\text{ mA/cm}^2$ in about 0.1-0.2 second. During the first stage oxygen is released on the titanium anode, titanium oxides and sulfates are formed on the surface and titanium ions leaved the anode are oxidized by oxygen near the surface of anode in the solution or react with NCC which has carboxyl groups as the active groups. The thin semiconductor layer formed on the surface of the titanium electrode has high resistance and electric current between electrodes is small, about $3-4\text{ mA/cm}^2$. At the same time the negatively charged carbon nanoparticles go away from the graphite cathode and the functional groups such as carbonyl ($>C=O$), hydroxyl ($-OH$), and carboxyl ($-COOH$) group are formed on the surface of carbon particles. During the second stage oxidation process is occurred at the carbon anode. The magnitude of repulsion forces formed between the stacked layers of graphite gets larger than that of van der Waals attraction forces between the layers, preparing a condition for formation of carbon nanoparticles when polarity of electrode will be changed. The surface of the titanium cathode is cleaned from the oxides and electric current between electrodes increases up to $180-200\text{ mA/cm}^2$. Titanium ions and charged particles of titanium oxide interact with carbon nanoparticles and form NCMC (Ti) [14]. Oxygen adsorbed on the surface of particles forms $-Ti(OH)-O-Ti(OH)-$, which can help the photogenerated holes h^+ to change into OH^\bullet free radical [3, 15]. Otherwise, the oxidization activity of OH^\bullet is the strongest in aqueous solution [16]. Typical TEM micrograph of NCMC (Ti) is given in Figure 3 and shows that nanoparticles have a spherical morphology. Measurements of particles sizes have shown that average dimension of nanoparticles is $6\pm 2\text{ nm}$.

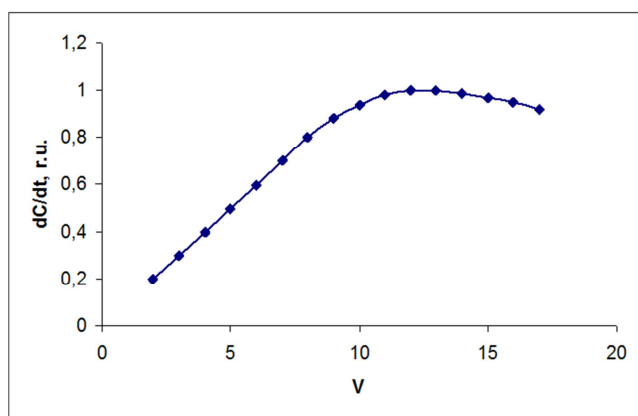


Figure 1. Dependence of the yield of titanium in six minutes after beginning the electrolysis process against electrolysis voltage.

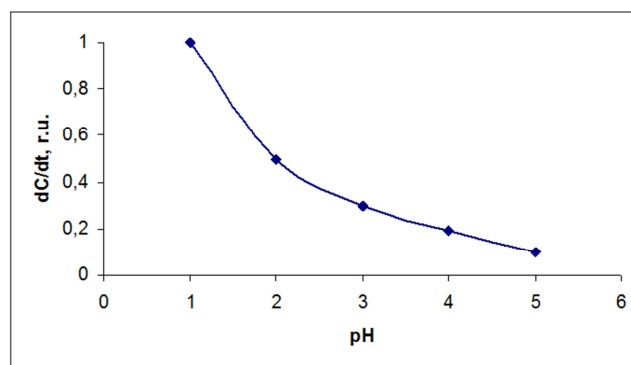


Figure 2. Dependence of the yield of titanium in six minutes after beginning the electrolysis process against pH of the solution.

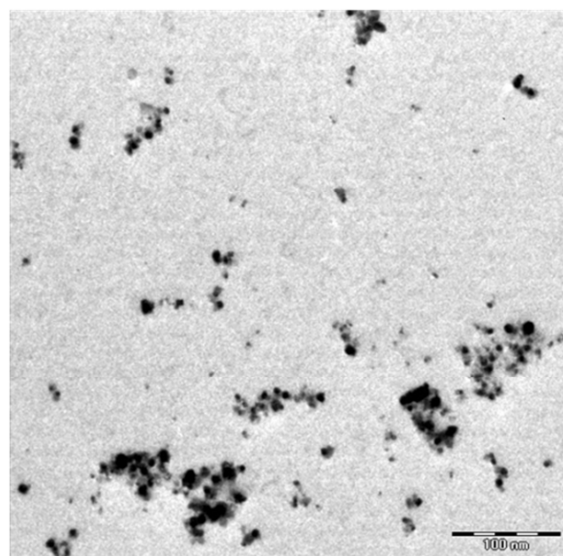


Figure 3. Typical TEM micrograph of NCMC (Ti).

Photodegradations of MeO and MeB solutions containing NCMC (Ti) as photocatalyst were analyzed in the pH value of 1.0, 2.0, 4.4 and 7.2. The relationships between the degradation degree and the pH value of the solutions under UV lamp and solar irradiation at temperature of 22°C and NCMC (Ti) concentration of 0.01 mg/l are shown in Figure 4 and Figure 5 respectively. These results indicate that a low pH value can facilitate the decolorization reaction of MeO. It means that the number of OH^\bullet radical increases on the surface of NCMC (Ti) particles in solution by trapping electrons and H_2O can be absorbed on the NCMC (Ti) surface and reacts with h^+_{VB} in Eq.(3), producing more OH^\bullet radicals under a lower pH value. It can promote the photogenerated electrons to transfer to the surface of NCMC (Ti) and to react with adsorbed oxygen. Rate of photodegradation processes depends on many factors: type of organic substances, concentration of NCMC (Ti), temperature of solutions and intensity of ultraviolet part of sunlight [3, 17]. For example, rate of photodegradation processes considerably increases with temperature rise. Dependence of this process on sunlight exposure time for MeB at 30°C is given in Figure 5.

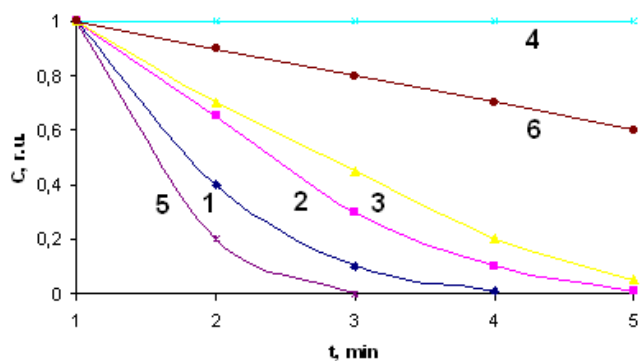


Figure 4. MeO degradation degree under UV lamp: pH = 2.2 (1), pH = 4.4 (2), pH = 6.0 (3) and without NCMC (Ti) (4). MeB degradation degree under UV lamp: pH = 7.2 (5) and without NCMC (Ti) (6). Concentration of NCMC (Ti) is 0.01 mg/l, temperature of solutions is 22°C.

The ability in photodegradation of *E. Coli* and PCBs by NCMC (Ti) were investigated in laboratory condition [17]. Colloidal solution of NCMC (Ti) was added to Petri dishes containing water with *E. Coli* and PCBs, put under the sunlight at 11 am and tested during 6 hours. Concentrations of NCMC (Ti) in mixed solutions were 1 µg/l and 10 µg/l. Dependences of bacteria and PCBs concentrations in water samples with temperature of 30°C irradiated by sunlight against exposure time are given in Figure 6 and Figure 7. The results show that water is disinfected during about 1 hour and PCBs is degraded during 5-6 hours.

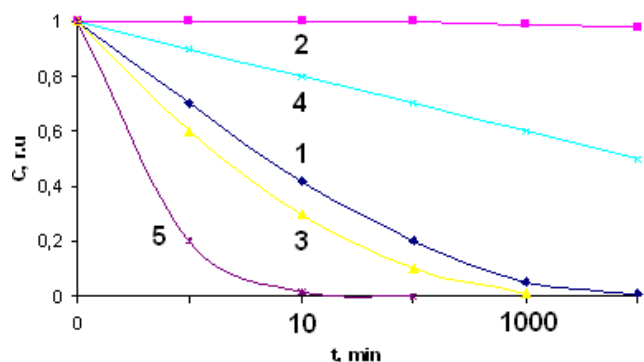


Figure 5. MeO degradation degree under solar irradiation with (1) and without NCMC (Ti) (2), MeB degradation degree under solar irradiation at 22°C (3) and 30°C (5) with NCMC (Ti) and at 22°C without nano-photocatalyst (4).

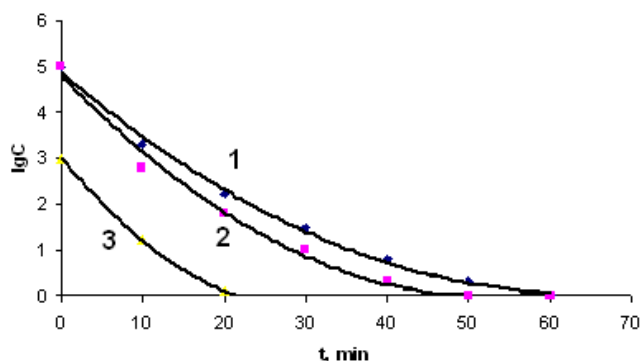


Figure 6. Photodegradation of *E. Coli* under solar irradiation by NCMC (Ti) with concentration of 1 µg/l (1) and 10 µg/l (2, 3). Temperature of solutions is 30°C.

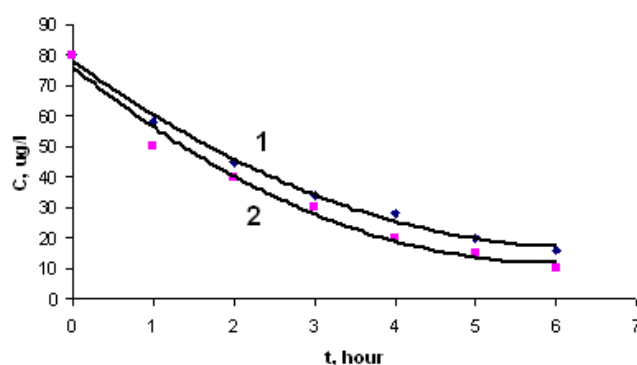


Figure 7. Photodegradation of PCBs under solar irradiation by NCMC (Ti) with concentration of 1 µg/l (1) and 10 µg/l (2). Temperature of solutions is 30°C.

5. Conclusion

Colloidal solutions of electrochemically synthesized NCMC (Ti) have shown a high efficiency as the nanotechnology-based photocatalyst. Photodegradations of MeO, MeB, PCBs and *E. Coli* go on at NCMC (Ti) concentration of 1-10 µg/l. Time of degradation of organic substances and bacteria under the UV lamp is about 3-5 minutes. Decoloration of MeO and MeB under sunlight goes on during 15-60 minutes, killing time of *E. Coli* is about 10-30 minutes, and destruction time of PCBs is about 6-8 hours. The application of the developed nanotechnology-based photocatalyst for water and wastewater treatment can be appropriate for developing countries or remote sites with no access to electricity.

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