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Microbial-free water using titanium dioxide nanoparticles: A simple and low-cost approach

Hafeez Anwar*[1], Yousaf Ali[1], Ayesha[1], Yasir Javed[1], Yasir Jamil[1], Naveed Ahmad[2] and Zahid Farooq[3]

[1]Department of Physics, University of Agriculture, Faisalabad, Pakistan, [2]Institute of Soil & Environmental Sciences, University of Agriculture, Faisalabad, Pakistan and [3]Department of Physics, University of Education Faisalabad Campus, Pakistan

Abstract

We report synthesis of TiO_2 nanoparticles using sol-gel method and their use as antimicrobial photocatalyst in water purification. The prepared nanoparticles were analyzed using X-ray diffraction and scanning electron microscopy. TiO_2 nanoparticles belonging to the phase anatase were obtained with average particle size ca. 22 nm as determined by Debye-Scherrer equation. For water purification treatment, transparent plastic bottles were coated on the inside with TiO_2 nanoparticles, filled with water samples and irradiated under sunlight for 24 hours. Samples were then analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS) and colony forming units (CFU). The results showed a considerable variation in all these parameters with approximately 100% microorganisms-free water as compared to uncoated water containers. This method is cheap and can be used at large scale for water purification.

Key words: Water Purification, Photocatalyst, Titanium dioxide, Antimicrobial Activity and TDS

Full length article **Corresponding Author*, e-mail: hafeez.anwar@gmail.com

1. Introduction

Availability of clean drinking water has become a big problem due to the rapid industrial growth, especially in developing countries. Water is the most important factor for the survival of living things. It is among one of the elements; playing key role for human health. The human body is build up by more than seventy percent of water. Throughout history there have been many occasions when hundreds of people have died due to diseases caused by contaminated water. Many diseases such as cholera, typhoid fever, food poisoning and hepatitis are caused by drinking unhealthy water. Microbial pathogens in drinking water are being considered for various gastrointestinal illnesses that have occurred in different parts of the world. Since microbes exist everywhere in our environment, their exposure to us cause harmless microbial flora in our bodies but the bad thing is that some microbes are pathogens like microsporidia and H. pylori, which can cause diseases and water is thought to be a likely a route of transmission of such microbes. It is of key importance that water used for drinking process must be free of germs and chemicals. Therefore, providing pure and inexpensive water to meet people requirement is a key challenge of 21st century. According to the guidelines of the World Health Organization (WHO), all the water intended for drinking, as well as treated water entering the distribution system, must not contain E. coli or thermo tolerant coliform and total coliform bacteria detectable in any 100 ml sample.

In current years, the significant attention has been given to photocatalysis development due to its extensive use in the field of energy and environment. Many metal oxides have been used as photocatalyst to convert solar energy into chemical energy [1–6]. Among these, titanium dioxide is low-cost, nontoxic and resistant to chemicals [7, 8]. It is a good photocatalyst and used in many applications including solar cells, fuel cell, sensors, pigment and environmental [9]. Titanium dioxide has capability of disintegrating organic toxins. If the light has energy greater than the band gap energy of titanium dioxide, then the charge carriers developed. The charge carriers developed by absorbing the UV light [10].

In addition to that TiO_2 is an excellent photocatalyst in environmental purification. When irradiated with UV light, TiO_2 nanopowders show strong oxidizability and reducibility [11]. Due to its low cost, stability nontoxicity in water, TiO_2 is used in water treatments by various research groups. TiO_2 based devices were used for decomposition of organic pollutants in domestic water. TiO_2 water purification devices photocatalytically dissolves organic contaminants into carbon dioxide [12]. TiO_2 show robust bactericidal activity, when exposed to near-UV light leading to instant increase in permeability to small molecules after 20 min [13].

In this work, a comparatively simple and cost-effective method for water treatment using TiO_2 nanoparticles was used. TiO_2 nanoparticles can be obtained using sol-gel technique. Water samples were investigated for the pH, electrical conductivity, presence of total dissolved solids (TDS) and colony forming units (CFU) such as bacteria, viruses and protozoa etc. in water.

2. **Materials and methods.**

Titanium tetraisopropoxide (TTIP), ethanol and HCl were purchased from Daejung, Sigma-aldrich and Lab scan respectively. All chemicals were of analytical grade and used without further purification.

2.1. Synthesis of TiO_2 nanoparticles

Synthesis of TiO_2 nanoparticles was carried out by sol-gel method. Titanium tetraisopropoxide (TTIP) was first dissolved in ethanol. The mixture of distilled water and HCl was then added dropwise under vigorous stirring at room temperature. In brief, 19 ml distilled water and 1.68 ml hydrochloric acid (HCl) were homogeneously mixed (solution A). In 54.8 ml ethanol, 5.5 ml titanium tetraisopropoxide was dissolved using magnetic stirrer (solution B). The molar ratio of titanium tetraisopropoxide and distilled water was almost be 1:4 [14]. As a result the milky solution was obtained. The solution was further stirred for 20 minutes. Then solution A was added into the milky solution drop wise. The final solution was stirred for 21 hours, and after centrifugation, the obtained gel was washed with distilled water to remove excess reactants. The gel was dried into an oven (VWR 1450M) at 80 ℃ for 1 hour and was calcinated in the furnace (SNOL N-8L) at 500 ℃ for 3 hours [15].

2.2. Characterization

To investigate the crystal structure and morphology of as prepared TiO_2 nanoparticles, X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies were performed. XRD patterns of TiO_2 was recorded using PAN analytic X'Pert PRO with λ =1.54056 Å which is the wavelength characteristic of the Cu-K_α radiation. SEM was performed on a JEOL JSM 5910 (Japan). After the synthesis and characterization of titanium dioxide (TiO_2), it was used for purification water. Solar Disinfection (SODIS) method was used which is a good technique to purify water. Water samples used in this work were collected from three different places labeled as Y_1, Y_2 and Y_3. Recycled transparent plastic bottles of same sizes were used as water containers. One of each sample was placed in dark to serve as control. Second series of samples with labels Y'_1, Y'_2 and Y'_3 (uncoated containers) were exposed to sunlight for 6 hours daily, for four days in total 24 hours (Figure 1 (a)). In the third series labeled Y''_1, Y''_2 and Y''_3, the inside of each containers (plastic bottles) was coated with a layer of as prepared TiO_2 nanoparticles and exposed to sunlight for 6 hours daily, for four days (24 hours), Figure 1 (b). All three samples were investigated for pH, electrical conductivity (EC), total dissolved solids (TDS) and colony forming units (CFU) for microbial count such as bacteria; virus and protozoa etc. pH of water was determined using pH meter model BL-4100S. Electrical conductivity was measured in µS/cm using EC meter (Jenway model 4510) with 230 V loaded power supply and conductivity measuring range 0-199 mS. Colony forming units (CFU) test was performed manually by using click counter, a pen and digital camera. Total dissolved solids (TDS) were measured from EC using the relation TDS (mg/l) = 0.64×EC (µS/cm).

Fig. 1(a): uncoated container, Fig. 1(b): TiO_2-coated container

3. Results and discussions

From XRD pattern (Figure 2), it can be observed that diffraction peaks with good crystalline quality are present corresponding to the phase anatase having tetragonal crystal structure. The miller indices (101), (004), (200), (105), (211), (204) and (220) correspond to the characteristic peaks of X-ray analysis pattern of the prepared titanium dioxide sample is in close agreement to the anatase characteristic peaks (JCPDS card No. 21-1272). Also, d-spacing values are very close to the reported values. Mean particle size was calculated by using well known Debye-Scherrer formula [16] and was found to be ca. 22 nm. The broadening of XRD peaks was a consequence of small particle size crystallites. The values of lattice constants were calculated as a =3.7829 Å and c=9.4713Å. The volume and density of crystallites were found to be 135.54 Å and 0.391 x 10^{-23} g/cm^3, respectively. Figure 3 shows SEM image of the as-prepared Ti_2O nanoparticles. It can be clearly seen that TiO_2 nanoparticles have spherical morphology.

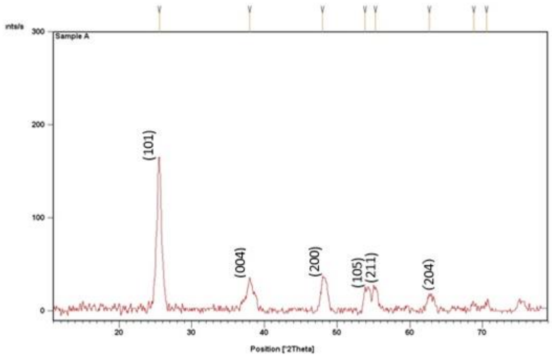

Fig. 2: XRD pattern of TiO_2 nanoparticles

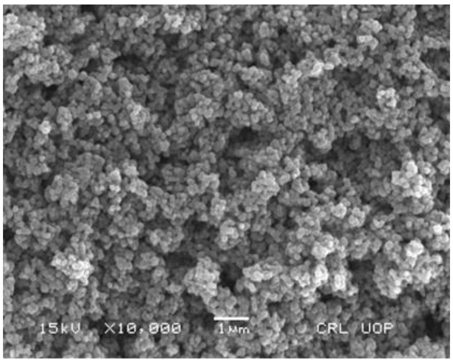

Fig. 3: SEM image of TiO_2 nanoparticles

Being a photocatalyst, the action of sunlight can be enhanced by TiO_2 nanoparticles. During this phenomenon, oxidation and reduction reactions take place resulting in the generation of hydroxyl free radicals (·OH) in water and superoxide ions ($O_2^{-\cdot}$) respectively. The demolition of pollutants through photocatalytic process, with the help of titanium dioxide is principally accompanied by a chain of hydroxylation reactions, starting with hydroxyl radicals (·OH). During this photocatalytic reaction, some of the possible modes for the ·OH generation are shown in Figure 4. In titanium dioxide semiconductor as photocatalyst, the electron-hole pair formation is occurred under UV light illumination. A hole is an electric charge carrier, carries a positive charge, and produces ·OH and H^+ ions when interact with water molecules. The interaction of electrons and dissolved oxygen results in the production of superoxide ions ($O_2^{-}\cdot$), which in return generate hydroxide ions (OH^-) and peroxide radicals (·OOH) when react with water molecules. Then the formation of ·OH and OH^- occurs due to combination of peroxide radicals with H^+ ions, and also the oxidation of OH^- to ·OH is caused by holes. Thus, the emergence of hydroxyl free radicals (·OH) is gradually assisted by all the species. These free radicals, being very strong oxidizing agents, balance the unpaired electrons in the vicinity of cells by disintegrating every cell during their attack on the cell structure of organic molecules. So, in this manner all the microorganisms are knocked down [17–19].

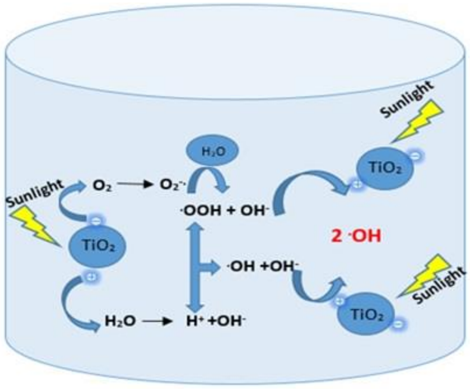

Fig. 4: Mechanism of radical generation

The results of pH, EC, TDS and CFU of all three samples (under dark, uncoated under sunlight and coated under sunlight) are shown in the bar graphs in Figures (5-9). These results showed that water has become totally pure after this treatment, by using titanium dioxide (TiO_2) in the sunlight, as our results are in the range of pure water. After these tests, we noted the number of microbes killed by titanium dioxide (TiO_2). Overall, we concluded that microorganisms killed under the sunlight, in titanium dioxide (TiO_2) coated samples were 100% and in the uncoated samples were 54%. Finally, by coating titanium dioxide (TiO_2), all microorganisms were killed successfully and the water became totally pure from microorganisms, as all results are in the range of pure water, Figure 10.

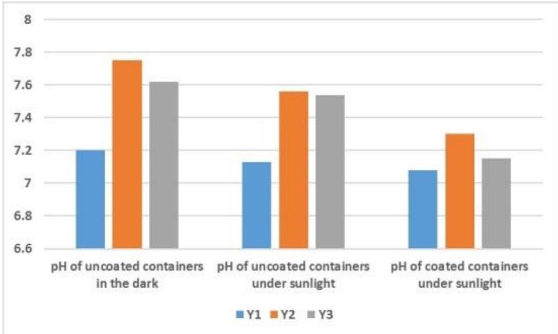

Fig. 5: Comparison of pH of three water samples

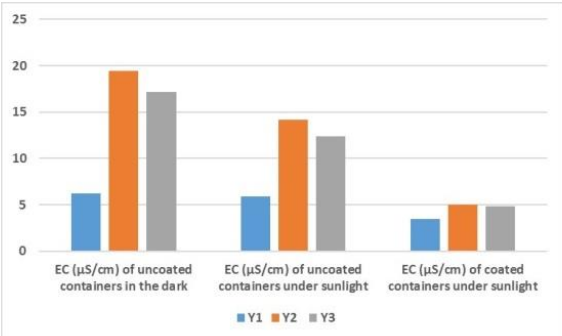

Fig. 6: Comparison of EC of three water samples

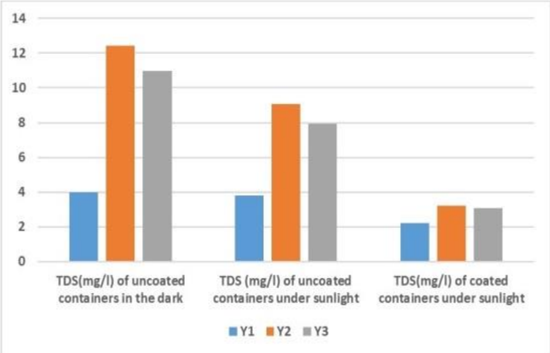

Fig. 7: Comparison of TDS of three water samples

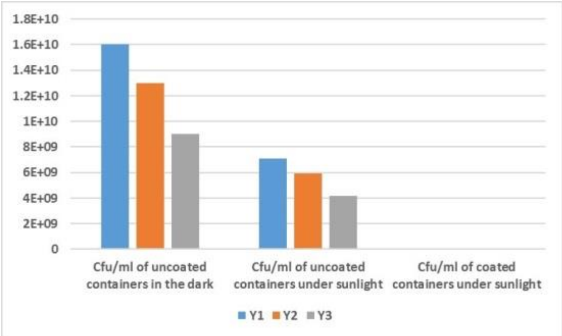

Fig. 8: Comparison of CFU for three water samples

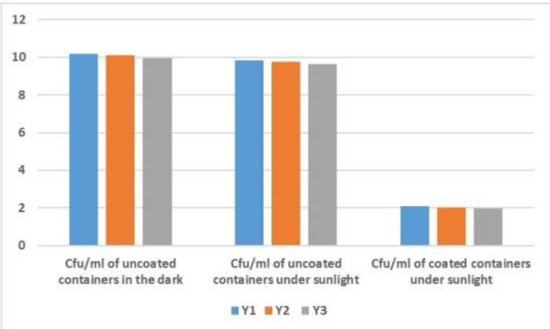

Fig. 9: Comparison of CFU values after taking Log

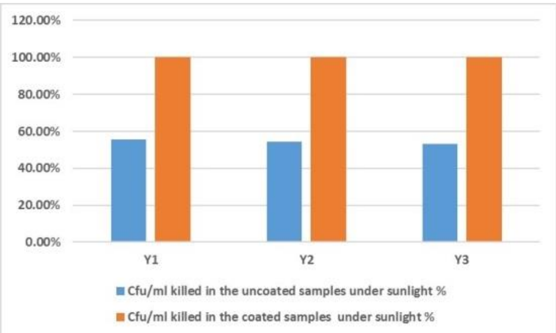

Fig. 10: Percentage of Cfu/ml killed in the uncoated and coated samples under sunlight

4. Conclusions

The aim of this work was to synthesize titanium dioxide (TiO_2) and to investigate its application for water purification as antimicrobial agent. The prepared TiO_2 was characterized structurally as well as morphologically using XRD and SEM. The XRD analysis such as peak positions, width analysis and the unit cell dimensions showed that the particles formed have nano dimensions and are pure in crystalline phase. The prepared TiO_2 nanoparticles were used for water purification by coating them on the insides of water containers. When irradiated with sunlight for 24 hours, approximately 100% bacteria were killed. Not only was this, the pH, TDS and EC of resulting water found to be close to that of pure water. We concluded that, by coating titanium dioxide (TiO_2), the activity of sunlight become more effective and killed microbes to get microbial-free water.

Declaration of Interest

The authors declare no declarations of interest.

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