

Characterization of BiVO₄ Modified TiO₂ and its Application in the Water Treatment

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Abstract— Pure drinking water is a fundamental right of living systems. However, water contamination is a significant problem in many regions. There are several methodologies for the degradation of pollutants. Among which photocatalytic oxidation/degradation of the pollutants has been considered as an environmentally friendly and low-cost methodology in the realm of water treatment. The anatase Titanium dioxide (TiO₂) has been known as an excellent material for the oxidation of the heavy metals from the potable water. Nevertheless, it absorbs in the UV region of the electromagnetic spectrum. Moreover, at this moment, the incorporation of the Bismuth vanadate (BiVO₄) into the anatase system, we are improving the properties of the TiO₂ so that the modified TiO₂ can have a better performance in the whole spectral regions. The Sol-gel technique has used for the synthesis of the modified TiO₂, and its properties have been studied using Xray diffraction analysis (XRD), Raman, Bandgap analysis, and BET (Braunner-Emmet-Teller) surface area measurement. Moreover, it is used for some preliminary tests for the removal of Arsenic total from water samples and also tested the effect of organic compounds and microorganisms present in water on the Arsenic removal.

Keywords—Sol-gel synthesis, BiVO₄ modified TiO₂, Characterizations, Arsenic removal, the effect of organic matter

I. INTRODUCTION

The water crisis is one of the major issues the world is going to face shortly. Anthropogenic causes such as population growth and industrialization are the primary reasons [1]. Several available methodologies are contributing towards the water treatment, and photocatalysis is identified as one of the best methodologies considering its lower cost of the process, simplicity in the experimentation, and also it does not form any harmful by-products during the process [2]. The photocatalysis is the process that is similar to the normal catalysis, where the presence of light accelerates the reaction. To begin with the process, we need to identify the best catalyst. TiO₂ is a commonly used photocatalyst. It is widely used considering its stability in the aqueous phase [3], low cost, and non-toxicity [4]. Arsenic, The P block element, which is the 20th most abundant element on the earth crust, has been identified as one among the heavily poisonous heavy metals including Cadmium (Cd), chromium (Cr), Mercury

(Hg), Nickel (Ni) and Lead (Pb) [5]. The concentration of the As in the earth crust has been reported as 0.5mg present in every 2.5kg of the crust.

Moreover, many countries, including Mexico, China, India, USA, Poland, Canada, etc., are affected by Arsenic contamination in the drinking water [6]. There are different sources of Arsenic such as Mining industries, Agrochemicals, Volcanic activities, Presence of the nearby mineral deposits, burning of the fossil fuels, wood preservatives, dissolution of the arsenic-containing rocks and soil, etc. [7]. Even there are inherent groundwater sources such as the ones present in Mexico. Most of these heavy metals, including Arsenic, can transform from their solid phase into the aqueous form and enter the food chain, being a silent threat to the living cells [5]. The wide bandgap of the TiO₂(~3.2 eV) made it possible to be efficient only in the Ultraviolet (Uv) region of the electromagnetic spectrum, which is only 3-5% [3] of the full sunlight spectra.

Furthermore, we have decided to have a modified TiO₂ material by introducing BiVO₄ (~2.4 eV) [8] and having a structure with improved photocatalytic properties. BiVO₄ has been used for this process, considering its low cost, chemical stability, non-toxicity, and antibacterial activity [9]. In this paper, we have discussed the synthesis, characterization, and preliminary experimental observations on arsenic removal.

II. EXPERIMENTAL DETAILS

A. Chemicals used

For the synthesis of the nanocomposites include bismuth nitrate ((Bi(NO₃)₂·5H₂O), ammonium meta-vanadate (NH₄VO₃), citric acid (C₆H₈O₇), and ammonium hydroxide (NH₄OH) has been used for adjusting the pH.

B. Synthesis of the Modified TiO₂

The modified TiO₂ has been synthesized by a sol-gel method. Two initial solutions have to be prepared (Solution A; the 0.01mol bismuth nitrate- 0.02mol citric acid in nitric acid and Solution B; 0.01mol ammonium metavanadate and 0.02mol Citric Acid in hot water). Both the solutions (A and B) were mixed under stirring. Once the solution is mixed up

well, the Anatase TiO₂ brought from Sigma Aldrich has to be introduced into the resultant solution (98 weight% of the final product). The pH was kept between 6.5 to 7. The solution kept under stirring has dried at 100°C and calcinated at 500°C to obtain the nanocomposite.

C. Preparation of Arsenic sample solution

The Arsenic (total) solution was prepared by using the 0.1302g of arsenic trioxide (As₂O₃) along with 1g of sodium hydroxide (NaOH) and also 20ml of hydrochloric acid (HCl). The solution is made up of 100mL using deionized water. The resultant solution is having the concentration of arsenic 1000ppm. Through-out the experiment, we have used the sample containing the 2ppm of arsenic by diluting the stock solution.

D. Photocatalytic oxidation test

The photocatalytic test has been carried out with the Laboratory made Solar simulator of variable intensities. The experiments have been performed under the intensity of 500w/m². We have used 300ml of the Arsenic sample solution with a concentration of 2ppm and the catalyst dosage of 1.5g/L under the natural pH of the solution (4.5-5). The test duration was 60 minutes, and the aliquot samples were taken at 0, 5, 10, 20, 30 and 60 minutes. The quantification has been done using the Absorbance spectroscopy; we used the Ammonium molybdate solution for the colored complex formation, which helps the quantification using the absorbance spectroscopy. The measurement was based on the absorbance peak at 871nm and the intensity of which is the basis of the further quantification.

E. Characterization

The structural analysis has been done using Bruker D2 Phaser X-ray Diffractometer (XRD). Raman spectral studies were performed on a Horiba-Jobin-Yvon spectrometer (Lab RAM HR800), with excitation radiation from He-Ne laser (wavelength= 632.8nm). The morphological analysis has been done employing TESCAN Scanning Electron Microscopy (SEM) VEGA3. The optical absorbance spectra of the samples were done with a UV-Vis spectrophotometer (Agilent Carry 5000). The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method on a Quantachrome Autosorb 1.

III. RESULTS AND DISCUSSION

A. Structural analysis

• XRD ANALYSIS

The X-ray diffractogram Fig. 1 of the nanocomposite is in comparison with that of the Monoclinic BiVO₄ and Anatase TiO₂ and is matched with the standard PDFs (JCPDS-00-14-0688 for BiVO₄) [10] and (JCPDS-00-0121-1272 For TiO₂) [11]. It has been observed that there are no diffractions observed from the monoclinic phase in the composite since their content is in a tiny percentage, possibly below limit detection. Moreover, the significant reflections from the TiO₂ anatase are present all along, keeping a good crystallinity of the material, and the position of the (101) reflection is practically the same in both samples. The crystallite sizes of the composites have been found using the Scherrer equation, and values are given in Table I. The crystallite size of the anatase TiO₂ is calculated as 15.11nm, whereas that of the nanocomposite showed an increase, 18.06nm. This is a consequence of the synthetic route and can be ascribed to a sintering process during calcination step.

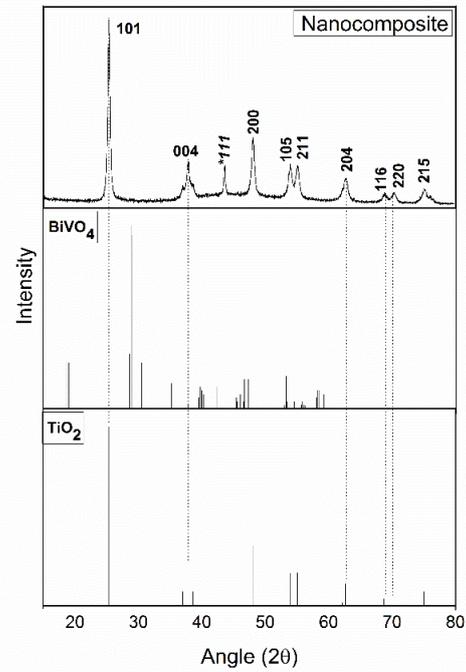


Fig. 1.XRD analysis of the nanocomposite in comparison with the standard PDFs.

TABLE. I CRYSTALLITE SIZE ANALYSIS

Sample	2 theta (Degrees)	FWHM	The crystallite size (nm)
TiO ₂	25.327	0.563	15.11
2%BiVO ₄	25.33	0.471	18.06

• RAMAN ANALYSIS

Raman analysis Fig. 2 of the nanocomposite has been done in comparison with the TiO₂ anatase for the identification of the vibrational modes of the molecules and hence for the structural identification of the sample. The peak around 154cm⁻¹ corresponds to the E_g vibrational mode of the anatase TiO₂ phase. 406.3, 526.4, and 648.8cm⁻¹ correspond to the A_{1g}, B_{2g}, and E_g vibrations of the same phase

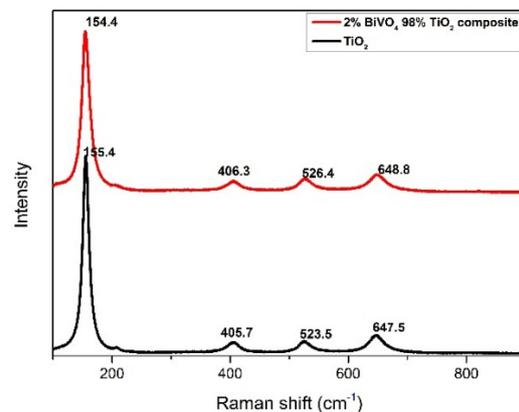


Fig. 2. Raman spectra of the modified TiO₂.

Furthermore, the Raman analysis agrees with the XRD analysis since it confirmed the presence of well-crystallized Anatase TiO₂. There seems a slight shift in the peaks of the composite material, and it is reported that the slight shift

along with the reduced intensity of the peaks in the composite can be due to the phonon confinement and oxygen deficiency due to the introduction of the BiVO_4 , which is a minor phase into the system. Moreover, from the Xray diffractogram, we have calculated the crystallite size. We have seen an increase, and this increase in the crystallite size can be why the slight broadening and reduced intensity of the nanocomposite peak [12].

B. Morphological Analysis

The morphological analysis has been done using the SEM in Fig. 3 a and b, and it is found that the modified material seemed to have an agglomerated spherical structure with aggregated particles.

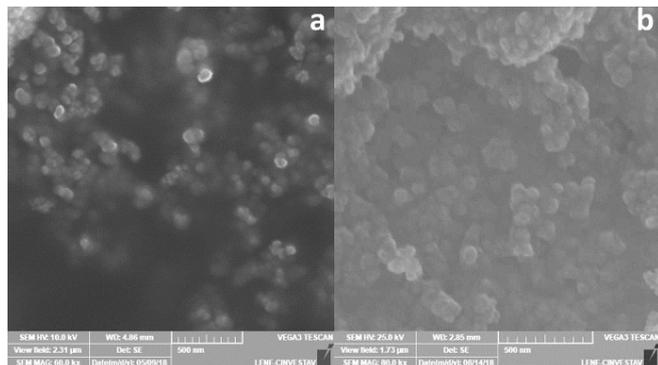


Fig. 3. SEM micrograph of a) Anatase TiO_2 b) modified TiO_2 .

C. Bandgap analysis

The bandgap has measured using the UV-Diffused reflectance spectroscopy and is plotted in Fig. 4, and the values are mentioned in Table II. The bandgap energy has been calculated, and it is found that the TiO_2 has a bandgap of 3.28eV belongs to the UV region. Moreover, BiVO_4 has a bandgap of 2.36eV, and that comes within the Visible region. The nanocomposite has shown a relatively lower value of the bandgap 3.03eV, and this could be due to the overlapping of the energy levels within the parent TiO_2 and BiVO_4 .

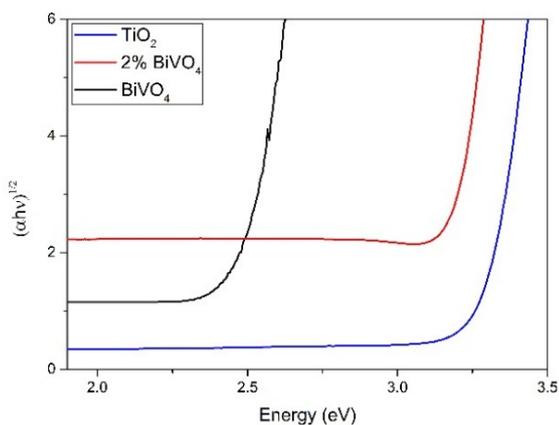


Fig. 4. The bandgap analysis of the modified TiO_2 in comparison with the parent materials

TABLE. II BANDGAP ANALYSIS

Material	Bandgap(eV)
TiO_2	3.24
BiVO_4	2.38
2% BiVO_4	3.03

D. BET- Surface area analysis

Surface area analysis has done using the BET method by measuring the nitrogen adsorption on the surface of the materials as a function of relative pressure (P/P_0), as in Fig. 5.

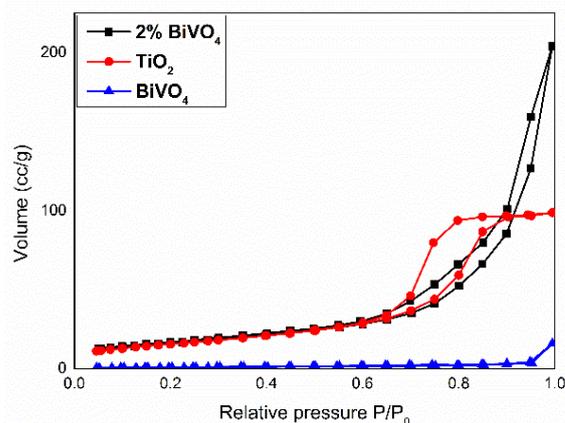


Fig. 5. BET Nitrogen adsorption-desorption isotherm.

The isotherms appeared as type 2 [13] within the relative pressure range from 0.05 to 1. The specific surface area of the modified TiO_2 was found to be $58.2\text{m}^2/\text{g}$, that of BiVO_4 was $29.6\text{m}^2/\text{g}$, and for TiO_2 alone, it was found to be $56.5\text{m}^2/\text{g}$, and pore diameter is found to be below 20nm as from the Fig. 6. The modified TiO_2 material is mesoporous since the pore diameter is below 20nm, which is in the range of the standard 2-50nm for the mesoporous materials.

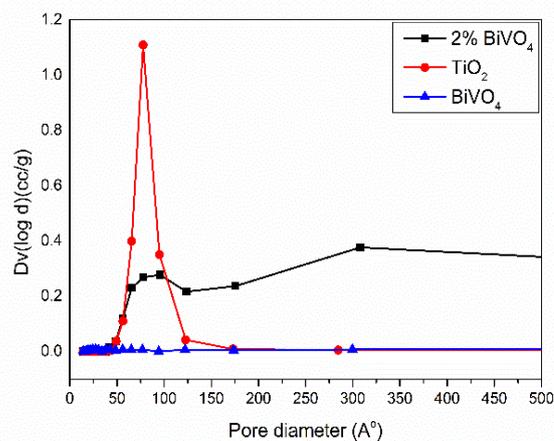


Fig. 6. The pore size distribution of the Modified TiO_2 in comparison with the parent materials.

IV. PHOTOCATALYTIC TEST RESULTS

A. Comparison of the efficiency of Modified TiO_2 with parent materials

The Fig. 7 shows the comparison of the Arsenic removal efficiency of the nanocomposite with 2% of BiVO_4 along with the parent materials (TiO_2 and BiVO_4).

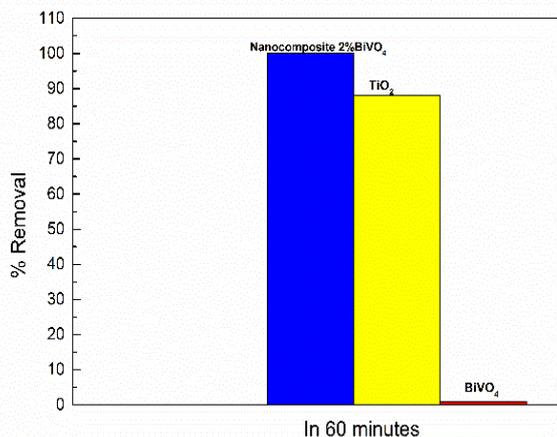


Fig. 7. Arsenic removal percentage within 60 minutes of irradiation.

Fig. 8 shows the kinetics of oxidation of As(III) using the nanocomposite, and it can be seen that there is complete oxidation of As(III) to As(V). Furthermore, it is observed that the nanocomposite material has shown a complete removal of total Arsenic within 60 minutes of irradiation. In contrast, the BiVO₄ has not exhibited any significant effect, whereas TiO₂ has removed 88% of total Arsenic within 60 minutes of irradiation, which is lower compared to the nanocomposite.

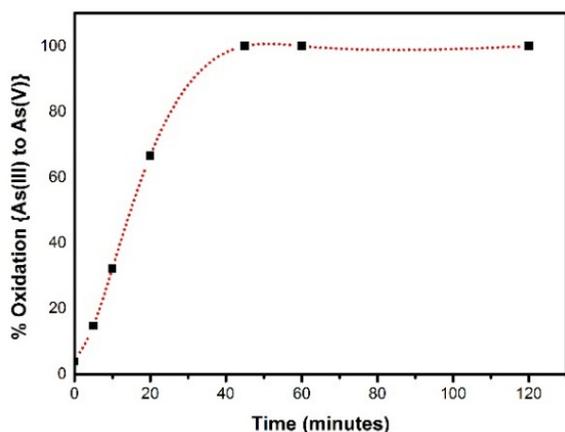


Fig. 8. Kinetics of Arsenic(III) oxidation.

B. Effect of Organic compound and microorganism on the Arsenic removal

A natural organic compound present in the water can alter the efficiency [14] of the Arsenic removal by the nanocomposite. As a part of the oxidation study of Arsenic, we have to consider the presence of both organic matter and the microorganisms in the process, since the water contains all these elements together before the purification procedure. Here we have used the Dye Acid Blue 113 (AB113) as the model organic compound and Escherichia coli K12 (*E. coli* K12) as the model microorganism, and the dependence of these in the oxidation has been studied. The pH of the experiment was the natural pH of the solutions itself (5-7). The photocatalytic disinfection study was performed with *E. coli* K12 bacterial cells, suspended in PBS solution after centrifuging the mother culture broth. The experiments were performed in triplicates, where 107 CFU/mL of initial concentration was used. A total of 100 mL mixture of bacterial cells, Arsenic, and the nanocomposite solution were placed in the dark for 30 mins for obtaining equilibrium. Under visible light irradiation, the samples were withdrawn

every 30 mins and were plated on nutrient agar. The standard plate count method was carried out to identify the bacterial viability. The plates were incubated overnight at 37° C, and the colonies were counted after the incubation. Furthermore, the Acid blue solution was taken with a concentration of 40mg/L.

The modified TiO₂ has been used to oxidize Arsenic (III) to Arsenic (V). We studied the effect of an organic compound and the microorganism in the process of removal of the total Arsenic, as in Fig. 9

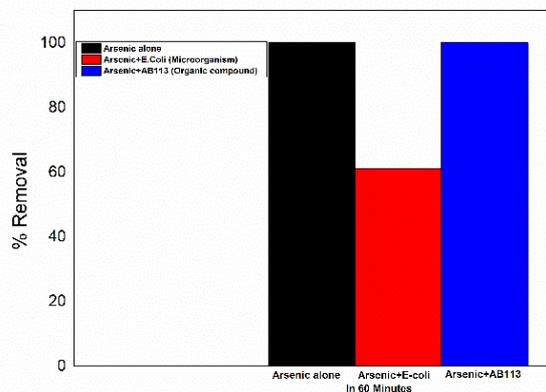


Fig. 9. Effect of organic compound and microorganism on the arsenic removal.

From Fig. 9, we can see that there is no noticeable effect of Organic compounds alone over the arsenic oxidation. In contrast, the microorganism is having considering effect where the Arsenic removal has reduced by 40% in the presence of the microorganisms, and this could be due to the adsorption of the microorganisms onto the catalytic surface, reducing the active sites.

V. CONCLUSION

The anatase TiO₂ has modified by introducing the BiVO₄, and the synthesis was achieved by Sol-gel methodology. The Characterizations have been done. The XRD analysis confirmed the formation of well-crystallized nanocomposite material. There observed no significant diffractions from the monoclinic BiVO₄ due to its low stoichiometry, which was below the detection limit of the diffractometer. However, there observed a shift in the diffraction angle of the nanocomposite. In the Raman analysis also has not shown the vibrations from the BiVO₄ phase, even though there observed a small shift in the peak positions and also observed a peak broadening and reduced intensity of peaks after the introduction of BiVO₄, which is due to the phonon confinement effects due to the oxygen deficiency by introduction of a minor phase, BiVO₄. The bandgap analysis has shown a slight change in the bandgap from 3.28 to 3.03eV after the BiVO₄ introduction. The BET analysis has confirmed the formation of a microporous nanomaterial with type 2 adsorption isotherm. Preliminary Arsenic removal tests have been carried out under the natural pH conditions, and the modified material has shown a complete removal of Arsenic compared to the pure TiO₂. The effect of the organic compound and microorganism has also been studied. It is observed that the organic compound that we have chosen, AB113 as a model, does not have any effect on photocatalysis. Whereas, in the presence of *E. coli* (model microorganism), the Arsenic removal efficiency of the modified TiO₂ reduced nearly 40%.

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