Vanadium doped titania nanoparticles for photocatalytic removal of heavy metals from aqueous solutions

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ABSTRACT
Sol-gel process with continuous ultrasonication was used to produce pure and vanadium doped titania powders. The amount of vanadium doped in titania was varied by using different initial concentrations of vanadium solutions. Scanning electron microscopy and particle size analyses showed formation of spherical shaped particles with diameter ranging from 3 to 11 nm. The average pore volume was 0.0248 cm³/g, and the surface areas of pure and V-doped titania were 62.9 and 66.1 m²/g, respectively. The maximum amount of vanadium doped on titania catalyst, as determined using energy dispersive X-ray spectroscopy was 1.7 wt%, and the X-ray diffraction patterns showed the presence of mainly anatase form of titania. The photocatalytic activities of pure and V-doped titania were tested for methylene blue, and the metal uptake was found to increase from 10 mg/g for pure titania to 17 mg/g for V-doped titania. Adsorption isotherms for removal of lead and zinc from aqueous solutions were generated under ultraviolet exposure for 24 h, and the results revealed that the photocatalytic activity was enhanced when titania was doped with vanadium.

ARTICLE HISTORY
Received 5 October 2020
Accepted 25 January 2021

KEYWORDS
Titania nanoparticles; vanadium doping; photocatalysis; adsorption isotherm; methylene blue

1. Introduction
Nano-sized titanium dioxide particles have gained wide attention in many physical and chemical applications. These include optical coating, manufacture of optoelectronic devices, photocatalysis applications for removal of dyes and heavy metals from aqueous solutions, and selective photoreduction of CO₂ for solar fuels [1–7]. Utilisation of nanocrystalline titania for the removal of toxic hydrocarbons and heavy metals from aqueous solutions has been shown to be effective in environmental clean-up. In this process, UV light is utilised to activate titania by the absorption of photons of ultra-band gap energy which leads to promotion of electrons (e⁻) from the valence band to the conduction band; this generates holes (h⁺) in the valance band. The photo generated e⁻/h⁺ pairs on the surface of the catalyst are highly oxidising and reducing, and could react with the adsorbed species on the catalyst surface to generate free radicals, hence can be used for...
the removal of heavy metal ions and hydrocarbons efficiently to obtain high reduction percentages similar to the values obtained by novel materials such as carbon materials derived from metal organic frameworks (MOFs), Zeolitic imidazolate frameworks (ZIFs) and graphene-based composites [8–10].

Several methods have been used for the synthesis of nanocrystalline titania, including sputtering, spray synthesis, chemical vapour deposition, and sol-gel method. Among these, sol-gel method is the most widely used as it is relatively simple and no special equipment are required. In order to enhance the photocatalytic activity of titania, it is crucial to prevent recombination of the photogenerated e-/h+ pair. One way to achieve this is by incorporating other metal oxides into the matrix of titania, which is known as doping [11]. The doped metals act as promoters on the surface to prevent any surface agglomeration and reduce the space charge region, and thereby separate the electron hole pair. The choice of metals to be doped on the surface of titania depends on its ability to form a homogeneous surface metal oxide [12–19].

Herein, nanocrystalline pure and vanadium-doped titania were synthesised via sol-gel process, and their photocatalytic activities were tested for the degradation of methylene blue (MB) at different pH values. The major objective of this study is to investigate the application of pure and V-doped titania for the removal of lead and zinc ions from aqueous solutions.

2. Material and methods

2.1. Materials

Titanium (IV) isopropoxide, hydrochloric acid, methanol, and ammonium metavanadate were acquired from Sigma-Aldrich and used without further purification. Deionised (DI) water was obtained from a Milli-Q water purification system (Millipore). All Pyrex glassware were washed with diluted nitric acid, soap, and DI water and dried in an oven at 75°C.

2.2. Methods

2.2.1. Syntheses of pure and vanadium doped titania

Nanocrystalline titania was synthesised using sol-gel process wherein a mixture of 5 ml of titanium isopropoxide (99.99%) and 25 ml of methanol at 5°C was subjected to continuous ultrasonication. Another mixture of 25 ml of methanol, 0.5 ml of HCl (1.3 M), and 0.5 ml of DI water was prepared and added drop wise to the first mixture of solvent and isopropoxide to prevent sudden formation of gel which may lead to incomplete reaction. The resulting sol was stirred for 1 h in an ultrasonic bath to prevent any agglomeration of the catalyst. The sol was dried in an oven for 12 h at 75°C, followed by crushing and calcination at 450°C for 4 h. A similar procedure was followed to prepare V-doped titania by replacing DI water with a solution of vanadium prepared by dissolving an appropriate amount of ammonium metavanadate in water. Different concentrations of vanadium solution were used to vary the amount of vanadium doped in titania, as shown in Table 1.

2.2.2. Adsorption isotherm experiments

For MB degradation experiments, a stock solution of 100 ppm was prepared by dissolving 100 mg MB in DI water. Different concentrations ranging from 10 to 100 ppm were prepared from the stock solution, and the pH of the adsorbate solution was maintained at 4,
and 10 using standard buffer solutions. For each concentration, 100 ml solution was taken and divided into half (50 ml) in two conical flasks; 0.1 g of the catalyst was added to one of them while the other was left as a blank. Both the blank and the catalyst containing flasks were exposed to ultraviolet (UV) light (300 nm) for 24 h at 25°C to ensure the equilibrium, and then the concentration of MB in all the samples was measured using an atomic absorption spectrophotometer. The difference between the concentrations of MB in the blank and the catalyst containing samples yielded the amount of MB removed by titania. A similar procedure was followed for the adsorption of Zn and Pb, where the stock solutions were prepared using zinc nitrate and lead nitrate, respectively, while all metals solutions were adjusted at pH of 2, based on several research articles suggesting optimum metals reductions at lower pH values [20,21]. All experiments were performed five times using the same catalyst at the same conditions for each measurement and the average was taken. Variations were found to be negligible (less than 6% maximum).

2.3. Characterisation

The microstructural analysis of the synthesised titania powders was performed using scanning electron microscopy (SEM; JOEL JSM-6460LU), and the particle size distribution was obtained using a particle size analyzer (PSA; Microtrac-Zetatrac, MICROMERTICS-S3500), where 0.05 wt% of the catalyst was ultrasonicated in a water bath for 15 min to obtain good dispersion. The amount of vanadium doped in titania was determined by energy-dispersive X-ray spectroscopy (EDS; OXFORD INCAx-SIGHT); its resolution at 5.9 keV is 137 eV. The surface area was measured using Brunauer, Emmett, and Teller technique (BET; MICROMERITICS-ASAP 2020) using liquid nitrogen. The crystalline phase and structure of the nanoparticles were characterised by X-ray diffraction (XRD).

3. Results and discussion

The synthesis of titanium dioxide takes place via two steps. First, the hydrolysis of titanium isopropoxide by acid takes place according to reaction (1):

$$\text{(RO)}_3\text{Ti} - \text{O} - \text{R} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{(RO)}_3\text{Ti} - \text{O} - \text{H} + \text{R} - \text{OH}$$  \hspace{1cm} (1)

The second step involves condensation of the produced hydroxides to form hydrated titanium dioxide as described by reaction (2):

$$2(\text{RO})_3\text{Ti} - \text{O} - \text{H} + \text{(RO)}_3\text{Ti} - \text{O} - \text{Ti} - (\text{RO})_3 + \text{H}_2\text{O}$$  \hspace{1cm} (2)

The produced hydrated titanium dioxide is thermally treated to produce titania nanoparticles. The shape and the size of the catalyst depend mainly on the ratio of titanium to water; generally, a high water content leads to fast hydrolysis of titanium isopropoxide and hence, formation of large aggregates [22].
3.1. Microstructural analysis

Figure 1 shows the SEM image of V-doped titania prepared at different Ti/H₂O ratios. At a high Ti/H₂O ratio (less amount of water), the catalyst particles are small and spherical. The particle size distribution is in the range of 3–11 nm as shown in Figure 2. As the amount of water increased (Figure 1(c)), larger aggregates tend to form from smaller particles, known as Ostwald ripening, wherein coarsening and aggregation compete with nucleation during hydrolysis. The extent of this aggregation is a direct result of the Ti/H₂O ratio; a higher ratio (>5) yields smaller particle size, and a smaller ratio may lead to combustion of residual hydrocarbon during calcination process, resulting in the formation of coke in the final catalyst [23].

BET analysis of pure and V-doped titania was carried out, and the results are shown in Table 2. The surface areas of pure and V-doped titania are similar (62.9 m²/g for pure titania and 66.1 m²/g for V-doped titania). This is because there is no separate growth of metal oxide on the surface of titania. Moreover, vanadium oxide is well dispersed on the surface, which was confirmed by the absence of any characteristic peaks of vanadium in the XRD patterns (discussed later). The results also indicated similar Langmuir surface areas and pore sizes. Figure 3 shows that the N₂ adsorption–desorption isotherm of V-doped titania is of type IV, typical of a mesoporous catalyst.

Titania exists in three phases, namely anatase, rutile, and brookite. Anatase is the most active phase and can be converted to rutile by thermal treatment at 500°C. The XRD pattern of 1.7 wt% V-doped titania is shown in Figure 4. Peaks corresponding to (101),
(004), (200), (105), and (220) planes were observed at 2θ values of 25, 36, 48, 54, and 62°, respectively. The presence of (101) peak at 2θ of 25° (JCPDS 21-1272) confirms that the main phase of titania formed is anatase. The additional peaks indicate the presence of rutile phase of titania and crystalline (lattice) distortion caused by the incorporation of

![Figure 2. Particle size distribution of V-doped titania (TiO₂/H₂O ratio of 10).](image)

### Table 2. BET analysis results of pure and V-doped titania.

| Property                                | Pure titania | V-doped titania |
|-----------------------------------------|--------------|-----------------|
| BET surface area                        | 62.9336 m²/g | 66.1237 m²/g    |
| Langmuir surface area                   | 88.1457 m²/g | 93.2200 m²/g    |
| Single point desorption Average pore volume | 0.023739 cm³/g | 0.024800 cm³/g |
| Average pore width (4V/A by BET)        | 61.5828 Å    | 5.7318 Å        |

![Figure 3. N₂ adsorption–desorption isotherm of V-doped TiO₂.](image)
vanadium because of the difference in atomic radii of vanadium (134 pm) and titanium (147 pm) as stated by Pauling principle [12,16,24].

The amount of vanadium doped on the surface of titania was measured using EDS, and the percentage of vanadium on the catalyst was verified using different initial concentrations of vanadium solution; the results are shown in Figure 5. At concentrations higher than 4000 ppm, the amount of vanadium doped in titania tends to remain constant at 1.7 wt%, which is attributed to saturation of the titania surface with vanadium oxide formed by oxygen–metal bond. The EDS graph of V-doped titania prepared at 5000 ppm...
concentration, as shown in Figure 6, shows the presence of minor amount of Cl originating from the HCl acid used in the synthesis process.

### 3.2. Photocatalytic degradation of MB

The effect of incorporation of vanadium into titania matrix on the degradation of MB is depicted in Figure 7. It is evident that the doping of vanadium in titania increases the catalyst uptake significantly from 10 to 17 mg/g. This enhancement in the photocatalytic performance of titania can be attributed to the increment in the surface barrier which leads to less space in the charge region. The resulting large electric field makes the electron hole pair more separated and hence, more efficient.

Figure 8 shows the effect of different solution pH on the degradation of MB using V-doped titania. The catalyst uptake increased from 14 mg/g at pH 4 to 16 mg/g at pH 6 and 20 mg/g at pH 10. This is because at higher pH, dimerisation of MB may take place during the period of adsorption resulting in the reaction of negatively charged hydroxyl group with MB in solution. In addition, physical interaction may occur between the negatively charged catalyst surface and the nitrogen charge on MB [25,26].

### 3.3. Adsorption of Zn and Pb

The adsorption of Zn and Pb was studied using pure and V-doped titania under the same conditions to determine the metal uptake for both catalysts. The photocatalysis pathway involves mass transfer of metal ions to the surface of the catalyst, followed by adsorption of metal ions to active surface sites, where photocatalytic degradation can occur. At these sites, photo-generated electrons and holes can be utilised for the reduction of the metal ions. Degradation is followed by desorption of the degraded products, and finally mass transfer of the products away from the catalyst surface.
Doping can enhance the optical properties and photocatalytic activity of TiO₂ by using band gap modifications to enhance absorption of light in Doping can also prevent electron-pair recombination and charge separation [27].

The photocatalytic removal data for Zn and Pb are shown in Figures 9 and 10, respectively. The results indicate that pure titania adsorbs Pb more efficiently than Zn. For pure titania, a maximum uptake of 7 mg Zn²⁺/g of solid was obtained, whereas that of Pb was 17 mg Pb²⁺/g of solid. In the case of V-doped titania, the maximum uptake of Zn increased from 7 to 11 mg Zn²⁺/g of solid, and for Pb, the maximum uptake increased from 17 to 26 mg Pb²⁺/g of solid. At optimum conditions, the reaction constants calculated using the kinetic model developed by Mirghani et al. [27] were 3.75 × 10⁻⁴ and 4.63 × 10⁻⁴ cm²/J for Zn and Pb respectively.

Figure 7. Photocatalytic degradation of MB using pure and V-doped titania.

Figure 8. Photocatalytic degradation of MB at different pH using V-doped titania.
Similar trends were reported for photocatalytic removal of Cr(VI) using TiO₂ doped with different transition metals. Removal efficiencies of Cr(VI) using Cu–TiO₂ and Fe–TiO₂ catalysts were 72.8% and 62.1%, respectively [28].

There are many factors that can justify the preference of specific adsorbents toward some adsorbates than others. The tendency of titania to uptake more Pb than Zn can be explained by the ratio of charge to volume. Both Pb and Zn are amphoteric oxides. Pb exhibits oxidation states of +4 and +2, while Zn has oxidation states of +2 and +1. The
atomic radii of Pb and Zn are 175 and 134 pm respectively. Hence, the higher oxidation state of Pb makes the surface of titania more attractive for Pb than Zn in this case. On the other hand, the electronegativity of Pb, which is 2.33 (Pauling scale) is higher than that of Zn (1.65 on Pauling scale); this makes the negatively charged surface of titania more attractive to Zn than Pb. However, the sum of these two factors (charge to volume ratio and electronegativity) makes titania more attractive for Pb than Zn, as indicated by the adsorption isotherms [29,30].

4. Conclusion

Pure and V-doped titania were synthesised via sol-gel process, and the microstructural analysis showed spherical shaped particles. The photocatalytic activity of the catalyst was tested for the degradation of MB at different pH values. It was found that the catalyst uptake increased as the pH of the solution increases. The effect of vanadium doping in titania was investigated by applying both pure and V-doped titania for the removal of Pb and Zn from aqueous solutions. The results revealed that the photocatalytic activity was enhanced when titania was doped with vanadium; the maximum Zn and Pb uptakes of the catalyst increased from 7 mg Zn^{2+}/g for pure titania to 11 mg Zn^{2+}/g for V-doped titania and from 17 mg Pb^{2+}/g for pure titania to 26 mg Pb^{2+}/g for V-doped titania, respectively.

Disclosure statement

No potential conflict of interest was reported by the author.

Funding

The author is thankful to King Abdu Aziz City of Science and Technology (KACST) for the financial support of this project and also extends gratitude to the Chemical Engineering Department at Najran University for their support to this research.

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