Photodegradation of Molasses by a $\text{MoO}_3\text{-TiO}_2$ Nanocrystalline Composite Material

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Abstract: A $\text{MoO}_3\text{-TiO}_2$ nanocrystalline composite material was prepared by a simple sol-gel method. The synthesized material was characterized by X-ray diffraction, scanning electron microscopy with an electron dispersion spectroscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy. Melanoidin is a dark brown pigment found in wastewater from the sugar industry and it pollutes water. This polluted water is generally referred to as molasses and it undergoes fermentation and is solely responsible for water, soil, and air pollution. The synthesized catalytic material was found to be effective in degrading molasses under UV-visible radiation. Analysis of treated and untreated molasses was carried out by measuring its color, chemical oxygen demand, biological oxygen demand, pH, and total dissolved solid. Results from these analyses indicate the effective photodegradation of the molasses. This methodology has several advantages such as high photocatalytic activity, non-toxicity, cleanliness, and reusability of the catalytic material.

Key words: sol-gel; molybdenum oxide; titanium oxide; photodegradation; molasses; pollution control

CLC number: O643

Document code: A

Received 1 August 2011. Accepted 13 October 2011.

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English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Coloured water and compounds that cause colouration are undesirable for the domestic or industrial use of water as coloured water indicates pollution [1]. The permissible limit of the colour intensity of water for use in domestic or industrial purposes is 15–20 units according to the world health organization [2]. Several new techniques for wastewater decolourization have emerged with improved performance and they are more environmentally favourable. This includes advanced oxidation processes such as heterogeneous photocatalysis, Fenton, photo-Fenton, and ozonation, which have received considerable attention because of their “green” nature in that innovative technologies are promoted that reduce or eliminate the use or generation of hazardous substances in the design, manufacturing, and use of chemical products.

Distilleries in India use sugarcane molasses as a raw material for the production of ethanol. The effluents from these distilleries contain a large amount of molasses in the spent-wash, which is highly coloured because of the presence of melanoidin pigments [3]. Molasses spent-wash pollutes the aquatic ecosystem because of its intense brown colour, which cuts off light, prevents photosynthesis, and causes anaerobic conditions. When it is disposed of in soil it acidifies the soil and thereby affects agricultural crops. The anaerobic digestion of molasses reduces chemical oxygen demand (COD) and biological oxygen demand (BOD), however, the dark colour persists and this imparts an odd

odour, hence, it is necessary to devise a method for the treatment of molasses. A literature survey reveals that the chemical treatment [4–6] and biological decomposition processes [7,8] are used to deal with this problem, however, these methods are expensive and time consuming.

Semiconductors and modified inorganic oxide materials can activate the photodegradation process because of their photocatalytic activity. Several researchers have used these materials as photocatalysts for the decomposition of organic pollutants [9–15]. The photocatalytic activity is explained on the basis of electronic transitions taking place between the valence and conduction band because of the generation of electron-hole pairs. Among various semiconducting materials, titanium oxide has been the most intensively investigated because of its merits from economic and ecological points of view [16–20]. However, because of its wide bandgap ($E_g \sim 3.2$ eV), TiO_2 absorbs only a small fraction of incident solar energy (4%) and therefore, its overall photocatalytic activity is very low. Therefore, reducing the bandgap to enhance photocatalytic activity is challenging. Several attempts have been made to reduce the bandgap so that the resultant material will give enhanced photocatalytic ability. It has been reported that the introduction of molybdenum effectively reduces the bandgap because of its higher electronegativity [21]. This modified TiO_2 has been used for the photodegradation of organic compounds in an aqueous medium by several workers [22–28].

The use of a $\text{MoO}_3\text{-TiO}_2$ nanocrystalline material as a photocatalyst was reported by Song et al. [29] and they found that the effective photodegradation of the gas-phase of propanol is not possible. A similar study was also carried out by Agarwal et al. [30] who found that self-organised nanostructures that consist of $\text{TiO}_2\text{-MoO}_3$ with different amounts of MoO_3 also did not degrade the organic compound to the required extent. In this paper, we report the synthesis and characterization of a new photocatalytic material sensitive to visible light and its applicability to the photodegradation of molasses.

1 Experimental

1.1 Synthesis of $\text{MoO}_3\text{-TiO}_2$ by the sol-gel method

Titanium (IV) butoxide (97%), anhydrous ethanol, iso-propanol (99%), and ammonium heptamolybdate (99%) from Sigma-Aldrich were used as received. The modified $\text{MoO}_3\text{-TiO}_2$ catalytic material was prepared by the sol-gel method. A solution containing 160 ml of ethanol and 20 ml of iso-propanol was mixed thoroughly with 20 ml (50 mmol) of titanium (IV) butoxide. The mixture was slowly dropped into 100 ml of deionised water to form a white precipitate. The reaction mixture was kept under constant stirring at 90 °C and an aqueous solution of ammonium heptamolybdate 20 ml (25 mmol) was added and thoroughly mixed. The excess water was evaporated on a water bath with continuous stirring. The resultant precursor was dried at 110 °C for 12 h and finally calcined at 500 °C for 2 h in an air atmosphere.

Pure MoO_3 catalyst was prepared by a conventional co-precipitation method. The solution was obtained by diluting an ammonium heptamolybdate (50 ml, 25 mmol) solution with deionized water. The system was kept under constant stirring and the pH was maintained at 8 by the simultaneous addition of 1:1 NH_4OH . Excess water was evaporated on the water bath with continuous stirring. The resultant precursor was then dried at 110 °C for 12 h and calcined at 500 °C for 2 h in an air atmosphere. TiO_2 was prepared by a similar process to that mentioned above for modified $\text{MoO}_3\text{-TiO}_2$ except for the addition of ammonium heptamolybdate.

1.2 Characterization techniques

X-ray diffraction (XRD) analysis of the calcined sample was carried out with a Phillips X-ray diffractometer in a diffraction angle range $2\theta = 20^\circ$ to 80° using $\text{Cu } K_\alpha$ radiation with a wavelength of 0.15405 nm. Surface morphology and elemental analysis of the samples were carried out using a JEOL-JEM 2300 (LA) scanning electron microscope with

an electron dispersion spectroscope (SEM-EDS) attachment. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (JASCO FTIR/4100, Japan) from 4000 to 500 cm^{-1} . The microscopic nanostructure and particle size were determined using a CM-200 PHILIPS transmission electron microscope (TEM) at 200 kV ($L = 600$, $\lambda = 0.0025\text{ nm}$).

1.3 Photocatalytic degradation activity

The catalytic photodegradation experiments were performed using 100 mg of photocatalyst placed in 200 ml of a solution of molasses spent-wash (0.03%). The suspension was maintained under stirring for 30 min to attain equilibrium. It was then irradiated using a 300 W mercury lamp for 120 min. To follow the photodegradation, samples were taken at 20 min intervals over a certain period and the absorbance was measured using a spectrophotometer at a λ_{max} of 475 nm. The photodegradation and decolourization of a brown pigment such as melanoidin is generally assessed by measuring the decrease in colour intensity of the molasses solution. The extent of decolourization is expressed in terms of the degree of absorbance against time at λ_{max} . Similarly, the effect of temperature on degradation was also determined at 40, 60, and 80 °C. Other parameters like COD, BOD, pH, and total dissolved solids (TDS) were measured using standard methods for the examination of water and wastewater before and after treatment [31].

2 Results and discussion

2.1 XRD analysis

A systematic XRD study was carried out to understand the phase symmetry of the calcined sample. XRD patterns of the calcined materials are shown in Fig. 1. The peaks shown at $2\theta = 23.3^\circ, 27.3^\circ, 29.5^\circ, 33.7^\circ, 38.9^\circ, 49.3^\circ, 64.8^\circ$, and 72.9° indicate hkl values for the (110), (021), (130), (111), (060), (002), (190), and (232) planes. All the XRD peaks confirm the orthorhombic structure of MoO_3 (JCPDS 76-1003) [32] with lattice parameters $a = 0.39628\text{ nm}$, $b = 1.38550\text{ nm}$, and $c = 0.36964\text{ nm}$. The strong and sharp peaks suggest that the as-prepared materials are crystalline. All the diffraction peaks agree with those of the anatase TiO_2 (JCPDS 84-1286) [33]. The peaks shown at $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ, 55.1^\circ, 62.6^\circ, 69.7^\circ$, and 75.1° correspond to the (101), (112), (201), (210), (203), (204), and (223) planes and these are due to the anatase phase of TiO_2 with lattice parameters $a = b = 0.3782\text{ nm}$ and $c = 0.9502\text{ nm}$.

Similarly, the peaks of the modified $\text{MoO}_3\text{-TiO}_2$ were identified and found to be strong and sharp. The peaks at 2θ

Fig. 1. XRD patterns of pure MoO₃ (1), pure TiO₂ (2), and modified MoO₃-TiO₂ (3) calcined at 500 °C.

= 23.2°, 27.2°, 29.6°, 33.5°, 38.9°, 49.3°, 64.8°, and 72.9° indicate *hkl* values for the (110), (021), (130), (111), (060), (002), (190), and (232) planes, which confirms the orthorhombic structure of MoO₃. The peaks at 2θ = 25.8°, 35.8°, 46.4°, 57.7°, 62.6°, 69.7°, and 77.4° indicate *hkl* values for the (101), (112), (201), (210), (203), (204), and (223) planes and are due to the anatase TiO₂.

2.2 SEM-EDS analysis

The surface morphology and elemental composition of the pure and modified form were investigated using SEM and EDS. Figure 2(a) shows the images of highly crystalline flakes of the orthorhombic structure of pure MoO₃ while Fig. 2(b) shows the crystalline structure of the anatase TiO₂. The sample has some sphere-like particles on its surface while agglomeration and randomness is apparent. Furthermore, Fig. 2(c) shows the presence of ultrafine particles with an approximate diameter of a few nanometres for the modified MoO₃-TiO₂. From the SEM images, it can be seen that the addition of MoO₃ shows an alteration in crystallite size and the deposition of TiO₂ on the surface of MoO₃ rods. These results clearly support the assertion that the calcined material is composed of mixed metal oxides.

According to the elemental analysis of the mixed metal oxide modified MoO₃-TiO₂ (Fig. 3), the calculated atomic

ratio of Mo:Ti:O is in good agreement with the expected bulk ratio, which indicates the uniform distribution of metallic species throughout the sample volume. The elemental analysis indicates that the minimum stoichiometric ratio is maintained and this is shown in Table 1.

Fig. 3. EDS spectrum of the modified MoO₃-TiO₂.

Table 1 Elemental analysis of the modified MoO₃-TiO₂

Element	Mass (%)	Atomic weight (%)
O	32.67	65.59
Ti	35.34	23.70
Mo	31.99	10.71

2.3 FT-IR study

Figure 4 shows the FT-IR spectra of different samples. The bands at 655, 815, and 993 cm⁻¹ in Fig. 4(1) are characteristic of the terminal molybdenum oxygen double bond (Mo=O). The band at 1616 cm⁻¹ is attributed to the H-O-H bending vibration mode of the adsorbed water. The additional band around 2340 cm⁻¹ is probably due to the adsorbed CO₂ stretching vibration. The broad band around 3480 cm⁻¹ is due to O-H stretching vibration modes of the adsorbed water on the surface of the powder [34,35]. The band at around 717 cm⁻¹ is due to the vibrational modes of the anatase structure at the terminal titanium-oxygen double bond (Ti=O). The band at 1629 cm⁻¹ is attributed to the H-O-H bending vibration mode of the adsorbed water and the additional band around 2339 cm⁻¹ is probably due to the adsorbed CO₂ stretching vibration while the broad band

Fig. 2. SEM images of pure MoO₃ (a), pure TiO₂ (b), and modified MoO₃-TiO₂ (c).

Fig. 4. FT-IR spectra of pure MoO_3 (1), pure TiO_2 (2), and modified $\text{MoO}_3\text{-TiO}_2$ (3).

around 3464 cm^{-1} is due to O–H stretching vibration modes of the adsorbed water [36].

The IR spectrum of $\text{MoO}_3\text{-TiO}_2$ in Fig. 4(3) shows the same bands as those observed with MoO_3 and TiO_2 but bands are present at higher frequencies in addition to a distinct band at 572 cm^{-1} , which may be due to the molybdenum oxygen bond vibration. Specifically, it is due to bridging Mo–O in the polymeric molybdate species. The addition of Mo shows the strong association between MoO_3 and TiO_2 as well as strong band for the microcrystalline MoO_3 species at 1000 cm^{-1} for Mo=O in MoO_3 . The bands at 885 cm^{-1} are related to the distorted splitting of bridging Mo–O–Ti in the outer layer of bulk $\text{MoO}_3\text{-TiO}_2$.

2.4 TEM analysis

The TEM images shown in Fig. 5 indicate the clarity of the obtained nanosized particles. The TEM image of pure MoO_3 in Fig. 5(a) shows the presence of highly crystalline nanorods of MoO_3 with a particle diameter that varies between 15.34 and 20.70 nm while its length is about 500 nm. Similarly, Fig. 5(b) shows the presence of highly crystalline nanoparticles of TiO_2 with an average particle size of 11.40–18.39 nm. In Fig. 5(c) the average particle size of the modified sample of $\text{MoO}_3\text{-TiO}_2$ ranges from 10.42 to 18.57 nm and the MoO_3 rod had an average diameter of 500 nm. TiO_2 deposition is clear on the surface of the MoO_3 rods.

2.5 Spectroscopic study

UV-visible absorption spectra of pure TiO_2 , pure MoO_3 , and modified $\text{MoO}_3\text{-TiO}_2$ are shown in Fig. 6. Pure TiO_2 absorbs light of wavelengths shorter than 400 nm because anatase TiO_2 has a bandgap of around 3.2 eV [37]. Interestingly, only pure MoO_3 gives a red shift for light absorption

Fig. 5. TEM images of pure MoO_3 (a), pure TiO_2 (b), modified $\text{MoO}_3\text{-TiO}_2$ (c), and high magnification of the modified $\text{MoO}_3\text{-TiO}_2$ (d).

and can absorb light beyond 400 nm because of its lower bandgap of 2.75 eV [38]. Modified $\text{MoO}_3\text{-TiO}_2$ has a bandgap of 3.0 eV, and hence it has a red shift [39]. This clearly indicates that the absorbed visible wavelength component of modified $\text{MoO}_3\text{-TiO}_2$ is more than that of pure TiO_2 and MoO_3 . Therefore, the modified $\text{MoO}_3\text{-TiO}_2$ mixed metal oxide system has more intensive visible light absorption than that of the pure component. Therefore, electron transfer may occur in the modified $\text{MoO}_3\text{-TiO}_2$ from MoO_3 to TiO_2 , as shown in Scheme 1.

2.6 Catalytic activity

To evaluate the photocatalytic activity of the modified and pure oxides, an equivalent volume of molasses was treated with the modified and pure oxides by exposure to UV-visible light radiation. A remarkable decrease in the concentration of TDS (Fig. 7) and colour intensity (Fig. 8) in the presence of modified $\text{MoO}_3\text{-TiO}_2$ material was ob-

Fig. 6. UV-Vis absorption spectra of pure MoO_3 (1), pure TiO_2 (2), and modified $\text{MoO}_3\text{-TiO}_2$ (3).

Scheme 1. Plausible electron transfer process.

served compared with pure metal oxides. This is attributed to a reduction in the bandgap of the modified MoO₃-TiO₂.

Fig. 7. Study of the TDS from the prepared catalytic materials. (1) Blank; (2) MoO₃; (3) TiO₂; (4) MoO₃-TiO₂.

The modified MoO₃-TiO₂ catalyst shows maximum decolourization within 120 min. Photodegradation was studied at different temperatures and we found that the decrease in colour intensity was dependent on temperature. The photodegradation rate increases with an increase in temperature from 40 to 80 °C. This increase may be due to different microstructures as shown in the SEM and TEM results. However, it is mostly due to the comparatively increased surface area and a decrease in crystallite size, which results in the absorption of light in the near-visible region. The colour of the molasses solution decreases to around 70% for

Fig. 8. Photodegradation kinetics of the molasses by the prepared catalytic materials. (1) Blank; (2) MoO₃; (3) TiO₂; (4) MoO₃-TiO₂.

Fig. 9. Photodegradation photographs of the molasses with untreated (a), UV radiation (b), UV radiation + MoO₃ (c), UV radiation + TiO₂ (d), and UV radiation + modified MoO₃-TiO₂ (e).

the modified catalytic material compared with the pure metal oxide, as shown in Fig. 9. This is attributed to the decomposition of melanoidin into colourless smaller fragments causing an overall decrease in absorbance. The colour of the solution is due to the presence of melanoidin, which contains C=C and C=N bonds and during decomposition these bonds may cleave to form simple, smaller fragments. This is responsible for the remarkable reduction in the colour intensity and the TDS [40].

The physico-chemical parameter of molasses before and after photodegradation is shown in Table 1. The maximum decolourization, decreases in COD, BOD, and TDS, elemental content was found in modified MoO₃-TiO₂ than as

Table 2 Physico-chemical parameters of the molasses before and after photodegradation

Sample	pH	COD (mg/L)	BOD (mg/L)	TDS (mg/L)	O. D. at 475 nm	Element content (%)								E. C. (mmhos/cm)
						Ca	N	P	K	Zn	Cu	Fe	Mn	
Before treatment	7.72	6550	575	8500	78	10	25.8	15.62	38.2	0.02	0.21	0.82	0.21	0.66
After treatment	8.27	641	55	4255	32	15	27.6	14.87	40.8	0.01	0.28	1.11	0.23	0.62
APHA	6.8	325	35	2500	—	21	—	—	—	—	—	—	—	—
BIS	7.2	250	30	2100	35	17	—	45	—	—	—	—	—	—

APHA: American Public Health Association. BIS: Bureau of Indian Standards. O. D.: Optical density. E. C.: Electrical conductivity.

occurs in pure MoO₃ and TiO₂ respectively.

3 Conclusions

A synthesized nanocrystalline composite material was successfully used for photocatalytic reactions. The addition of MoO₃ to TiO₂ showed high activity for the photodegradation of molasses. XRD, SEM-EDS, FT-IR, and TEM were useful in detecting the presence of molybdenum oxide species on the TiO₂ surface. Because the newly modified MoO₃-TiO₂ material has an increased surface area compared to the pure oxides, a higher amount of absorption of molasses containing melanoidin is possible. The modified material has a reduced bandgap and can absorb more light in the near-visible region and thus accelerate the rate of decomposition.

Acknowledgements

The authors are grateful to the Head of the Department of Chemistry at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, for providing all the necessary and required facilities to carry out the work.

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