Green synthesis of vanadium oxide–zirconium oxide nanocomposite for the degradation of methyl orange and picloram

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Abstract
The vanadium oxide–zirconium oxide nanocomposite (V₂O₅/ZrO₂ NC) was synthesized by green method using Daphne alpine (D. alpine) leaves extract. The pore size and surface area was studied by N₂ adsorption-desorption process using Brunauer-Emmett-Teller (BET) methods and S_BET was found to be 214 m² g⁻¹. The crystalline nature and other crystal properties was investigated by x-ray diffraction (XRD) and the calculated average crystallite size is 41.74 nm. The morphology of the V₂O₅/ZrO₂ NC was examined by scanning electron scanning microscopy (SEM) and transmission electron microscopy (TEM). The thermal stability was examine by thermogravimetric analysis and a total of 11.73% weight loss was observed. The optical property was studied by diffuse reflectance spectroscopy (DRS) and band gap was found to be 3.93 eV. The surface function group was studied the Fourier transform infrared (FTIR) spectroscopy. The photocatalytic performance of V₂O₅/ZrO₂ NC was examined against methyl orange and picloram and 76.94% and 86% were degraded in 75 min respectively.

1. Introduction

Ecological pollution is one of the critical subject for research due to rapid discharge of organic pollutants in water bodies. The rapidly growing industrialization and advances agriculture results in advent of chemicals and their transformed products in ecological system, which led to the undesirable effect on environment. The azo dye such as methyl orange constitute more than 50% of the global dye production (700 000 ton per year) is used in the pharmaceuticals, textile and paper printing industries about 15% of them discharge into effluent stream [1, 2]. The effective removal of methyl orange is challenging due to its high stability in water, low biodegradation rate and carcinogenic nature [3, 4]. The picloram is herbicide belong to family of pyridine carboxylic acid with surface plasmon resonance at 405 nm and is widely used to control variety of weeds and woody plant grow in rice, sugarcane and cereals field [5]. The picloram is white powder at room temperature released into ground water since it is not evaporated and hydrolyzed. The picloram is carcinogenic in nature and causes reproductive toxicity and genotoxicity in animals as well as human being [6]. The organic dyes and pesticides are highly hazardous to human and other aquatic organisms. The removal of these organic compounds is essential to ensure human health and life of aquatic biota [7]. The use of reliable procedure is essential for the complete remediation of toxic organic compounds from water resources without causing any harm. The photocatalytic degradation is favorable method for removal of hazardous organic compounds from water bodies owing to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic product and removal pollutant in ppb range [2, 8].

The transition metal oxides have been a focus of research in recent years in view of their fundamental and technological aspects including mechanical, thermal, optical, and electrical characteristics [9]. Among them, the oxide of zirconium and vanadium are very effective in term of photocatalytic activity. The ZrO₂ with wide band
gap in range of 5.0–5.5 eV is extensively used as photocatalyst due to its physical nature, chemical inertness, low toxicity, photo-thermal stability, high corrosion resistance and low thermal conductivity [10]. On other hand, V2O5 have narrow band gap ~2.3 eV, which can spread the light absorption to visible region [11–16]. The coupling of two or more active components effectively make hetero-structure like SnO2 aerogel/reduced graphene oxide nanocomposite coupling and Ag2CO3/β-bi2WO6 heterojunction are a more powerful method to overcome the drawbacks of all traditional photo catalysts [17–19].

To the best of our knowledge, the V2O5/ZrO2 NC is yet to synthesize by using plant material. Thus, the present research work was planned to synthesize V2O5/ZrO2 NC using D. alpine leaves extract and the physicochemical properties were studied by N2 adsorption-desorption, XRD, TEM, SEM, TG/DTG, DRS and FTIR techniques. The synthesized V2O5/ZrO2 NC were used as photocatalyst for the degradation of methyl orange degradation of methyl orange and picloram in aqueous solution in the presence of simulated solar light source. A set of mathematical equations was used to determine the percentage degradation and degradation rate constant for the photochemical reactions.

2. Materials and methods

2.1. Materials

The analytical grade chemical purchased from Sigma Aldrich are ammonium meta-vanadate, zircon (IV) chloride, methyl orange, picloram and ethanol. Deionized water were used throughout the research work and all the glass wares were treated with 15% (v/v) solution of nitric acid for 3 h, washed with deionized water and dried in oven at 100 °C.

2.2. Preparation of plant leaves extract

For the preparation extract, the D. alpine leave were collected from northern area was washed with deionized water and were dried in the absence of sunlight. The 20 g of the leave was added into beaker containing 1000 ml of deionized water and were heat for 3 h at 60 °C. The crude extract form was filtered through Whatmann No. 1 filter paper and then centrifuged at 4000 rpm for 20 min. The upper layer of the leave extract was stored in air tight bottle at 4 °C for further use.

2.3. Synthesis of V2O5/ZrO2 NC

For the synthesis of V2O5/ZrO2 NC, 50 ml of ammonium meta-vanadate solution (5 mM) was mixed with 20 ml of the D. alpine leave extract under stirring and heating till formation of gel. Similarly, The 20 ml of the leaves extract was added to the 50 ml of zircon (IV) chloride solution (5 mM) at constant heating and stirring till the gelation. Both gels were then mixed together under vigorous stirring for 3 h at room temperature and the resultant light green colored product was aged for 24 h. The well settled product was collected by centrifugation at 4000 rpm for 15 min. The residue obtained were rinsed three time with deionized water followed by ethanol and were dried in electric oven at 100 °C. The dried sample were stored in air tight bottle and subjected to further experiments.

2.4. Characterization

The surface areas, pore volume and size of V2O5/ZrO2 NC was measured by N2 adsorption-desorption using Quantachrome Quadrasorb SI (Quantachrome Instrument, Odelzhausen, Germany) and the sample under vacuum was degassed at 200 °C for 16 h. The crystalline nature of V2O5/ZrO2 NC was studied by using analytical X-pert pro (PW3040/60) diffractometer in the 2θ range of 20° to 80°. The surface morphology was observed with scanning electron microscopy model JEOL 5910 (Japan) and transmission electron microscopy Model Hitachi TEM HT7700. The Perkin Elmer Model 6300 TG/DTG analyzer was used for thermal (TG/DTG) analysis. A sample of known amount was heated up to 1000 °C, starting from 40 °C with heating rate 10 °C min−1 under air atmosphere. The DRS model UV–vis/NIR spectrometer lambda 950 with integrated sphere of 200–250 nm was used to study optical property was studied. Fourier transform infrared analysis was performed with a Shimadzu FT-IR spectrophotometer model 8400 S in the range of 4000–400 cm−1.

2.5. Photocatalytic experiment

The photocatalytic activity of V2O5/ZrO2 NC was conducted in aqueous solution to degrade methyl orange and picloram. The photocatalytic experiment was carried out in a Pyrex double walled beaker having inlet and outlet valve used for cooling purpose by connecting with water pipe. The aluminum foil was used to cover reactor containing 50 ml of methyl orange and 0.02 g of the catalyst so that light interaction was avoided and was stirred in dark for 30 min established adsorption/desorption equilibrium. Afterward, the solution was irradiated under stimulated solar source and after specific time interval, 3 ml of reaction was centrifuged for 5 min at 4000 rpm.
and upper portion was then analyzed by double beam spectrophotometer and absorbance maxima was noted as function of time. Similar procedure was repeated for the photo-degradation experiment of picloram.

3. Result and discussion

3.1. Physiochemical properties

The mesoporous nature of the V$_2$O$_5$/ZrO$_2$ NC was determined by the type VI N$_2$ adsorption desorption isotherm (figure 1). The adsorption maximum was appeared in the range of 0.55 to 0.85 p/p$_0$ forming H2 (b) hysteresis loop, assigned to mesoporous nature of the sample. The BET and BJH methods were utilized to measure specific surface area and pore size distribution. The S$_{BET}$ was measured to be 214 m$^2$ g$^{-1}$, whereas the pore size and pore volume was found to 2.3 nm and 0.36 cc g$^{-1}$. The reaction temperature might be cause of the high surface area, which during condense phase(gel) formation form meta phase(sol) govern the nucleation and growth followed by Ostwald ripening [20]. Thus, the particles size, interfacial energy and growth rate is influence by the temperature [20]. The slow nucleation and growth due to low reaction temperature leads to formation of small size nanomaterial, which are of high surface area as compared to large size particles. The x-ray diffraction pattern of the V$_2$O$_5$/ZrO$_2$ NC given in figure 2, shows the characteristic Bragg’s reflection at the corresponding 2 theta position. The diffraction bands appeared at 2theta position with corresponding hkl values position are 21.40 (200), 28.16 (103), 34.04 (004), 36.67 (213), 42.80 (303), 43.68 (400), 56.43 (501) are match with the diffraction bands listed in the JCPDS card 00-023-0720. The diffraction peaks confirm the synthesis of nano sized V$_2$O$_5$ exhibiting tetragonal geometry. The set of Bragg’s reflection appeared at 2 theta position are 23.53, 24.90, 30.66, 32.92, 48.56, 49.32, 50.94, 59.82 and 63.69 with the corresponding miller indices (015), (009), (018), (110), (1112), (211), (122), (1019) and (11 18) respectively. These bands along with hkl values are in close agreement with those listed in the reference card 00-073-0958, owing to the rhombohedral geometrical shape of ZrO$_2$. The crystallite size calculated by considering the FWHM of the diffraction bands for V$_2$O$_5$ and ZrO$_2$ are 48.63 and 34.05 nm respectively.

The low to high magnified TEM micrographs of V$_2$O$_5$/ZrO$_2$ NC shown in figure 3, shows that the mono-disperse particles are interconnected with each other. The micrographs shows that dense structure formed due to agglomeration of particle, however some particles with distinct boundaries also found. The particles are found to be different in size and shape and exhibits smooth surface. The size of particle calculated from these TEM micrograph are ranging from the 34–50 nm. The low to high magnified SEM micrographs of V$_2$O$_5$/ZrO$_2$ NC shown in figure 4, explain the morphology of the sample. The highly agglomerated particles forming compact solid in background, however, the individual particles are present on the surface, exhibits smooth surface. The majority of the particles with distinct boundaries are varies in size and shape, however few particles with nearly spherical shape are also present. The SEM particles was found in the range of 45–80 nm.

The TGA curve of V$_2$O$_5$/ZrO$_2$ NC given in figure 5, shows total weight loss of 11.73% in three stages between 45 to 630 °C. The weight losses at 47.78 and 110 °C are due to ethanol traces loss and adsorbed moisture meanwhile the weight loss at 530 °C assigned to chemically sorbed water [21]. The DTG sharp intense curve at
63.98 °C shown in figure 5 is associated with loss of ethanol traces while small endothermic peak between 281.6 °C to 361.8 °C are due to loss of loosely bounded water molecule. A couple of peak at 519 and 528 are small exothermic and endothermic peaks may be because of burning of organic compound and removal of
chemisorbed. The diffuse reflectance spectrum V$_2$O$_5$/ZrO$_2$ NC was measured in the range of 250 to 600 nm as given in figure 6. The DRS spectrum shows that the transmittance edge is positioned at 315.88 nm. The band gap energy calculated on the basis of absorbance edge are 3.93 eV. The band gap energy of V$_2$O$_5$/ZrO$_2$ NC is found different from that of the ZrO$_2$ and V$_2$O$_5$, suggesting that the formation of new material [17, 18]. The Fourier transform infrared spectrum of V$_2$O$_5$/ZrO$_2$ NC shown in figure 7 exhibits a broad band assigned to stretching vibration of OH group around 3499 cm$^{-1}$. The peaks appeared around 3000 and 2942 cm$^{-1}$ is for C-H bending whereas the band at 1725 cm$^{-1}$ may be due to carbonyl group of ester and carboxylic acid. The bands at 1433 and 1220 cm$^{-1}$ are attributed to N=O bending mode and carbonyl stretching respectively. The band at 1085 cm$^{-1}$ is for vandyl stretching mode and band at 779 cm is attribute to the bridging metal-oxygen-metal (V-O-V) [22]. The bands at 1364 and 903 cm$^{-1}$ is attribute to V$_2$O$_5$–ZrO$_2$ NC indicates Zr–O–V stretching [23]. The band at 779 cm$^{-1}$ is assigned to ZrO$_2$ while those located at 524 cm$^{-1}$ is for the symmetric stretching of V–O–V [10].

3.2. Photocatalytic activity
The photocatalytic efficiency of the synthesized V$_2$O$_5$/ZrO$_2$ NC was examined against the methyl orange and picloram in the range of 200–600 nm and surface plasma resonance was observed at 464 and 405 nm respectively. The 50 ml aqueous solution of the methyl orange and picloram was individually added into separated reactors containing 0.02 g of the V$_2$O$_5$/ZrO$_2$ NC (0.4 g l$^{-1}$) was covered with aluminum foil and stirred to established adsorption/desorption equilibrium. After dark test, the photocatalytic reaction was irradiated under the simulated solar light source and the 3 ml of the sample was examined by double beam
Figure 7. FTIR spectrum of V$_2$O$_5$/ZrO$_2$ NC.

Figure 8. Degradation profile (a), Percentage degradation (b), Kinetic isotherm (c) and Schematic mechanism (d) for the degradation of methyl orange and picloram in the presence of V$_2$O$_5$/ZrO$_2$ NC.
spectrophotometer after specific interval of time. The degradation profile shown in figure 8(a) shows gradual reduction in the absorbance maxima as a function of time. The performance of the catalyst was seen to enhance with increasing the irradiation time under simulated solar light. The percentage degradation shown in figure 8(b), was calculated by using the following equation (equation (1)) where the \( C_o \) is the initial concentration and \( C_t \) is equilibrium concentration [24]. The 76.94% and 86% of the methyl orange and picloram were found to degrade in 75 min respectively. The Langmuir–Hinshelwood kinetics model (equation (2)) was applied to the experimental data to determine the degradation rate constant, where \( k \) is degradation rate constant, \( C_o \) is initial concentration while \( C \) is the concentration of organic compound at time (t). The plot \( \ln(C_o/C) \) against time (t) (figure 8(c)) shows linear relationship suggesting that the photocatalytic reaction follow pseudo first order reaction [25]. The degradation rate constant shows that 0.017 73 and 0.026 21 amount of methyl orange and picloram degraded in per min.

\[
\% \text{ degradation} = \frac{C_o - C_t}{C_o} \times 100
\]

\[
\ln(C/C_0) = -kt
\]

The heterojunction of ZrO2 and V2O5 is illuminated with simulated solar light the electrons excited from valence band to conduction band, generating holes in the valence band. The formation of powerful oxidizing agents on the surface of metal oxide is promoted by light irradiation which leads to the decomposition of organic pollutants. The schematic mechanism of electron excitation and holes creation for V2O5/ZrO2 NC is best explained by set of reactions shown in figure 8(d). When a photon having equal or higher energy than the band gap of the catalyst, strike on the surface of catalyst, the outermost electron of both oxides gets excited into conduction band and simultaneously same amount of holes were generated in the valence band. The photo-generated electron transfer from conduction band of ZrO2 to the conduction band of V2O5 while the generated holes in valence band of V2O5 accumulated in valence band of ZrO2, shows that the electron and hole are efficiently separated [26]. Afterward, the surface hydroxyl group of the catalyst were trapped by photo-generated holes (h+), producing hydroxyl radicals (OH). The superoxide anion radicals (O2-) is an additional source of hydroxyl radicals, formed by the reaction of excited electron with absorbed oxygen. The methyl orange and picloram get oxidized by hydroxyl radicals (OH) and leads to the production of intermediates organic molecules which were further converted into carbon dioxide and water [27].

4. Conclusion

The V2O5/ZrO2 NC was successfully synthesized via biological route using D. alpine leaves extract. The physicochemical properties were studied by different techniques, which confirm the synthesis of highly crystalline V2O5/ZrO2 NC with high surface area. The mesoporous particles exhibits smooth surface and all the particles observed SEM and TEM micrographs are fall in nano range. The thermal treatment of V2O5/ZrO2 NC shows that the composite are highly stable up to 1000 °C, whereas the weight loss is due to the loss of water molecules. The band gap determine for the synthesized V2O5/ZrO2 NC is different for that of V2O5 and ZrO2 nanostructures suggest the formation of new material. The synthesized V2O5/ZrO2 NC was utilized to encounter the water pollution cause due to the methyl orange and picloram and were photo-catalytically eliminate from the aqueous solution. The performance of synthesized photocatalyst was found to increasing the irradiation time and was more efficient against found against picloram as compared to methyl orange. The V2O5/ZrO2 NC may also use against other organic pollutants and also as adsorbent for the adsorption of heavy metal ions from aqueous solution in future.

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