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Nanostructured zirconium tungstate and its bionanocomposite with chitosan: Wet peroxide photocatalytic degradation of dyes

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ABSTRACT

In this study nanoclusters of zirconium tungstate (ZrW) were synthesized hydrothermally in a stainless steel autoclave and its bionanocomposite with chitosan (CZrW) was fabricated. The synthesized ZrW and CZrW were characterized by UV, FTIR, XRD, TEM Raman and TGA techniques and further explored for their catalytic potential in degradation of dyes. ZrW and CZrW exhibited high photocatalytic activity for degradation of cationic and anionic dyes as well as their binary mixture under ambient conditions using H_2O_2 . It was observed that CZrW was more effective in degradation of dyes as compared to ZrW while ZrW was more efficient in mineralization. The high catalytic activity can be attributed to the possible formation of surface peroxy complexes by ZrW and CZrW. Furthermore the green catalyst could be reused for degradation of dyes for three cycles without significant loss in efficiency. This study opens new avenues in designing CZrW based green catalysts for degradation of dyes.

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1. Introduction

Catalytic oxidation using hydrogen peroxide is known to be superior in comparison with other methods [1–5] for degradation of recalcitrant dyes. Among the various catalysts being used for degradation of dyes, ion exchange materials as catalysts are highly specific and selective for water treatment studies due to which scientists opt to exploit these materials for various applications [6,7].

Zirconium tungstate belongs to the cubic AM_2O_8 family ($A=Zr, Hf$; $M=Mo, W$). The tungstates are thermodynamically stable at high temperatures [8,9]. Zirconium tungstate (ZrW_2O_8) is a unique ceramic oxide that exhibits a negative coefficient of thermal expansion (CTE) over a wide temperature range [10]. ZrW_2O_8 based materials have been used in a wide range of applications such as low CTE polymer composites [11,12], substrates for mirrors and optical devices [6], microelectronics [7] and construction materials [13]. ZrW_2O_8 was also discovered to be a novel photocatalyst for hydrogen production from photocatalytic water splitting [14].

The synthesis of ZrW_2O_8 nanoparticles has been attempted through either sol–gel [15,16] or hydrothermal methods [17,18]. Lo et al. [19] reported a sol–gel/reverse micelle technique, which resulted in parallelepiped nanoparticles. Zhang et al. [16] also utilized the sol–gel technique for the synthesis of ZrW_2O_8 , which were further electro-spun to produce ZrW_2O_8 nanofibers. Xing et al. [17] used a hydrothermal method in HCl medium for synthe-

sis of ZrW_2O_8 nanorods with widths ranging from 40 to 500 nm. Kozy et al. [18] obtained smaller ZrW_2O_8 nanoparticles of different morphologies through careful control of hydrothermal reaction variables such as nature of acid, concentration, and reaction time. Perottoni et al. [20,21] have shown that ZrW_2O_8 undergoes an irreversible pressure-induced amorphization above 1.5 GPa. The amorphous phase of zirconium tungstate reverts to α - ZrW_2O_8 upon annealing at about 900 K at ambient pressure [22]. Of all the methods the sol–gel/hydrothermal technique is popular due to its ease in processing methodology and control on the morphology of the particles [23–25].

In hydrothermal synthesis, zirconium tungstate is prepared by decomposition of the precursor $ZrW_2O_7(OH_xCl_{2-x}) \cdot 2H_2O$ at relatively lower temperatures [17,26,27]. Furthermore, ZrW can be incorporated into various polymer matrices to form composites utilized in a wide range of applications [28,29] with an extensive potential for reuse. Hongchao et al. had utilized zirconium tungstate/epoxy nanocomposites [30] for the application in microelectronic insulation industry. Niwas et al. had investigated the adsorption of phosphamidon on the surface of styrene supported zirconium (IV) tungstophosphate [31]. Viswanathan and Meenakshi had investigated the adsorption of fluoride onto chitosan supported zirconium (IV) tungstophosphate composite [29]. These composite ion exchangers have the desired properties of both organic and inorganic counter parts put into one molecule with the required selectivity, specificity as well as wide range of applicability, making them amenable for their use in environmental remediation.

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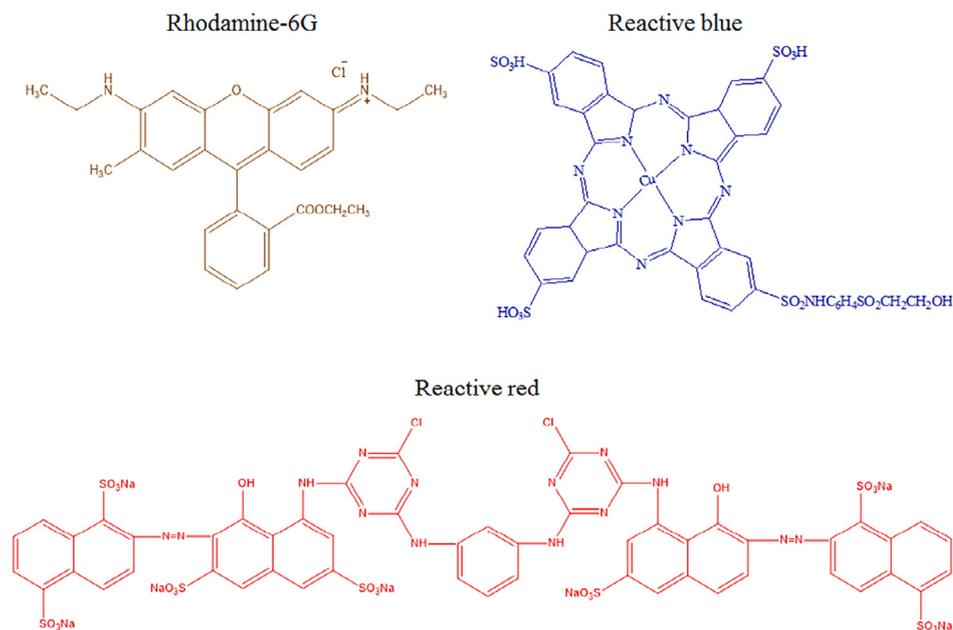


Fig. 1. Structure of dyes.

However till date chitosan supported zirconium tungstate has not been explored as a catalyst for degradation of dyes. The goal of this study was to synthesize nano form of precursor zirconium di(hydroxo)aquatungstate(ZrW) in the absence of acid, its nanobiocomposite with chitosan (CZrW) and further investigate the potential of ZrW and CZrW as catalysts for degradation of dyes. The degradation of anionic dyes Reactive Blue-21 (RB-21), Reactive Red-141 (RR-141), cationic dye Rhodamine-6G (Rh-6G) (Fig. 1) and their binary mixtures Reactive Blue-21 + Reactive Red-141(RB + RR), Reactive Red 141 + Rhodamine-6G(RR + RH) and Reactive Blue-21 + Rhodamine-6G(RB + RH) with ZrW and CZrW as catalysts have been investigated.

2. Experimental section

2.1. Materials and methods

Sodium tungstate (Na_2WO_4 , Merck; 99.9%), zirconium oxy chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Spectrachem), commercially used dyes (Fig. 1) Reactive Blue-21 (RB-21), Reactive Red-141 (RR-141), Rhodamine-6G (Rh6G) and hydrogen peroxide (H_2O_2 , Fisher Scientific; 30% solution), were used in this study without further purification.

2.2. Synthesis of zirconium tungstate

Zirconium tungstate (ZrW) was prepared by adding an aqueous solution of sodium tungstate to an aqueous solution of zirconium oxychloride in 2:1 molar proportion under stirring condition, at room temperature. White precipitates of zirconium tungstate were formed which were further stirred for 2 h for complete precipitation and were then kept in autoclave for 3 h. The precipitates were then centrifuged and washed several times with conductivity water and dried at 40°C to obtain ZrW.

2.3. Synthesis of chitosan–zirconium tungstate nanocomposite (CZrW)

1% Chitosan solution (100 mL) in acetic acid was added to 10 g of synthesized zirconium tungstate nanoparticle solution in stirring

condition. After few minutes (~ 10 min) fibrous white colored material was formed which was autoclaved for 3 h to obtain chitosan–zirconium tungstate nanocomposite (CZrW). The precipitates were then centrifuged and washed with conductivity water and dried at 40°C .

2.4. Individual and binary dye degradation experiments

The respective individual dye solutions, Reactive Blue-21 (RB-21), Reactive Red-141 (RR-141) and Rhodamine-6G (Rh-6G) and binary mixture of dye solutions (RB + RR, RR + RH, RB + RH) were prepared by dissolving the required amount of dyes in 100 mL of DDW. Samples were prepared by mixing 3 mL of the dye solution, 0.5 mg catalyst and $100 \mu\text{L}$ of 30% H_2O_2 in a cuvette. The cuvette was then inserted in the spectrophotometer, Scans were started immediately after the addition of nanoparticles, and the solution was left untouched until completion. Absorbance was monitored at the respective absorption maximum wavelengths of the dyes.

2.5. Characterization of the zirconium tungstate and chitosan–zirconium tungstate nanocomposite

The dried ZrW and CZrW were diluted with potassium bromide (KBr) at a ratio of 1:100 and the FTIR spectra were recorded. X-ray diffraction patterns were measured by a Rigaku ultima-3 diffractometer $\text{Cu K}\alpha$ radiation of wavelength 1.54184 \AA . Thermogravimetric analysis was done using EXSTAR6000 TG/DTA 6300 model instrument. Raman analysis was done using Horiba LabRAM HR Raman & PL instrument. TEM images were recorded using Philips (Model CM200) transmission electron microscope. Energy Dispersive X-Ray Spectroscopic (EDS) analysis were obtained using a SEM/EDX (JEOL, model JSM-5610LV) microscope operating at 200 KV. Surface area was measured using BET analyzer (Micromeritics, model ASAP 2020). The XPS analysis was done using VG Scientific ESCA LAB Mk-II Spectrometer. All degradation experiments were monitored by UV spectrophotometer (JASCO V-630 and TOC analysis of the degraded dye solution was done using a Shimadzu make TOC analyzer.

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