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Hydrothermal Assisted Synthesis of $FeWO_4$ for Degradation of 2-Nitrophenol under Visible Light Illumination

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ABSTRACT

In this paper, the iron tungstate ($FeWO_4$) particles were synthesized by a simple, facile and green hydrothermal approach using sodium tungstate and iron nitrate. The synthesized material have been characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), fourier transform infrared (FTIR) and UV-Visible diffuse reflectance spectrophotometer (UV-Vis DRS). These results reveal that the hydrothermally synthesized $FeWO_4$ material is a promising photocatalyst for the degradation of 2-Nitrophenol (2-NP) under visible light illumination.

Keywords : $FeWO_4$, Hydrothermal, 2-Nitrophenol And Visible Light Irradiation.

I. INTRODUCTION

The aromatic nitro-compounds are the lethal stuffs resulted in severe environmental pollution. Among them, nitro-phenols are persistent substances and widely used in chemical industry, pharmaceuticals, herbicides and dyes [1]; even at trace level the nitro-phenols toxicity effect on humans, animals and plants [2]. Especially, 2-nitrophenol (2-NP) is the hazardous organic pollutant with high toxicity [3, 4] and much attention in the production of chemical intermediates, explosives, fungicides, gas, herbicides, insecticides, pharmaceuticals, pesticides, petroleum, pigments, rubber chemicals, synthetic dyes, textile and wood [5, 6]. Hence, the elimination of 2-NP from wastewaters and drinking water is should be necessary.

Recently, advanced oxidation processes (AOPs) have been widely proved to be a benign method to elimination of toxic organic and inorganic pollutants from wastewater [7, 8]. AOPs are resultant in the production of hydroxyl radicals for the degradation of pollutants. Consequently, AOPs have great future and widely used [9].

Metal tungstates (MWO_4) with M = Mn, Fe, Co, Ni and Cu which are belongs to inorganic functional materials for various technological applications such as microwave, scintillation, optical modulation, magnetic and writing-reading-creasing devices, optical fibres, humidity sensors and photoluminescence materials [10-12]. $NiWO_4$, $CaWO_4$, $ZnWO_4$, $SrWO_4$, $SnWO_4$, $PbWO_4$, $BaWO_4$, $CdWO_4$ and $CuWO_4$ [13-21] have been reported earlier. In recent years, ferrous tungstate ($FeWO_4$) has great attention in photocatalysis due to it exhibits excellent visible light absorption capacity with a narrow band gap [22]. In this paper we aim at synthesis of iron tungstate ($FeWO_4$) via simple, green hydrothermal method and evaluate the photocatalytic degradation of 2-NP.

II. METHODS AND MATERIAL

Iron (III) nitrate hexahydrate ($Fe(NO_3)_2$), sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) were purchased from Sigma Aldrich), Merck), were used without further purification.

2.1. Synthesis of $FeWO_4$

All the chemicals were analytical grade and purchased from Sigma Aldrich, India. In a typical procedure, equimolar (1:1) ratios of $Fe(NO_3)_2$ and Na_2WO_4 were dissolved in 30 ml distilled water. After stirring for 20 min, the homogeneous green solution was transferred into a 50 ml teflon-lined autoclave with sealed and placed in an oven, heating at 180 °C for 3 h. After the reaction, the autoclave was cooled to attain room temperature. The suspension was centrifuged sequentially with both distilled water and ethanol; the resulting black precipitate was finally dried in an oven at overnight. The same procedure was adopted for 1:2 and 2:1 molar ratios of $Fe(NO_3)_2$ and Na_2WO_4.

2.2. Characterization

The crystalline size and phase formation of $FeWO_4$ were testes using XRD (Bruker) with Cu-K α radiation in the 2θ range from 10 to 80^0 in scanning rate of 2^0/min. The function groups were measured by FTIR (IR Prestige 21) with the scan from 400- 4000 cm^{-1}. The morphology of as prepared $FeWO_4$ was studied using FESEM (JEOL JSM-6700F). The elemental analysis was done using EDX. The bandgap energy of $FeWO_4$ was measured using diffuse reflectance spectra (Shimadzu, 2600R) with scanning of 200-800 nm with $BaSO_4$ as reference.

2.3 Evaluation of photocatalytic activity

The Photocatalytic activity of the $FeWO_4$ was evaluated by the degradation of 2,-NP under visible light illumination. The photocatalytic activities of the samples were evaluated by the degradation of 2-NP under visible light irradiation at ambient temperature using a 400 W metal halide lamp with a 420 nm cut-off filter as the light source. In each experiment, powder photocatalyst (50 mg) was dispersed in 50 mL of 2-NP aqueous solution (10 mg/L). Before irradiation, the suspensions were vigorously stirred for 30 minutes in dark condition to attain an establishment of adsorption–desorption equilibrium between the photocatalyst and 2-NP molecules. During the photoreaction, 5 mL suspensions from each sample were taken at every 15 minutes interval, followed by centrifugation to remove the photocatalyst. Finally, the centrifuged solutions were detected using a UV–Vis spectrophotometer (Shimadzu, 2500, India) at its maximum absorption wavelength of 350 nm. The degradation efficiency was calculated by using equation (1)

$$\% \text{ of degradation} = (C_0\text{-}C_t/C_0)\text{x}100 \quad \text{----} \ (1)$$

Where C_0 is the initial concentration and C_t is the concentration at time t of 2-NP solution.

III. RESULTS AND DISCUSSION

3.1 Structure and Morphology

Fig.1 (a-c) shows the XRD patterns of as-prepared three different ratios of $FeWO_4$. The strong and sharp diffraction peaks at 2θ=25°, 29°, 34°, 36°, 41°, 50°, 55°, 64° and 65° which are well in agreement with the standard JCPDS (Card No. 71-2391) [23]. All of diffraction peaks are well according with the, suggesting the monoclinic phase of the $FeWO_4$. No impure peaks could be detected, suggesting the high purity of the $FeWO_4$ was synthesized by hydrothermal method.

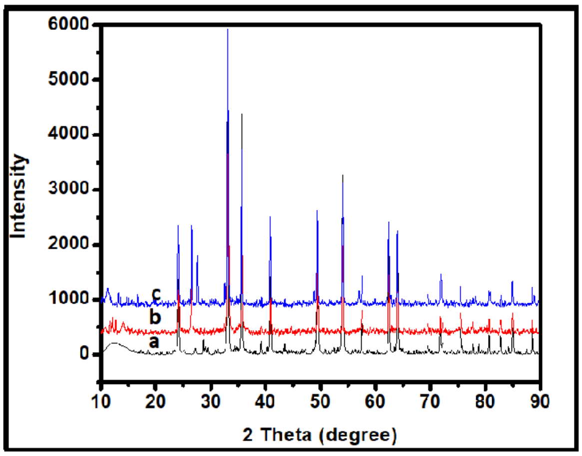


Fig.1: XRD patterns of a) 1:2, b) 1:1 and c) 2:1 ratios of $FeWO_4$

The FTIR spectra of prepared photocatalyst $FeWO_4$ was shown in Fig.2 (a-c), in which the two major characteristic peaks at 567 and 842 cm^{-1} corresponds to W-O and Fe-W-O [24]. All the characteristic peaks of three different molar ratios of $FeWO_4$ could be appearing too similar.

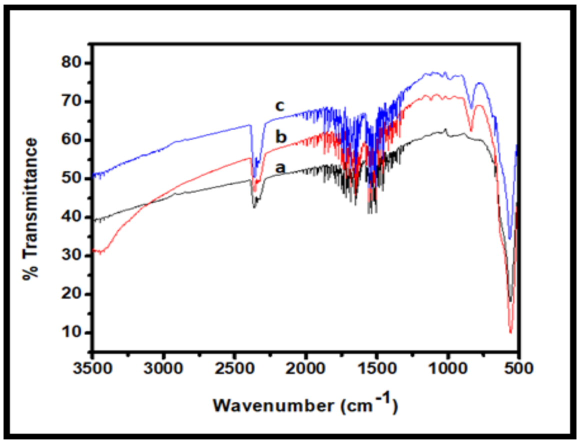


Fig.2: FTIR spectra of (a) 1:2, (b) 1:1 and (c) 2:1 ratios of $FeWO_4$

Fig.3 (a-c) shows the bandgap of as-prepared different molar ratios of $FeWO_4$ photocatalyst was measured using equation (2). The absorption peak edge

$$E_g = 1240/\lambda_{max}\ (eV) \quad ---------- \quad (2)$$

E_g: Band-gap energy and

λ_{max}: maximum absorption wavelength.

wavelength at 627, 637 and 647 nm corresponding to their bandgap of 1.97, 1.94 and 1.91 eV for 1:2, 1:1 and 2:1 molar ratios of nanostructure $FeWO_4$ respectively. This is evident that 2:1ratio of $FeWO_4$ somewhat decrease the bandgap. Consequently, larger portion of $Fe(NO_3)_2$ effects on decreasing of bandgap and suggest that it has photocatalytic degradation ability by capturing the visible light.

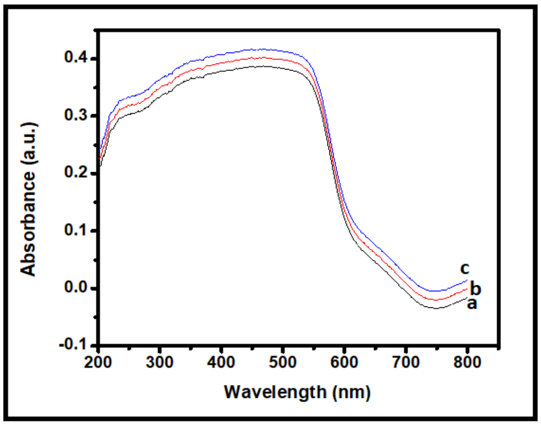
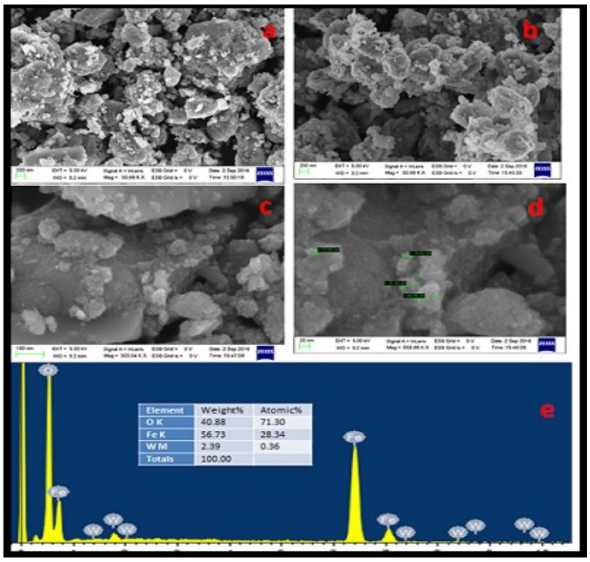


Fig.3: UV DRS spectra of (a) 2:1, (b) 1:1 and (c) 1:2 ratios of $FeWO_4$

Fig.4 (a-d) implies the FESEM micrographs of $FeWO_4$ (2:1) photocatalyst. These results display flake-like shapes with wrinkles. The size of the $FeWO_4$ nanoparticles is 30–45 nm view from 200-20 nm. The EDX patterns of $FeWO_4$ (2:1) shown in Fig.4 (e). The $FeWO_4$ pattern indicates the obtained product is composed of Fe, W and O elements with atomic ratio 56.73:2.39:40.88 which is consistent with the stoichiometric ratio and declares the formation of pure $FeWO_4$.

3.2 Photocatalytic activity of $FeWO_4$

The photocatalytic activities of prepared $FeWO_4$ nanostructures toward 2-NP degradation was investigated under visible light irradiation for 90 minutes using UV-Vis spectrophotometer under similar conditions such as catalyst dose 30 mg, pH (8) and 50 mL of 2-NP suspension (Fig.5 (a-c)). The results obviously declared that 2:1 molar ratio of $FeWO_4$ exhibits better photocatalytic activity towards 2-NP degradation than $FeWO_4$ (1:2 and 1:1). It was more than partially degraded 62% of 2-NP than 1:2 and 1:1 which degraded very slow 29 and 38% respectively was shown in Fig.5 (d). This is due to wider bandgap of $FeWO_4$ (2:1).



Element	Weight%	Atomic%
O K	40.88	71.30
Fe K	56.73	28.34
W M	2.39	0.36
Totals	100.00	

Fig.4: (a-d) FESEM micrographs and (e) EDX of 2:1 $FeWO_4$

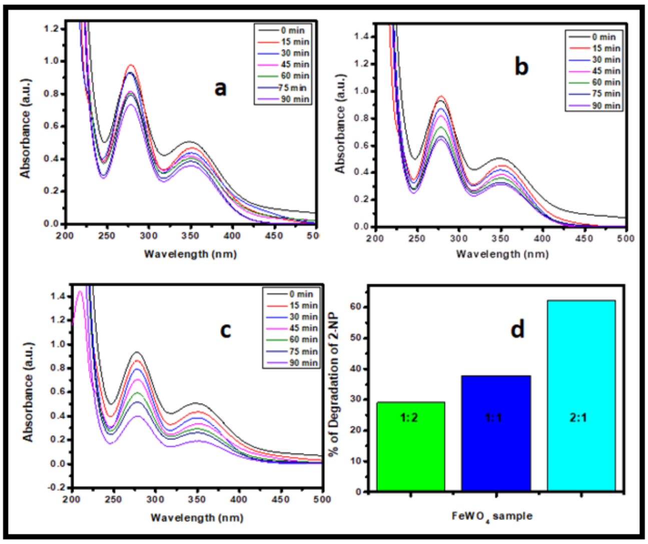


Fig.5: photocatalytic degradation of 2-NP by $FeWO_4$ (a-c) at different molar concentrations of catalyst and (d) comparison of % of dye degradation.

The Langmuir-Hinshelwood (L-H) model was applied to study the kinetics of as-prepared photocatalyst. The L-H equation can be expressed as following when the initial concentration of 2-NP is relatively lower [25].

$$\ln (C_0/C) = Kt \quad ----------- \quad (3)$$

Where C_0 is the initial concentration of 2-NP,

C is the concentration at time t,

K is the apparent first-order rate constant and t is the reaction time.

Fig.6 (a) revealed that the plot $\ln(C_0/C)$ Vs time is approximately linear. The photocatalytic degradation of 2-NP dye using prepared nanostructures followed pseudo first-order kinetics and the apparent pseudo first-order rate constants (K) were calculated to be 0.002, 0.008 and 0.038 for 1:2, 1:1 and 2:1 of $FeWO_4$ respectively were presented in Table.1.

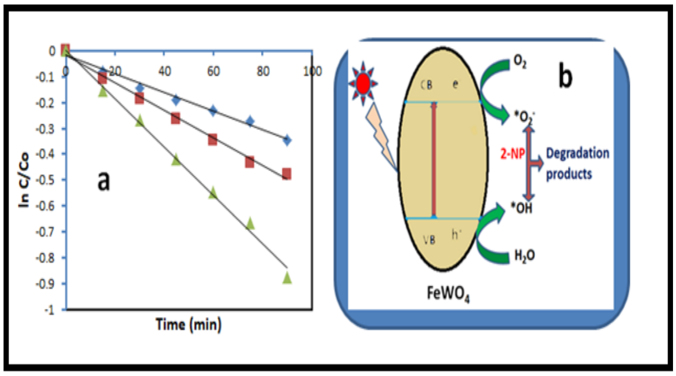


Fig.6: (a) Rate kinetic order and (b) Possible mechanism of photocatalytic degradation

Table.1: Regression coefficient (R^2) and rate order Kinetics (k) of $FeWO_4$ photocatalyst.

Catalyst	R^2	Rate constant ($k \times 10^{-3}$)
$FeWO_4$ (1:2)	0.98	0.2
$FeWO_4$ (1:1)	0.99	0.8
$FeWO_4$ (2:1)	0.99	3.8

Based on these results we proposed a plausible mechanism (Eq 4-7) for the degradation of 2-NP pollutant by prepared $FeWO_4$ (Fig.6 (b)). Initially, $FeWO_4$ was irradiated by light; it absorbs energy which is equal or higher than its bandgap energy and to form electron-hole pairs. The electron jumps from valance band (VB) to conduction band (CB) resultant in formation of holes in VB and electrons in CB respectively. The electron reduces the oxygen and produce super oxide radicals ($^*O_2^-$) similarly the holes oxidise the H_2O and renders hydroxyl radicals (*OH). The *OH radicals have great potential in the degradation of 2-NP pollutant [26, 27] into degradation products such as H_2O and CO_2.

$$FeWO_4+hv \rightarrow FeWO4+e^{-}+h^{+} \quad \text{--- (4)}$$

$$e^{-}+O_2 \rightarrow {}^{*}O_2^{-} \quad \text{--- (5)}$$

$$h^{+}+2H_2O \rightarrow {}^{*}OH \quad \text{--- (6)}$$

$${}^{*}O_2^{-}/{}^{*}OH+2\text{-NP} \rightarrow \text{Degradation products} \quad \text{--- (7)}$$

IV. Conclusions

$FeWO_4$ monoclinic tungstates with different molar ratios of 1:2, 1:1 and 2:1respectively, were synthesized hydrothermally using $Na_2WO_4{\cdot}2H_2O$ and $Fe(NO_2)_3$ solutions as precursors. The prepared photocatalyst was examined for photocatalytic degradation of organic pollutant, 2-NP under visible light irradiation for 90 minutes. The results clearly revealed that the $FeWO_4$ (2:1) shows better photocatalytic activity towards organic pollutant, 2-NP degradation under visible light illumination.

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