ORIGINAL ARTICLE

Preparation and characterization of PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite: Catalytic activity for synthesis of Arylidene Barbituric acid derivatives

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Abstract
PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite was successfully synthesized and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). Also, the catalytic activity of PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ has been considered in the synthesis of two arylidene barbituric acid derivatives. The FT-IR and XRD results confirmed the synthesis of PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite. According to Scherre equation and the main peak at about $2\theta = 41.72°$, the average crystalline size of the nanoparticles determined at about 75 nm. Catalytic activity results show that the as-prepared composite is as an efficient catalyst. This study suggests that other PVC composites could be explored as a new catalyst for synthesis of other arylidene barbituric acids.

Keywords: *Catalyst; Characterized; Composite; FT-IR; PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$; SEM.*

INTRODUCTION

Due to low production cost, good chemical resistance, excellent electrical properties and also insulation performance, poly(vinyl chloride) (PVC) is one of the major thermoplastics that widely used in various application such as medical equipment's, pipe and etc [1, 2]. Also wide used in the world with a global demand exceeding 35 million tons per year [3]. In such applications, PVC is more economical than wood, metals, and ceramics. The high chlorine content in the polymer is a disadvantage from an environmental point of view. In addition, PVC has low thermal and photochemical stability and under high temperatures, the PVC is degraded by dehydrochlorination to the release of hydrochloric acid (HCl), with the formation of a polyene structure [4]. Thermal decomposition of PVC in the presence of various metal oxides had been studied and indicted that the accelerate decomposition of PVC to aromatic compounds [5, 6]. Recently, the modified PVC composites used as a support for the catalysts of organic compounds are reported in the literature [7-10]. These modified PVC prepared by the elimination of hydrogen chloride with the insertion of polar groups had caused changes in the color of polymer from white to orange [7-10]. The presence of NH groups on PVC is suitable for the adsorption of active substances such as drugs, fertilizers, herbicides and dyes [11-13]. Arylidene barbituric acid derivatives are important organic compounds that are used in various fields such as Antibacterial, antiurease and antioxidant [14] and also prepared by various techniques [15-20].

In the present paper, PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite was successfully prepared and characterized by FT-IR, XRD and SEM techniques. In addition, catalytic activity of PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ has been considered in the synthesis of two arylidene barbituric acid derivatives (Fig. 1).
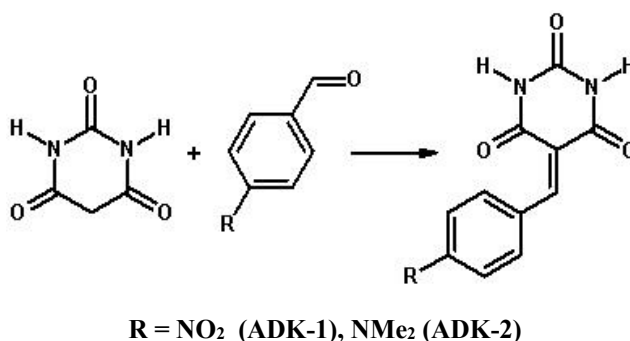
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R = NO₂ (ADK-1), NMe₂ (ADK-2)

Fig. 1: Synthesis of two arylidende barbituric acid derivatives.

EXPERIMENTAL

Materials and methods

Poly(vinyl chloride), nickel chloride, ferric chloride, NaOH, ethanol, baribituric acid and various aldehydes were purchased from Aldrich company and used as received without further purification. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. Optical absorption measurements were done using a UV-Vis spectrophotometer in the wavelength ranges of 200-800 nm at room temperature. X-ray powder diffraction was done with a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation in the range $2\theta = 10°–80°$. SEM images were obtained by scanning electron microscope SNE 4500-M.

Preparation of PVC/NiFe₂O₄/Fe₂O₃

PVC (2 g) was dispersed in to 15 mL of H_2O and stirred for 5 min, then, an aqueous solution of 0.81 g $FeCl_3 \cdot 6H_2O$ and 0.06 g $NiCl_2 \cdot 4H_2O$ (in 15 mL H_2O) was added and mixture was stirred for about 0.5 h at 50 ºC. Finally, 10 mL of NaOH (0.24 M) was added drop by drop and the mixture was stirred for about 1 h at 75 ºC. The brownish-black precipitates were filtered and dried at 25 ºC (r.t.) for 3 days and characterized by FT-IR, XRD and SEM.

Catalytic activity

In order to investigate the catalytic activity of the PVC/NiFe₂O₄/Fe₂O₃, it was used in the synthesis of arylidene barbituric acid derivatives (Scheme 1) as below optimization procedure: Barbituric acid (5 mmol) was dissolved in hot-water, followed by addition of 0.02 g PVC/NiFe₂O₄/Fe₂O₃ and stirred

for about 10 min. Then, the ethanolic solution of various benzaldehydes (5 mmol) was added to the reaction mixture and stirred until the color precipitate of the products has been prepared. The color solid products were filtered and dissolved in hot-ethanol and then filtered off to separate the PVC/NiFe₂O₄/Fe₂O₃. By slow evaporation of ethanolic solution after several days the solid crude arylidene barbituric acid derivatives have been prepared and filtered off. The arylidene barbituric acid derivatives have been characterized by FT-IR and UV-Vis spectroscopy. Also, melting points of the products were recorded.

RESULTS AND DISCUSSION

FT-IR spectra of PVC and PVC/NiFe₂O₄/Fe₂O₃

PVC/NiFe₂O₄/Fe₂O₃ composite was prepared using the reaction of PVC, $FeCl_3$ and $NiCl_2$ in presence of NaOH. The chemical structure of PVC and PVC/NiFe₂O₄/Fe₂O₃ was studied by FT-IR spectroscopy and the results presented in Fig. 2. The FT-IR revealed several peaks which were assigned to the various groups such as OH stretching (3431 and 1631 cm⁻¹) concerning to the water molecules adsorbed on the surface of compounds [21], C-H aliphatic stretching (2969, 2912, 2850) of PVC [9] and the peaks at 689, 614 and 427 cm⁻¹ concerning to Fe-O and Ni-O stretching [22].

XRD patterns of PVC and PVC/NiFe₂O₄/Fe₂O₃

The XRD diffraction analysis was performed for PVC and PVC/NiFe₂O₄/Fe₂O₃ composite. In the XRD of the as-prepared PVC/NiFe₂O₄/Fe₂O₃ (Fig. 3) the four broad peaks at $2\theta \approx 17$, 19, 24.5 and 40º could be assigned to the PVC [23]. The intensity of them was decreased in the XRD pattern of
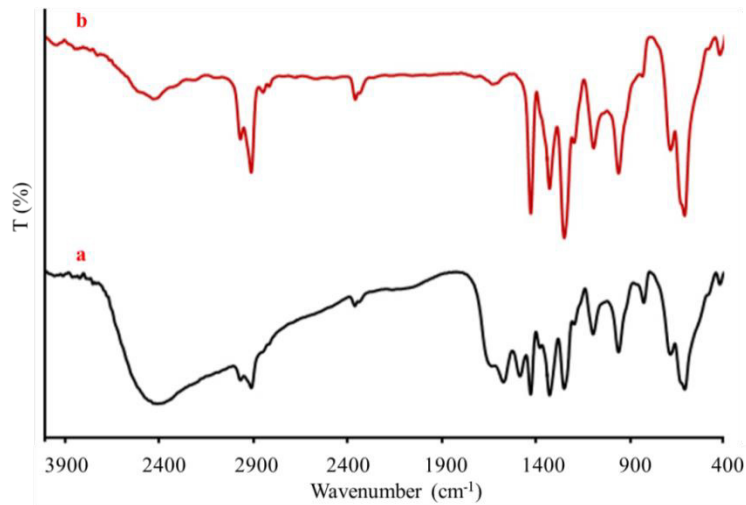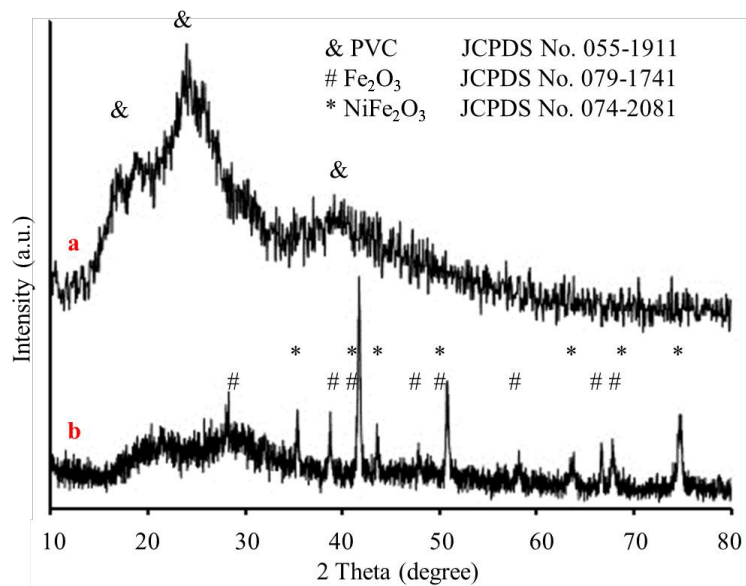
Fig. 2: FT-IR spectra of a) PVC and b) PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite.

Fig. 3: XRD pattern of a) PVC and b) PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$.

the PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$. In XRD pattern of PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$, there are sharp and narrow peaks at 2θ ≈ 28.18, 38.78, 41.72, 47.90, 50.77, 58.13, 66.65, 66.65, 67.82º, assigned to the α-Fe$_2$O$_3$ with JCPDC card No. 079-1741 [24] and at 2θ ≈ 35.34, 41.72, 43.61, 50.77, 63.79 and 78.73º, assigned to the NiFe$_2$O$_4$ with JCPDC card No. 074-2081 [25]. According to Scherre equation and the data for shape phase appeared at 2θ = 41.72 º, the average crystalline size of the NiFe$_2$O$_4$ and Fe$_2$O$_3$ nanoparticles determined at about 75 nm.

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

In this equation, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and ϑ is the diffraction angle.

SEM images of PVC and PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$

SEM images of the PVC and PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ have been presented in Figs. 4a and 4b. Spherical shape of PVC (Fig. 4a) and also spherical shapes nanoparticles of NiFe$_2$O$_4$ and Fe$_2$O$_3$ (Fig.
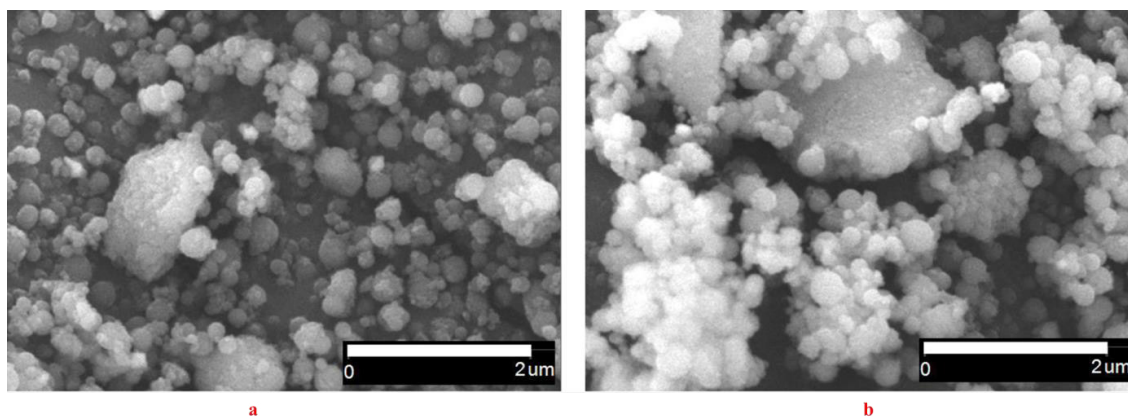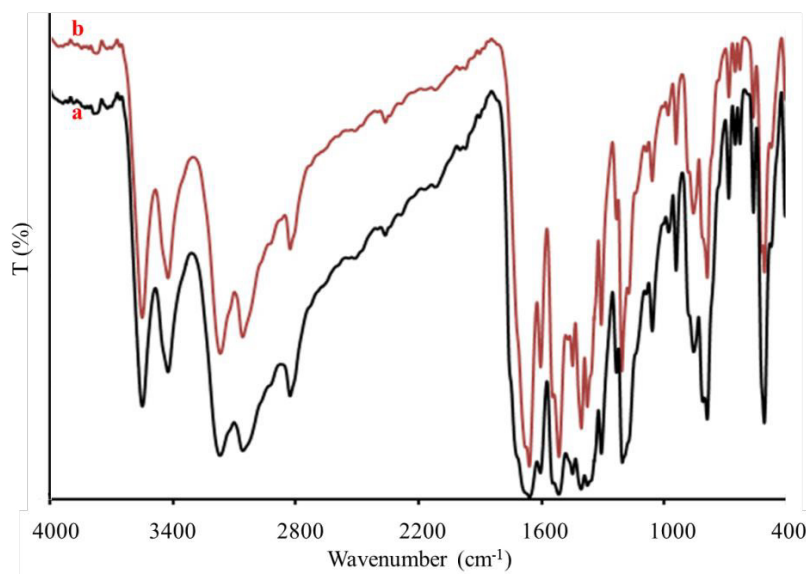
Fig. 4: SEM images of a) PVC and b) PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$.

Fig. 5: FT-IR spectra of a) ADK-1 and b) ADK-2.

4a) loaded on PVC are seen. However, there is an agglomerated between the particles.

Characterization of arylidene barbituric acid derivatives

The color of barbituric acid is white, while the color of ADK-1 is pale-brown (Fig. 5a) and ADK-2 is orange (Fig. 5b), this color change confirmed the preparation of ADK-1 and ADK-2. Melting point of ADK-1 is about 275 ºC and is more than melting point of ADK-2 (239), due to the NO$_2$ group that cause increasing hydrogen bond in ADK-2.

Table 1 shows the conditions under which various derivatives of arylidene barbituric acid have been prepared. The yield of the products is

very low in acetonitrile, dichloromethane and is a medium in ethanol and water, while the yield increased to ≥ 95% using a water-ethanol (l:1 v/v) mixture. Preparation of ADK-2 (30 sec) is faster than ADK-1 (180 sec), because N(Me)$_2$ is an electron donor while NO$_2$ is an electron acceptor. Results in this MS are better than the previous paper [16]. For example, the yield and time for the preparation of ADK-2 (entry 2 in Table 1) is higher than this compound prepared by Rajput and Kaur [16]. By increasing the catalyst, the yield of ADK-1 and ADK-2 increased from 80 to 86 and 91 to 95%. Also by changing the solvent from ethanol to ethanol-water the yield of ADK-1 and ADK-2 increased. In the absence of the PVC/

Table 1. Optimization of the preparation of arylidene barbituric acid derivatives.

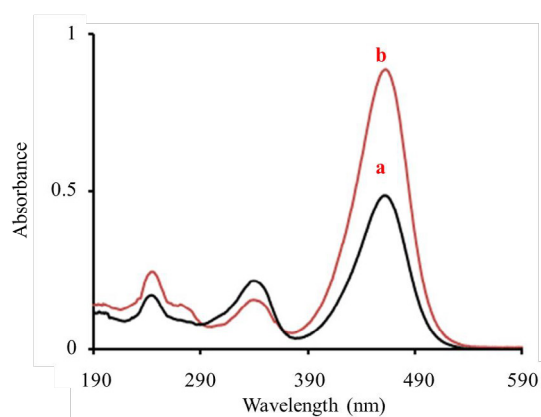| Entry	R	Time (min)	Yeild (%)	Catalyst amount (g)	Solvent
1	NO$_2$	3	86	0.02	Ehanol-Water (1:1)
2	N(Me)$_2$	0.5	95	0.02	Ehanol-Water (1:1)
3	NO$_2$	5	80	0.01	Ehanol-Water (1:1)
4	N(Me)$_2$	1	91	0.01	Ehanol-Water (1:1)
5	NO$_2$	15	82	0.02	Ethanol
6	N(Me)$_2$	4	88	0.02	Ethanol
7	NO$_2$	22	75	0.01	Ethanol
8	N(Me)$_2$	7	79	0.01	Ethanol

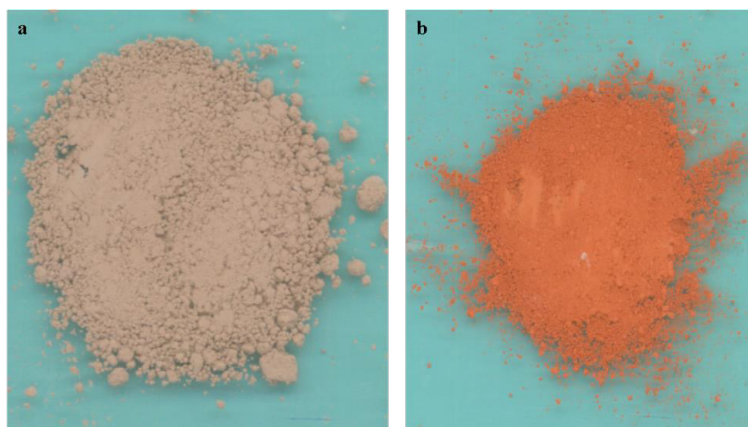Fig. 6: UV-vis spectra of a) ADK-1 and b) ADK-2.

Fig. 7: The color of a) ADK-1 and b) ADK-2.

NiFe$_2$O$_4$/Fe$_2$O$_3$, only a trace (< 50%) of ADK-1 and ADK-2 was obtained that is agreement by previous reports [26]. This reaction is clean, simple and the progress and completion of it was monitored by formation of colored precipitate product. The compounds were recrystallized by for purification and characterized by FT-IR (Figs. 5a and 5b) and UV-vis (Figs. 6a and 6b) spectroscopies. Until now, there are many reports on the preparation of arylidene barbituric acid by various catalysts such as BiCl$_3$ (yield of 85 %) [27], NaCl (yield of 68 %) [28] and CoFe$_2$O$_4$ (yield of 94%) [16].

FT-IR spectra of ADK-1 and ADK-2 are presented in Figs. 6a and 6b, respectively. The sharp peaks at about 3550 and 3424 cm^{-1} assigned to the symmetric and asymmetric N-H stretching.

Two peaks appeared at about 3168 and 3059 cm^{-1} corresponding to the sp^2 C-H (phenyl and ethylenic groups). The sharp and broad peak at about 1660 cm-1 confirmed the presence of carbonyl groups. The aromatic C=C and NO$_2$ vibration are appeared at about 1515-1540 cm^{-1}. Finally, the peak appeared at about 1200 cm^{-1} is assigned to C-N stretching. As seen in Fig. 6, the FT-IR spectrum of ADK-1 and ADK-2 compounds is very similar and confirmed the same structure of them.

UV-Vis spectra

The UV-vis spectra of ADK-1 and ADK-2 are presented in Figs. 7a and 7b, respectively. As shown in Fig. 7, there is one sharp peak in visible region at about 463 nm, could be assigned to the n→π* of C=O groups, and two weak and broad peaks at violet region at 339 and 244 nm, could be assigned to the π→π* of C=C groups of phenyl and ethylene groups. The sharp peak at visible region confirmed that the ADK-1 and ADK-2 be colorful.

CONCLUSIONS

New PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite has been prepared and characterized by FT-IR, XRD and SEM and used as new catalyst for preparation of arylidene barbituric acid derivative. The result confirmed that the PVC/NiFe$_2$O$_4$/Fe$_2$O$_3$ composite is good catalyst. This catalyst produces the ADK-1 and ADK-2 compounds in a very short time and with high yields. Therefore, it can be used in the preparation of other arylidene barbituric acid derivative.

ACKNOWLEDGMENT

CONFLICT OF INTEREST

Authors have no conflict of interest.

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