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First electrospun immobilized molybdenum complex on bio iron oxide nanofiber for green oxidation of alcohols



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ABSTRACT

Bio iron oxide was synthesized from natural Sesbania sesban plant and modified by a molybdenum complex (Fe₂O₃/MoSB). Fe₂O₃/MoSB was deposited on polyvinyl alcohol (PVA) using a conventional single nozzle electrospinning technique (PVA/Fe₂O₃/MoSB). TEM, SEM, AFM, FT-IR, TGA, EDAX, and elemental analysis were used to determine fiber compositional information. The catalytic efficiency of electrospun PVA/Fe₂O₃/MoSB nanofiber in the oxidation of alcohols was exploited. The green reactions were conducted at solvent free conditions as a green media in the presence of H₂O₂ to have the desired aldehydes and tert-butyl hydrogen peroxide to obtain acid products in high yields and excellent selectivity. The survival of this nanocomposite was investigated and it could be reused and recycled in consecutive runs.

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1. Introduction

Todays, development of electrospun nanocomposites reinforced polymer fiber materials with intention to stimulate interests in both academia and industry makes them highly attractive [1]. Electrospun nanofiber have great potential for synthesis of next-generation polymer nanofibers [2,3]. Continuity, diverse material choice, controlled diameter/structure, possible alignment/assembly, and mass production capability are comprehensive advantages of electrospun nanopolymers [3-5]. Inorganic nanofibers, with smaller pores and higher surface area than regular fibers, have enormous catalytic applications [6,7]. Despite enormous efforts devoted to explore industrial applications of electrospun nanofibers, there are limited attempts to employ these nanofibers for reinforcement in polymer nanohybrids [8,9]. Among all polymers, polyvinyl alcohol (PVA) due to its low cost, high hydrophilicity, and excellent chemical resistance has used in broad application areas. PVA is a synthetic water-soluble hydrophilic polymer and the degree of polymerization or the degree of hydrolysis can effect on its properties such as adhesives, emulsificantes, and paper industry applications [1,10]. Modified PVA with metal oxides, with different mechanical, thermal and chemical stability, has already been proven as an effective way to produce new materials with specific properties and high performances [11-13]. In many recent studies, iron nanoparticles (NPs) for environmental remediation have indicated excellent potentials [14,15]. Microwave assisted synthesis, ultrasonication assisted synthesis, coprecipitation, chemical reduction methods, and hydrothermal methods are the methods for iron oxide synthesis. While, the most commonly used conventional strategy for the synthesis of the nanoparticles are chemical physical and biological methods [16-18]. However, they need expensive instruments, high energy, usage of toxic reducing agents maintaining the cell culture, and recovery steps [19]. The undesirable features of traditional reagents and methods have forced chemists to use phyto-mediated synthesis to reduce the costs of chemical production [20,21]. Hence, the synthesis of nanoparticles using the plant extract has several advantages [22-24].

On continuing our work on the green catalytic system [25-29], bio α -Fe₂O₃ was synthesized using Sesbania sesban plant and molybdenum complex was supported on it and nanofiber of immobilized molybdenum complex on α -Fe₂O₃ in the presence of PVA was synthesized through electrospinning

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Scheme 1. The synthesis of electrospun PVA/Fe₂O₃/MoSB nanofiber.

(PVA/Fe₂O₃/MoSB). As our acknowledgment, this work is the first report of catalytic potential of an electrospun nanofiber base on one transition metal complex in oxidation reactions. Here, we describe catalytic properties of PVA/Fe₂O₃/MoSB in the presence H_2O_2 as an ideal oxidant to aldehyde products and t-BuOOH as a common oxidant to produce the acid products.

2. Material and methods

Sesbania sesban was provided from University of Jiroft. 2amino pyridine was purchased from Across Company. 3chloropropyltrimethoxysilane and Polyvinyl alcohol were procured from Alderich and Merk Company, respectively. FT-IR spectra were recorded by FT-IR spectrophotometer (NICOLET iS10). Thermo stability of PVA/Fe₂O₃/MoSB was investigated by Simultaneous Thermal Analyzer. Synthesis of iron oxide nanoparticles was performed by furnace (FANAZMA GOSTAR). Shape and morphology of PVA/Fe₂O₃/MoSB was considered by TEM microscope (Philips CM30). X-ray energy-dispersive spectroscopy (EDS) detector (IE 300X,Oxford, UK) attached to the SEM was analyzed the elemental composition of materials. For AFM images of PVA/Fe₂O₃/MoSB, an atomic force microscopy (DME Model Igloo) was performed. Electrospinning instrument was used for synthesis of PVA/Fe₂O₃/MoSB (Nanoazma company, Iran).



Fig. 1. The FT-IR of PVA, Fe₂O₃/MoSB, and PVA/Fe₂O₃/MoSB.

3. Experimental

3.1. Green synthesis of iron oxide (α -Fe₂O₃)

4 gr of Sesbania sesban wood powder was added to 200 ml of distilled water at 90 °C for 10 min. A KOH solution (0.01 M) was then added drop wise (drop rate = 1 mL.min-1) at room temperature to reach the reaction pH to 9. 170 ml of the obtained extraction solution was added to 130 ml of distilled water and 200 ml of FeCl₃.6H₂O solution (0.05 M). The mixture of reaction was heated to 80 °C for 2.5 h. The resulting α -Fe₂O₃ was separated by an external magnet, washed with water and dried in oven under vacuum. The as-synthesized sample was heated by the furnace at 250 °C for 7 h [30].

3.2. Synthesis of immobilized molybdeum complex on functionalized α -Fe₂O₃ (Fe₂O₃/MoSB)

A mixture of 3-chloropropyltrimethoxysilane (0.5 mmol, 0.1 mL) and triethylamine as a catalyst (0.01 mL, 0.07 mmol) was added to suspend iron oxide (0.1 g) in dry ethanol (20 mL) and was refluxed for 24 h. Chloro functionalized iron oxide was separated by centrifuge machine at 3000 rpm for 5 min and washed with toluene and water mixture for three times. The resulting product was dried under vacuum.

0.94 gr of chloro-functionalized iron oxide was added to 2.5 mg of 2-amino pyridine in ethanol (20 ml) and this reaction mixture was heated to 80 °C for 8 h. The resulting ligand (Fe₂O₃/SB) was separated through centrifugation at 300 rpm for 5 min and washed three times by ethanol and dried at room temperature [31,32]. 2.31 gr of ammonium hepta molybdate salt was added to suspension of supported ligand of iron oxide (0.2 gr) in 4 ml of distilled water and refluxed for 8 h at 80 °C. The F₂O₃/MoSB washed three times with distilled water and dried at room temperature.

3.3. Electrospinning procedure of Fe₂O₃/MoSB (PVA/Fe₂O₃/MoSB)

4 gr of Fe₂O₃/MoSB was dispersed to 4 mL of water within a half hour and was added to 1.6 gr of PVA in 12 mL of water. The mixture of reaction was irradiated with ultrasound for 30 min. Prepared solution was placed under magnetic stirrer for 8 h at 80 °C.

The electrospinning of final prepared solution was done at an electrical voltage of 25 kV at room temperature under atmospheric pressure. The polymer fibers were injected using a syringe needle (5 ml) with a needle [1.23 mm outer diameter (OD) and 0.83 mm internal diameter (ID)] at a flow rate of 0.3 ml/h. The grounded target was placed at 12 cm from the needle tip.

3.4. General procedure for oxidation of alcohols using H_2O_2

To a mixture of alcohol (1 mmol) and electrospun PVA/Fe₂O₃/MoSB nanocomposite (0.003 g) under solvent free conditions, 0.6 mmol H₂O₂ (12 μ L) was added and the reaction mixture was stirred at 80 °C for 7 h.

3.5. General procedure for oxidation of alcohols using t-BuOOH

To a mixture of alcohol (1 mmol) and electrospun PVA/Fe₂O₃/ MoSB nanocomposite (0.005 g), 0.6 mmol t-BuOOH (57 μ L) was added under solvent free conditions and the reaction mixture was stirred at 80 °C for 6 h.

3.6. Reusability of catalyst

To a mixture of benzyl alcohol (1 mmol, 0.1 mL) and PVA/Fe₂O₃/MoSB nanofiber (0.003 g) under solvent free conditions was added H_2O_2 (0.6 mmol, 12 μ L) and the reaction mixture was stirred at 80 °C for 7 h. After completion of the reaction, 1 mL ethyl acetate was add and catalyst was separated by centrifugation. PVA/Fe₂O₃/MoSB nanocomposite as the isolated solid phase was dried under air and reused for next runs. According to the above-mentioned procedure, catalyst recovery was also considered in the oxidation of benzyl alcohol under solvent free conditions using t-BuOOH as an oxidant.

4. Result and discussion

Bio iron oxide nanoparticles was synthesized by Sesbania sesban and these green α -Fe₂O₃ nanoparticles were then allowed to react with an appropriate concentration of 3-



Fig. 2. The analysis spectrum of the PVA/Fe₂O₃/MoSB.

Table 1 The weight percentage of each element in the $PVA/Fe_2O_3/MoSB$.

Element	Series	Wt%	At%
Carbon	K series	46.06	54.83
Nitrogen	K series	3.51	3.59
Oxygen	K series	41.72	37.28
Aluminum	K series	7.80	4.14
Chlorine	K series	0.01	0.0
Iron	K series	0.08	0.02
Molybdenum	L series	0.69	0.1



Fig. 3. TGA curves of PVA/Fe₂O₃/MoSB composite nanofibrous (dash line) and PVA.

chloropropyltrimethoxysilane to give chloro-functionalized α -Fe₂O₃. The obtained chloro-functionalized iron oxide was reacted with 2-amino pyridine to produce immobilized 2-amino pyridine on bio chloro-functionalized iron oxide (Fe₂O₃/SB). To this end, the reaction of Fe₂O₃/SB with ammonium heptamolybdate in water led to the formation of F₂O₃/MoSB. Nanofiber of PVA/Fe₂O₃/MoSB was synthesized by electrospinning of F₂O₃/MoSB base on polyvinyl alcohol as a polymer (Scheme 1).

FT-IR spectra of PVA, $Fe_2O_3/MoSB$, and $PVA/Fe_2O_3/MoSB$ were shown in Fig. 1. In the case of PVA, the most intensive band that appeared at 3900 cm⁻¹ corresponds to the asymmetric stretching

vibrations of an alcoholic O-H. The bands observed at 1440 and 640 cm−1 are corresponded to the CH₂ bending and stretching modes [8,10,33]. In the case of Fe₂O₃/MoSB, the C-O stretching vibration appeared at 1130 cm⁻¹ [2,5,8]. The band observed at around 627–648 cm⁻¹was assigned to the stretching vibrations of Metal-Oxygen (Fe-O) bond in this bio iron oxide nanoparticles [34]. The peaks observed at 2910, 2930 and 1475 cm⁻¹ in the FT-IR spectrum of Fe₂O₃/MoSB was related to the stretching and bending of the CH₂ bonds, respectively [35]. Si-O stretching bond was detected in the region 1000–1110 cm⁻¹. A stretching vibrational about 3434 cm⁻¹ are attached to the O-H surface. Observed peak at 1629 cm⁻¹ is confirmed a stretch for the vibrational mode of water. It is the V2 bending mode of the water molecules adsorbing on the surface. In the FT-IR spectrum of PVA/Fe₂O₃/MoSB, additional stretches at 2957 and 2834 cm⁻¹ are related to aryl C–H stretches. The amine group stretch is found at 1292 cm⁻¹ (C-N). The peaks at 1610, 1496, and 763 cm⁻¹ for the 2-amino pyridine, and 462 cm⁻¹ for Mo-N bond were indicated a minor amount of complex in the structure of PVA/Fe₂O₃/MoSB [36]. Therefore, FT-IR of PVA/Fe₂O₃/MoSB confirmed the presence of the supported molybdenum complex on bio-iron oxide nanoparticles in this nanocomposite.

Also, EDAX measurements (see Fig. 2) provided the direct evidence for chemical analysis. The presence of Fe Mo, Si, Cl, C, and O were confirmed as elements in PVA/Fe₂O₃/MoSB. The strong signal was due to the alumina from the Al substrate on which the fibers were collected [2]. The weight percentage of each element shows in Table 1. The high percentage of oxygen suggests the presence of PVA polymer with high number of OH groups in the sample.

The thermal behavior of PVA and PVA/Fe₂O₃/MoSB composite nanofiber was analyzed through thermal gravimetric analysis (Fig. 3, dash line) [37]. The thermal stability and content of organic functional groups on the surface were considered. The PVA nanofiber had three main weight loss stages: the first one, up to 210 °C was related to the evaporation of water and volatile compounds. From 230 to 380 °C, we have second stage corresponding to the polymer chain. At higher than 400 °C, the breakage the main chain of PVA was happened [38]. By comparison, the PVA nanofiber undergoes total thermal oxidation between 460 and 700 °C, the presence of Fe₂O₃/MoSB was confirmed. In fact, the remaining mass after the polymer decomposition in PVA/Fe₂O₃/MoSB is due to the molybdenum complex [39]. According to the TGA curves, the



Fig. 4. TEM image (a), SEM image (b), two-dimensional (4c) and three-dimensional (4d) AFM topography images of electrospun PVA/Fe₂O₃/MoSB nanofiber.



Scheme 2. Oxidation of alcohols catalyzed by PVA/Fe₂O₃/MoSB under solvent free condition using H_2O_2 and t-BuOOH to obtain corresponding aldehyde or ketones and acid products.

amount of transition metal complex in $PVA/Fe_2O_3/MoSB$ is estimated to be 5%.

In continuing our characterization of PVA/Fe₂O₃/MoSB composite nanofibrous, the TEM images of the pure nanofibers with different diameters showed the uniform structures (Fig. 4a). When this nanocomposite nucleate and grow during the electrospinning process, the Fe₂O₃/MoSB move to the surfaces of the nanofibers PVA because of the internal radial orientation of the electrostatic field and the rapid evaporation of the solvents. In fact, Fig. 4a shows the high-resolution TEM image of the PVA/Fe₂O₃/MoSB nanofiber and the short distances of straight chain separated each other [40]. The PVA chains are elongated and self-oriented side by side along the fiber axis and the straight molecular segments in these chains are at least 40-70 nm long. Also, the SEM of PVA/Fe₂O₃/MoSB confirmed the irregular white and gray dots on the straight chain of PVA, which are $Fe_2O_3/MoSB$ (Fig. 4b). The aggregation of the $Fe_2O_3/MoSB$ MoSB was observed and the average size of them was estimated about 30 nm.

Two-dimensional (Fig. 4c) and three-dimensional (Fig. 4d) AFM topography images of PVA/Fe₂O₃/MoSB were used to determine fiber compositional information. Representative AFM-phase was gave good information about surface morphology this nanofiber. AFM images were derived from 5.1 μ m * 5.1 μ m scans part of the samples. The AFM-phase image (Fig. 4a) shows the aggregation of the hydrophobic parts of the immobilized molybdenum complex on iron oxide nanoparticles in the PVA/Fe₂O₃/MoSB [41,42]. Three-dimensional AFM topography image, 5.1 μ m² *1.1 μ m framework, showed that nanofibers with high porosity was formed [43].

4.1. Green oxidation of alcohols catalyzed by PVA/Fe₂O₃/MoSB

Catalytic potential of PVA/Fe₂O₃/MoSB was evaluated in the oxidation of alcohols as green chemistry point of view (Scheme 2). Different factors such as various temperatures, solvents, catalyst amounts, and oxidants were optimized in the oxidation of alcohols catalyzed by PVA/Fe₂O₃/MoSB nanofiber (Fig. 5). This nanocomposite was initially evaluated for the oxidation of benzyl alcohol with H₂O₂ as ideal oxidant under solvent free conditions as a green media. This reaction did not proceed in the absence of the catalyst under any conditions [44]. While, PVA/Fe₂O₃/MoSB (0.003 g) was used into the reaction mixture, the conversion rate was enhanced significantly and benzaldehyde was obtained in 65%



Fig. 5. The effect of solvents (a), catalyst amount (b), temperature (c), time (d), and oxidant (e) on the oxidation of alcohols catalyzed by electrospun PVA/Fe₂O₃/MoSB nanofiber.

and 100% yield after 5 and 7 h at 80 °C, respectively. When the same amount of PVA, Fe₂O₃, and Fe₂O₃/MoSB was applied as heterogeneous catalysts in this green system. Trace, 20, 44% of related products were achieved, respectively. Virtually, no catalytic activity was observed in commonly used organic solvents. The examination of six solvents, such as dichloromethane (DCM), dichloroethane (DCE), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), water (H₂O) and solvent free conditions, showed that solventless and acetonitrile promoted the yield of the aldehyde products (Fig. 5a). Solvent free conditions were selected due to easy separation of the products and catalyst. On the other hand, the yields of reactions were crucially affected by the catalyst amounts. Best yield of aldehyde product was achieved by using 0.003 g of the electrospun nanofiber (Fig. 5b). It seems that higher temperatures up to 80 °C was required to furnish favored yields of the benzaldehyde under the catalytic influence of PVA/Fe₂O₃/MoSB (Fig. 5c). Under these optimum conditions, benzyl alcohol converted completely to the related aldehyde product within 7 h (Fig. 5d). To consider the oxidizing potential of other common oxidants, benzyl alcohol was subjected to the oxidation protocol using O2, H2O2, t-butylhydroperoxide (t-BuOOH), NaIO₄, and Oxone[®], TB (Fig. 5e). The interesting results were observed at the presence of PVA/Fe₂O₃/ MoSB nanocomposite. At the same condition, benzyl alcohol was oxidized to benzaldehyde completely using H₂O₂, while, t-BuOOH was produced the benzoic acid as sole product. It seem that t-BuOOH is a strong oxidant, even more effective than hydrogen peroxide, therefore, it was used in the agrochemical and pharmaceutical industries instead of other organic peroxides [40]. Oxidation of benzyl alcohol under the optimized conditions (0.005 g of PVA/Fe₂O₃/MoSB under solvent free conditions at 80 °C within 6 h) using 0.06 mmol of t-BuOOH, gave solely benzoic acid in 100% yield (Support information, S1-S4).

PVA/Fe₂O₃/MoSB was shown high efficiency and selectivity toward oxidation of a wide range of primary and secondary alcohols under optimized conditions using H₂O₂ and t-BuOOH (Table 2). The secondary alcohols were subjected in this green system and high conversion and excellent selectivity were achieved. Generally, the secondary alcohols were oxidized more difficult than of primary alcohols. Ester products were not observed in this clean strategy (Table 2, entries 1–4). A number of primary substituted benzylic alcohols, like benzyl alcohol, were oxidized smoothly to their corresponding aldehydes using H₂O₂ and acid products in the presence of t-BuOOH (Table 2, entries 5-12). It should be noted the electronic and steric demands of the substrate could effect on the yield of products. In fact, by changing the oxidant, the formation of acid or aldehyde products was controlled completely. Desired aldehyde and acid products were obtained in yields ranging from 85% to quantitative in the presence of both oxidants.

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Table 2	2
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The oxidation of different alcohols catalyzed by electrospun PVA/Fe₂O₃/MoSB nanocomposite under solvent free condition using H₂O₂ and t-BuOOH.

Entry	Alcohol	Product	Conversion%(selectivity of aldehyde) ^a	Conversion% (selectivity of acid) ^b
1	ОН	> Contro	100	90
2	ОН		90	95
3	ОН		85	100
4	ОН		70	90
5	ОН	O SH	90 (100)	100 (100)
6	Н3С ОН	H _{+C}	100 (100)	100 (100)
7	HO		100 (100)	90 (100)
8	ОН	ОН	100 (98)	90 (100)
9	ОН	H H	100 (100)	100 (100)
10	СІ	H Cl	85 (100)	85 (85)
11	О2N ОН	02N	95 (100)	100 (90)
12	СІ	CI CI	90 (100)	90 (95)

^a The reactions were run under air for 7 h at 80 °C under solvent free condition using H₂O₂ as a green oxidant.

^b The reactions were run under air for 6 h at 80 °C under solvent free condition using t-BuOOH.

Encouraged by the impressive results obtained for indicating its relative stability of PVA/Fe₂O₃/MoSB biopolymer in the heterogeneous oxidation system, the recycling of the catalyst was investigated (Fig. 6). After performing the oxidation reaction of benzyl alcohol with this biopolymer nanofiber under the present conditions, EtOAc was added to work-up. The catalyst was separated by the centrifuge from the reaction mixture, washed with EtOAc, dried at room temperature, and reused for a consecutive run under the

same reaction conditions. The average yield of benzaldehyde for five consecutive runs was 95%, which clearly demonstrates the practical reusability of this catalyst. These benefits along with excellent conversion and selectivity of wide range of alcohols using the present green system were addressed one novel environmental and industrial strategy.

Ultimately, we compared the result and conditions used in this work for oxidation of benzyl alcohol (Table 3) with some reports



Fig. 6. The reusability of $PVA/Fe_2O_3/MoSB$ in the oxidation of benzyl alcohol under solvent free condition using H_2O_2 and t-BuOOH.

Table 3

Comparison of the results and conditions used for oxidation of benzyl alcohol catalyzed by $PVA/Fe_2O_3/MoSB$ with some other catalysts reported in the literature.

Entry	Catalyst	Conditions	Time (h)	Conversion %	Ref
1	(DODA) ₄ PMo ₁₁ VO ₄₀	Solvent-free/H ₂ O ₂ /90 °C	6	53	[45]
2	PVA/Fe ₂ O ₃ /MoSB	$Solvent-free/H_2O_2/80^{\circ}C$	7	100	This work
3	PVA/Fe2O3/MoSB	Solvent-free/t-BuOOH/ 80 °C	6	100	This work
4	Cetyl-HoWlO/H	Solvent- free/H ₂ O ₂ / 60 °C/under N ₂	6	94	[46]
5	PW-NH 2 -IL-SBA-15	Solvent-free/H ₂ O ₂ / 100 °C	6	86 (16 ^a)	[48]
6	Cu-DAPyPTS -MCM-41-W	Solvent-free/t-BuOOH/ 100 °C	4 h	62 (68 ^a)	[49]
7	MnO ₂	Water/t-BuOOH/40 °C	7	38 (66 ^a)	[50]
8	MnO ₂	Water/H ₂ O ₂ /40 °C	5	1	[50]
9	Ceric ammonium nitrate	EtOAc/t-BuOOH	20	85	51

^a Yield of benzoic acid.

using catalysts. The superiority of biocatalyst is established with respect to solvent nature, temperature, oxidant, and reaction time.

5. Conclusion

In conclusion, Iron oxide nanoparticles was prepared from Sesbania sesban plant and an electrospun nanofiber was synthesis from one novel molybdenum complex base on natural bio-iron oxide nanoparticles for the first time. This bio nanofiber was applied as a heterogeneous catalyst for selective oxidation of primary and secondary alcohols. High and excellent aldehyde and acid products was gained under solvent free conditions using H₂O₂ and t-BuOOH oxidants, respectively. A long-term stability, using ideal oxidant, easy work-up, and solventless show the great potential in scalability with relatively low catalyst loading. These features as concepts in economical and sustainable modern oxidation systems along with good reusability of the bio-catalyst render a practical strategy to address the environmental and industrial applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.07.003.

References

- X. Jia, Y. Li, Q. Cheng, S. Zhang, B. Zhang, Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate, Eur. Polym. J. 43 (2007) 1123–1131.
- [2] S. Anitha, D.J. Thiruvadigal, T.S. Natarajan, In-situ preparation of high optical quality ZnO nanoparticles in nanofibrous PVA matrix, Mater. Lett. 65 (2011) 2872–2876.
- [3] H.R. Pant, D.R. Pandeya, K.T. Nam, W. Baek, S.T. Hong, H.Y. Kim, Photocatalytic and antibacterial properties of a TiO₂/nylon-6 electrospun nanocomposite mat containing silver nanoparticles, J. Hazard Mater. 189 (2011) 465–471.
- [4] T. Subbiah, G.S. Bhat, R.W. Tock, S. Parameswaran, S.S. Ramkumar, Electrospinning of nanofibers, J. Appl. Polym. Sci. 96 (2005) 557–569.
- [5] A.M. Abd El-aziz, A. El-Maghraby, N.A. Taha, Comparison between polyvinyl alcohol (PVA) nanofiber and polyvinyl alcohol (PVA) nanofiber/hydroxyapatite (HA) for removal of Zn²⁺ ions from wastewater, Arab. J. Chem. 10 (2017) 1052–1060.
- [6] N. Gogoi, G. Borah, P.K. Gogoi, T.R. Chetia, TiO₂ supported gold nanoparticles: an efficient photocatalyst for oxidation of alcohol to aldehyde and ketone in presence of visible light irradiation, Chem. Phys. Lett. 692 (2018) 224–231.
- [7] B.N. Yılmaz, T. Baran, A. Menteş, Production of novel palladium nanocatalyst stabilized with sustainable chitosan/cellulose composite and its catalytic performance in Suzuki-Miyaura coupling reactions, Carbohydr. Polym. 118 (2018) 596–604.
- [8] S. Mirzaeea, S.F. Shayesteh, Ultrasound induced strain in ultrasmall CoFe₂O₄@ polyvinyl alcohol nanocomposites, Ultrason. Sonochem. 40 (2018) 583–586.
- [9] J. Zhang, Y. Wang, H. Ji, Y. Wei, N. Wu, B. Zuo, Q. Wang, Magnetic nanocomposite catalysts with high activity and selectivity for selective hydrogenation of *ortho*-chloronitrobenzene, J. Catal. 229 (2005) 114–118.
- [10] A.B. Salunkhe, V.M. Khot, N.D. Thorat, M.R. Phadatare, C.I. Sathish, D.S. Dhawale, S.H. Pawar, Polyvinyl alcohol functionalized cobalt ferrite nanoparticles for biomedical applications, Appl. Surf. Sci. 264 (2013) 598–604.
- [11] L. Peiyang, D. Jiachun, L. Ying, L. Wei, W. Kun, K. Litao, Z. Shaozhong, Y. Shanhui, Z. Zhigang, L. Xuguang, Y. Yongzhen, G. Feng, One-step solution combustion synthesis of Fe₂O₃/C nano-composites as anode materials for lithium ion batteries, J. Alloy. Comp. 590 (2014) 318–323.
- [12] Q.J. Chun, R.C. ling, D.Y. Lei, C.Y. Ping, M. Zhou, C.X. Guo, Facile synthesis of multifunctional graphene oxide/AgNPs-Fe₃O₄ nanocomposite: a highly integrated catalysts, Chem. Eng. J. 211–212 (2012) 412–420.
- [13] I.S. Chronakis, Novel nanocomposites and nanoceramics based on polymer nanofibers using electrospinning process-A review, J. Mater. Process. Technol. 167 (2005) 283–293.
- [14] Y. Wei, Z. Fang, L. Zheng, T. Tan, E.P. Tsang, Green synthesis of Fe nanoparticles using Citrus maxima peels aqueousextracts, Mater. Lett. 185 (2016) 384–386.
- [15] K.K. Chul, K.E. Kwon, LJ. Won, M.S. Lyul, K.Y. Sung, Synthesis and characterization of magnetite nanopowders, Curr. Appl. Phys. 8 (2008) 758–760.
- [16] S. Afsheen, T.M. Bilal, T. Iqbal, A. Liaqat, M. Abrar, Green synthesis and characterization of novel iron particles by using different extracts, J. Alloy. Comp. 732 (2018) 935–944.
- [17] P.B. Bhat, R. Rajarao, V. Sahajwalla, B.R. Bhat, Immobilized magnetic nano catalyst for oxidation of alcohol, J. Mol. Catal. Chem. 409 (2015) 42–49.
- [18] S.B. Babic, V. Jokanovic, D. Milivojevic, M. Pozek, Z. Jaglicic, D. Makovec, O.N. Jovic, M. Markovic, Ultrasmall iron oxide nanoparticles: magnetic and NMR relaxometric Properties, Curr. Appl. Phys. 18 (2018) 141–149.
- [19] C.M. Martínez, G.M. López, J.L. Barriada, R. Herrero, Green synthesis of iron oxide nanoparticles. Development of magnetic hybrid materials for efficient As(V) removal, Chem. Eng. J. 305 (2016) 83–91.
- [20] D. Mukherjee, S. Ghosh, S. Majumdar, K. Annapurna, Green synthesis of a-Fe₂O₃ nanoparticles for arsenic(V) remediation with a novel aspect for sludge management, J. Environ. Chem. Eng 4 (2016) 639–650.
- [21] S. Sangami, B. Manu, Synthesis of Green Iron Nanoparticles using Laterite and their application as a Fenton- like catalyst for the degradation of herbicide Ametryn in water, Environ. Technol.Innovat. 133 (2017) 1864–2352.
- [22] A. Naeimi, M. Amini, Biosorption of cadmium using a novel, renewable and recoverable modified natural cellulose bearing chelating Schiff base ligand based on 2-hydroxy-5-methyl benzaldehyde, Iran. Polym. J. (Engl. Ed.). doi: 10.1007/s13726-018-0623-8.
- [23] F.E. Ghadi, A.R.Ghara, A. Naeimi, Phytochemical fabrication, characterization, and antioxidant application of copper and cobalt oxides nanoparticles using *Sesbania sesban* plant, Chem. Pap.. doi: 10.1007/s11696-018-0506-7.
- [24] A. Naeimi, M. Honarmand, O. Jawhid, Iron Porphyrin Immobilized on Natural Cellulose Polymer Extracted from Sesbania Sesban Plant: a Novel, Eco-friendly and Cost Effective Catalyst for green Oxidation of Organic Compounds in Water, Accepted in Cellulose Chemistry and Technology.
- [25] A. Lopez-Moreno, D. Clemente-Tejeda, J. Calbo, A. Naeimi, F.A. Bermejo, E. Orti, E.M. Perez, Biomimetic oxidation of pyrene and related aromatic hydrocarbons Unexpected electron accepting abilities of pyrenequinones, Chem. Commun. 50 (2014) 9372–9375.
- [26] A. Naeimi, S. Saeednia, M. Yoosefian, H. Rudbari, V.M. Nardo, A novel dinuclear schiff base copper complex as an efficient and cost effective catalyst for oxidation of alcohol: synthesis, crystal structure, and theoretical studies, J. Chem. Sci. 127 (2015) 1321–1328.

- [27] M. Honarmand, A. Naeimi, M. Zahedifar, Nanoammonium salt: a novel and recyclable organocatalyst for one-pot three-component synthesis of 2-amino-3-cyano-4H-pyran derivatives, J. Iran. Chem. Soc. 14 (2017) 1875–1888 (B).
- [28] A. Naeimi, A. Amiri, Z. Ghasemi, A novel strategy for green synthesis of colloidal porphyrins/silver nanocomposites by Sesbania sesban plant and their catalytic application in the clean oxidation of alcohols, J. Taiwan Inst. Chem. Eng 80 (2017) 107–113.
- [29] E. Tajik, A. Naeimi, A. Amiri, Fabrication of iron oxide nanoparticles, and green catalytic application of an immobilized novel iron Schiff on wood cellulose, Cellulose 25 (2018) 915–923.
- [30] A. Naeimi, S. Saeednia, Morphology control of colloidal silver nanoparticles using sesbania sesban, Bioinspired, Biomimetic Nanobiomaterials. doi: 10.1680/jbibn.17.00023.
- [31] V. Jassal, U. Shanker, S. Gahlot, Green synthesis of some iron oxide nanoparticles and their interaction with 2-Amino, 3-Amino and 4-Aminopyridines, Mater. Today 3 (2016) 1874–1882.
- [32] X. Liu, C. Manzur, N. Novoa, S. Celedón, D. Carrillo, Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: synthesis, functional materials properties, and applications to catalysis, Coord. Chem. Rev. 357 (2018) 144–172.
- [33] K. Arul, E. Manikandan, P.P. Murmu, J. Kennedy, M. Henini, Enhanced magnetic properties of polymer-magnetic nanostructures synthesized by ultrasonication, J. Alloy. Comp. 720 (2017) 395–400.
- [34] N. Anand, K.H.P. Reddy, T. Satyanarayana, K.S.R. Rao, A magnetically recoverable γ-Fe₂O₃ nanocatalyst for the synthesis of 2-phenylquinazolines under solvent- free conditions, Catal. Sci. Technol 2 (2012) 570–574.
- [35] P.A. Hasannejad, M. Shekouhy, N. Golzar, A. Zare, M.M. Doroodmand, Silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB- DABCO): a highly efficient, reusable and new heterogeneous catalyst for the synthesis of 4H-benzo[b]pyran derivatives, Appl. Catal. Gen. 402 (2011) 11–22.
- [36] D. Girija, H.S. Bhojya Naik, B.V. Kumar, C.N. Sudhamani, K.N. Harish, Fe3O4 Nanoparticle Supported Ni(II) Complexes: a Magnetically Recoverable Catalyst for Biginelli Reaction, doi:10.1016/j.arabjc.2014.08.008.
- [37] S. Yang, P. Lei, Y. Shan, D. Zhang, Preparation and characterization of antibacterial electrospun chitosan/poly (vinyl alcohol)/graphene oxide composite nanofibrous Membrane, Appl. Surf. Sci. 435 (2018) 832–840.
- [38] K.C.S. Figueiredo, T.L.M. Alves, C.P. Borges, Myoglobin entrapment in

poly(vinylalcohol) dense membranes, Braz. J. Chem. Eng. 31 (2014) 747-756.

- [39] A.K. Sahu, G. Selvarani, S. Pitchumani, P. Sridhar, A.K. Shukla, N. Narayanan, A. Banerjee, N. Chandrakumar, PVA-pssa membrane with interpenetrating networks and its methanol crossover mitigating effect in DMFCs, J. Electrochem. Soc. 155 (2008) 686–695.
- [40] X. Liu, J. Ma, X. Wu, L. Lin, X. Wang, Polymeric nanofibers with ultrahigh piezoelectricity via self-orientation of nanocrystals, ACS Nano 11 (2017) 1901–1910.
- [41] A. Wali, Y. Zhang, P. Sengupta, Y. Higaki, A. Takahara, M.V. Badiger, Electrospinning of non-ionic cellulose ethers/polyvinyl alcohol nanofibers: characterization and applications. Carbohydr. Polym. 181 (2018) 175–182.
- [42] N.E. Zander, K.E. Strawhecker, J.A. Orlicki, A.M. Rawlett, T.P. Beebe, Coaxial electrospun poly(methyl methacrylate)_Polyacrylonitrile nanofibers: atomic force microscopy and compositional characterization, J. Phys. Chem. 115 (2011) 12441–12447.
- [43] K.H. Prasad, S. Vinoth, P. Jena, M. Venkateswarlu, N. Satyanarayana, Electrospinning of non-ionic cellulose ethers/polyvinyl alcohol nanofibers: characterization and applications, Mater. Chem. Phys. 194 (2017) 188–197.
- [44] J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng, Z. Wang, A metal-free catalytic system for the oxidation of benzylic methylenes and primary amines under solvent-free conditions, Green Chem. 11 (2009) 1973–1978.
 [45] Z. Du, H. Miao, H. Ma, Z. Sun, J. Ma, J. Xu, Trace water-promoted oxidation of
- [45] Z. Du, H. Miao, H. Ma, Z. Sun, J. Ma, J. Xu, Trace water-promoted oxidation of benzylic alcohols with molecular oxygen catalyzed by vanadyl sulfate and sodium nitrite under mild conditions, Adv. Synth. Catal. 351 (2009) 558–562.
- [46] R. Siozaki, A. Inagaki, H. Kominami, S. Yamaguchi, J. Ichihara, Y. Kera, Catalytic properties of holmiumdecatungstate modified with cetylpyridinium cation [(C, H,N(CH,) sCH 3)7H2H-(III) W10036; Cetyl-HoWIO] for H, O,-oxidation of alcohols and olefins and its working states under an organic-solvent-free condition, J. Mol. Catal. Chem. 124 (1997) 29–37.
- [48] Y. Pérez, R. Ballesteros, M. Fajardo, I. Sierra, I. del Hierro, Copper-containing catalysts for solvent-free selective oxidation of benzyl alcohol, J. Mol. Catal. Chem. 352 (2012) 45–56.
- [49] C. Bhaumik, D. Stein, S. Vincendeau, R. Poli, E. Manoury, Oxidation of alcohols by TBHP in the presence of sub-stoichiometric amounts of MnO₂, C. R. Chim. doi:10.1016/j.crci.2016.02.012.
- [50] R.R. Gowda, D. Chakraborty, Ceric ammonium nitrate catalyzed oxidation of aldehydes and alcohols, Chin. J. Chem. 29 (2011) 2379–2384.