

Recyclable Nanomagnetic Fe₃O₄@APTES Catalyst Role on the Hydrolysis of Polycarbonate Wastes

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Abstract. In this research, the effect of (3-Aminopropyl) triethoxysilane (APTES) modified Fe₃O₄ (Fe₃O₄@APTES) core-shell nanomaterials as the recyclable heterocatalyst on the recovery of bisphenol-A (BPA) from hydrolysis of polycarbonate (PC) wastes were investigated. In the evaluated reactions, water and diethylene glycol (DEG) were used as the green solvent composition and the water as well as magnetic heterocatalyst content were optimized. By examining the results of the above-mentioned reactions, it was observed that by using 25 pbw of water and 2 pbw of magnetic heterocatalyst (both based on total waste and solvent weights), BPA achieved in 100% yield. The Fe₃O₄@APTES nanomaterials as the heterocatalyst can be recovered and reused up to five intervals with our significant activity losses. The resulting BPA and nanomaterials has been characterized by X-ray diffraction (XRD), and spectroscopic methods (¹H NMR, ¹³C NMR, FT-IR).

Keywords: Bisphenol-A; Chemical recycling; Fe₃O₄@APTES nano-heterocatalyst; Hydrothermal condition; Hydrolysis; Polycarbonate wastes.

Resumen. En esta investigación, el efecto de (3-aminopropil) trietoxisilano (APTES) modificó los nanomateriales de Fe₃O₄ (Fe₃O₄@APTES) como heterocatalizador reciclable en la recuperación de bisfenol-A (BPA) de hidrólisis de policarbonato (PC). En las reacciones evaluadas, se utilizaron agua y dietilenglicol (DEG) como la composición del disolvente verde y se optimizó el contenido de agua y de heterocatalizador magnético. Al examinar los resultados de las reacciones mencionadas anteriormente, se observó que al usar 25 pbw de agua y 2 pbw de heterocatalizador magnético (ambos basados en residuos totales y pesos de solventes), el BPA alcanzó un rendimiento del 100%. Los nanomateriales Fe₃O₄@APTES como heterocatalizador pueden recuperarse y reutilizarse hasta cinco intervalos con nuestras importantes pérdidas de actividad. El BPA y los nanomateriales resultantes se han caracterizado por difracción de rayos X (XRD) y métodos espectroscópicos (¹H RMN, ¹³C RMN, FT-IR).

Palabras clave: Bisfenol A; Reciclaje químico; Nano-heterocatalizador Fe₃O₄@APTES; Condición hidrotermal; Hidrólisis; Residuos de policarbonato.

Introduction

Plastics such as polycarbonate (PC) (e.g., DVDs, CDs, airplane and automobile windows, safety goggles, and computer parts) and poly (ethylene terephthalate) (PET) (e.g., PET bottles and film) made from fossil resources has been widely employed because of its high durability, excellent transparency, and good mechanical properties. Recently, the disposal of plastic products and materials has become a challenge to the achievement of sustainable societies and the development of resources recycling [1]. In the following, a

number of studies on the chemical recycling of PC wastes are reviewed. Do *et al.* [2], has studied methanolysis of the PC into bisphenol-A (BPA) and dimethyl carbonate (DMC) using 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD) as an organocatalytic and DMC itself under mild condition. Beneš and coworkers [3], have reported the microwave-assisted degradation of the PC wastes to suitable polyols for preparing of polyurethanes (PUR) foams in optimal conditions. Depolymerization of PCs sample by the Taguchi research group to BPA was investigated using two crystallite sizes of Cerium (IV) oxide (CeO_2) crystal (75 nm, and 7.40 nm) as the catalyst [1]. In another study, calcium-functionalized mesoporous γ -alumina ($\text{Ca-Al}_2\text{O}_3$) was used for alcoholysis of PC [4]. Of course, many other suggestions have been made by other scientists for the chemical recycling of PC wastes, from which one can refer to methods hydrolysis [5-8], pyrolysis [9-11], aminolysis [12, 13], glycolysis [14, 15], and alcoholysis [16-18]. Fe_3O_4 is well known as the strongest magnetic nanomaterials (MNMs) of all natural minerals on earth [19]. Due to the unique features, Fe_3O_4 has been considered for use in a variety of applications [20-28]. On the other, unmodified MNMs tend to aggregate because of their high specific area and strong inter particle interaction, which limit their utilization. Therefore, it is necessary to develop strategies for the chemical stabilization of the naked MNMs against aggregation over a long period. Although the development of more efficient and versatile approaches to functionalized MNMs is very important [29]. Recently, various studies have been carried out on the use of modified Fe_3O_4 as the effective heterocatalyst in the synthesis of organic materials, two of which are as follows; the functionalization of silica-coated Fe_3O_4 magnetic nanomaterials ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) using chlorosulfonic acid ($\text{Fe}_3\text{O}_4@-\text{SiO}_2-\text{SO}_3\text{H}$) as an organic-inorganic hybrid heterocatalyst has been introduced in the one-pot synthesis of 1,8-dioxo-octahydroxanthenes derivatives [30]. In another particular case, Jafarzadeh's research group has used magnetically recoverable trifluoroacetic acid-immobilized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES core-shell nanocatalyst for the Friedländer synthesis of quinolines under solvent-free condition [31]. Our research group has carried out in the past extensive studies on the chemical recycling of PC wastes to recover BPA as the valuable materials in the presence of sodium hydroxide (NaOH) as the homogeneous catalyst, water [32] and glycerin/water [33], and sorbitol/glycerin/water [34] under hydrothermal conditions and ethylene glycol (EG) [35] and glycerin/water [36] under microwave irradiation. Recently our research group, depolymerization of PC wastes was carried out to recover bis (4-hydroxybutyl hydrogen carbonate) of BPA (DHB-BPA), mono (4-hydroxybutyl hydrogen carbonate) of BPA (MHB-BPA) and BPA itself in the presence of (1,4-butanediol and water) as the solvent composition, nanoparticles TiO_2 (NPs- TiO_2) and microparticles TiO_2 (MPs- TiO_2) as the recyclable solid supports and NaOH as the homogeneous catalyst under simple heating method [37]. In addition, we recovery of pure BPA has been studied using hydroglycolysis of PC wastes in diethylene glycol (DEG) and water as the green solvent composition, NPs- TiO_2 and MPs- TiO_2 as the recyclable solid supports and NaOH as the homogeneous catalyst conditions [38]. Finally, we investigated the performance of magnetite nanomaterials coated with amine modified silica nanoshell ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$) as an available, efficient, reusable heterocatalyst and inexpensive for recovering of BPA with yield 100% from hydrolysis of PC wastes at atmospheric pressure using water and DEG mixture without the disadvantages of traditional techniques [39]. In this research and in the continuation of previous works, our group has decided to use modified Fe_3O_4 as the heterocatalyst with unique features in the chemical recycling of PC wastes. Further, we have investigated the effect of magnetite nanomaterials coated with (3-Aminopropyl) triethoxysilane (APTES); as the recyclable heterocatalyst on the hydrolysis of PC wastes in order to recover pure BPA without using any homogeneous and traditional catalyst. Thus, nano- Fe_3O_4 coated with APTES using chemical co-precipitation method as a recyclable heterocatalyst, and using water and DEG as the green solvent composition have been used in the recovery pure BPA as valuable material of PC wastes.

Experimental

Materials

The iron trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), iron dichloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99.70%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.70%), ammonia (NH_3 , 25%-28%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), acetic acid (CH_3COOH), APTES (97%), DEG, methanol (CH_3OH), acetone ($\text{C}_3\text{H}_6\text{O}$), NaOH, and hydrogen chloride solution (HCl, 37%) bought from Merck (Darmstadt, Germany). Water for doing of reactions was twice-distilled. PC was received CDs and DVDs wastes and the thin layer of aluminum was separated completely

and the large particles of PC wastes broken into the arbitrary sizes and shapes, washed with NaOH solution and hot water and dried being charged in the reactor.

Instruments

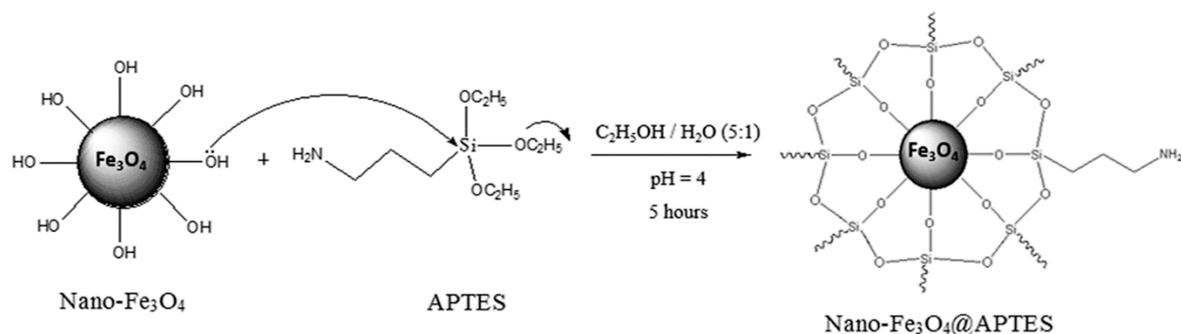
^1H NMR and ^{13}C NMR spectra were carried out using a BPUKER 300 instrument (Bruker, Billerica, Massachusetts, USA) with chloroform-d (CDCl_3) as a solvent and tetramethylsilane (TMS) as an internal standard. Fourier transform infrared spectroscopy (FT-IR) spectra was done by using a BRUKER Tensor 27 (Bruker, Billerica, Massachusetts, USA) with KBr pellet press (sample/KBr mass ratio of 1:100) between 400-4000 cm^{-1} . MNMs were characterized using an X-ray powder diffraction (XRD, Model: GNR, Novara, Italy). The XRD information was obtained on an APD-2000 diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$, GNR, Novara, Italy) from 20° to 80° (2θ). For preparing of the heterocatalyst and drying reaction products, an ultrasonic device (Hielscher, UP200S, Oderstraße 53, 14513 Teltow, Germany), and a vacuum oven (Wisd, WOV-70, DAIHAN Scientific, Seoul, South Korea) were used, respectively. Melting point (mp) was determined on a Gallenkamp electrothermal 9100 (CO, UK).

Preparation of nano- Fe_3O_4

Nano- Fe_3O_4 were synthesized by applying previously reported conditions [40]. The nano- Fe_3O_4 were prepared through co-precipitation by ferric and ferrous (2/1, in moles/moles) precursors using reported method. Typically, 0.015 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.0075 mol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in twice-distilled water 1000 ml. The solution was subsequently heated to 90°C and N_2 was continuously purged in solution, for O_2 exhausting. NH_3 (30 ml, 25-28 %) was added drop wise and reacted for an additional 6 h with adjusting of pH around 10. The precipitate was separated by decantation and washed with ethanol and twice-distilled water. To obtain well dispersed nano- Fe_3O_4 , the precipitate was added to citric acid (500 ml, 0.20 M) and treated with ultrasonic. Finally, unreacted acid was removed and precipitate dried in oven in 40°C overnight.

Preparation of nano- Fe_3O_4 @APTES

For the synthesis of nano- Fe_3O_4 @APTES in the first step, nano- Fe_3O_4 (500 mg) was dispersed in 600 ml ethanol/twice-distilled water (5/1) and sonicated for 20 min by the addition of acetic acid and adjusting of pH=4. Then, 4 ml APTES was added to the solution and the mixture was stirred mechanically at room temperature for 4 h. Finally, the core-shell nanomaterial was separated and washed with twice-distilled water for four times and then dried at 45°C in oven overnight and characterized [41] (Scheme 1).



Scheme 1. Modification of nano- Fe_3O_4 with APTES.

General procedure for hydrolysis of PC wastes

At first, DEG and water (total weights 2.50 g) as the green solvent composition, 0.08 g of nano- Fe_3O_4 @APTES as the heterocatalyst (2 % based on total waste and solvent weights), and 1.50 g of PC wastes were introduced into a 50 ml two-necked flask and placed under reflux and magnetic stirrer. Then the reaction mixture was refluxed under atmospheric pressure and the reaction time was carefully measured until complete PC wastes. Then, the reaction mixture cooled to room temperature. In the next step, hot water and methanol were used to crystallize the BPA and nano- Fe_3O_4 @APTES as the heterocatalyst are separated by external magnetic field. Then, HCl solution (37%) added drop wise until the BPA is completely crystallize and

products are separated by filtration. In the following, washed by twice-distilled water for several times, dried at 80 °C in vacuum oven for 5 h and the obtained product was characterized. The heterocatalyst/PC wastes and total solvents/PC wastes mass ratios were 0.053 and 1.66, respectively. All results are reported in Table 1.

Table 1. Effects of DEG/Water composition in the hydrolysis reaction of PC wastes.

Entry	DEG:Water [g]	Reaction time [min]	BPA recovery yield [%]
1	2.25: 0.25	358	70
2	2.00: 0.50	228	80
3	1.75: 0.75	170	88
4	1.50:1.00	135	100

Reaction conditions: PC wastes (1.50 g), nano-Fe₃O₄@APTES (0.08 g).

Results and discussion

Characterization of nano-Fe₃O₄ and nano-Fe₃O₄@APTES using FT-IR, and XRD

FT-IR spectroscopy was used to confirm the correctness of the surface of the nano-Fe₃O₄ with APTES (Fig. 2). As can be seen, bands centered at 586 cm⁻¹, 2918 cm⁻¹, and 1639 cm⁻¹ related to the Fe–O stretching vibrations (ν), ν O–H, and O–H bonding vibration (σ), respectively in the FT-IR of nano-Fe₃O₄. Moreover, the absorption peak in the 588 cm⁻¹ corresponding to Fe–O–Si vibrations that overlaps with the Fe–O vibrations. The band related to Si–O–Si vibrations sat 1073 cm⁻¹ is present in the FT-IR of nano-Fe₃O₄@APTES. Two bands of 1748 cm⁻¹ and 3448 cm⁻¹ related to ν and σ of the free NH₂. Finally, bands 2853 cm⁻¹ and 2922 cm⁻¹ are devoted to the ν of the C–H groups on the APTES.

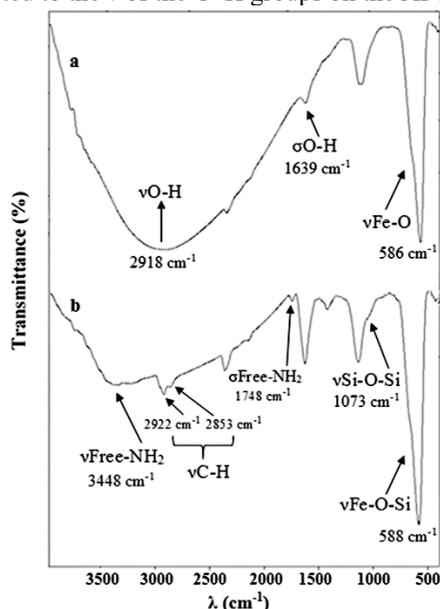


Fig. 2. FT-IR spectrums of magnetic nanomaterials; (a) nano-Fe₃O₄, and (b) nano-Fe₃O₄@APTES.

The XRD pattern of nano-Fe₃O₄ and nano-Fe₃O₄@APTES are shown in Fig. 3. The position ($^{\circ}$ 2Theta) and the ratio of the intensities of all peaks in the XRD pattern of nano-Fe₃O₄@APTES are consistent with the XRD pattern of nano-Fe₃O₄, indicating the preservation of the cubic spinel structure and the non-phase change during coating of the nano-Fe₃O₄ [41, 42]. The average nano-Fe₃O₄@APTES diameter was estimated to be 29.4 nm from the XRD results with Debye-Scherrer's equation in the $^{\circ}$ 2Theta= 35.52°. Debye-Scherrer's Eqns.1 where K is a constant (generally considered as 0.94), β is the corrected diffraction line full-width at half-maximum (FWHM), θ is Bragg's angle and λ is the wavelength of Cu Ka (1.54 Å) [43].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

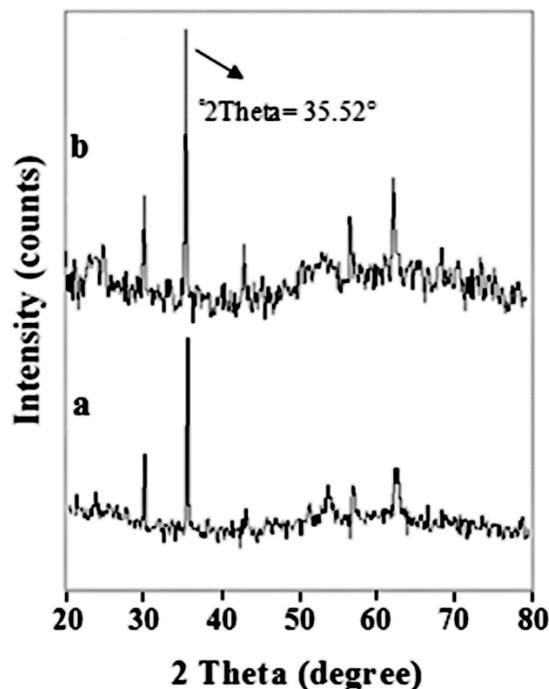


Fig. 3. XRD patterns of magnetic nanomaterials; nano-Fe₃O₄ (a), and nano-Fe₃O₄@APTES (b).

The role of solvents composition on hydrolysis of PC wastes

In order to investigate the effect of water on the hydrolysis of PC wastes, four reactions were carried out in the presence of nano-Fe₃O₄@APTES as the heterocatalyst, and the results are summarized in Table 1. According to the results, by increasing the amount of water in the role of the leading agent of the reaction, the reaction time is reduced and the reaction efficiency is increased.

The role of nano-Fe₃O₄@APTES as heterocatalyst on hydrolysis of PC wastes

In order to investigate the effect of nano-Fe₃O₄@APTES as the heterocatalyst on the hydrolysis of PC wastes, four reactions were carried out in the presence of nano-Fe₃O₄@APTES (0.0345 to 0.10) as the heterocatalyst, DEG (2.00 g), water (0.50 g), and PC wastes (1.50 g) and the results are collected in Table 2. According to the results, with the increase for nano-Fe₃O₄@APTES, the reaction time is reduced and the efficiency of the reaction is increased. Moreover, with 0.10 g of nano-Fe₃O₄@APTES as the heterocatalyst, BPA can be obtained at 100%.

Table 2. Effects of Nano-Fe₃O₄@APTES as heterocatalyst in the hydrolysis reaction of PC wastes.

Entry	Nano-Fe ₃ O ₄ @APTES [g]	Reaction time [min]	BPA recovery yield [%]
1	0.0345	300	70
2	0.05	270	75
3	0.08	228	80
4	0.10	120	100

Reaction conditions: DEG (2.00 g), water (0.50 g), PC wastes (1.50 g).

Reusabiliting of nano-Fe₃O₄@APTES as the heterocatalyst

In order to recovery the nano-Fe₃O₄@APTES as the heterocatalyst, DEG (2.00 g) and water (0.50 g) as solvents and nano-Fe₃O₄@APTES (0.08 g) as the heterocatalyst, they were added to the reaction medium and 1.50 g of PC wastes was dissolved in 228 min and check the amount of PC dissolved using the method described in general procedure section. The nano-Fe₃O₄@APTES were extracted with the external magnetic field and washed several times with acetone and water. All these steps were repeated five times in constant time and the results are presented in Fig. 4. In the following, we compare the five times recovered nano-Fe₃O₄@APTES with the virgin catalyst using FT-IR and find that there are APTES coatings on nano-Fe₃O₄ (Fig. 5). As shown in the results, the amount of PC wastes dissolved in each period of the reaction is reduced and according to these results, the activity of the nano-Fe₃O₄@APTES as the heterocatalyst has decreased after five recoveries. Reducing the activity of nano-Fe₃O₄@APTES as the heterocatalyst may be due to a reduction in the amount of heterocatalyst in the recovery processes.

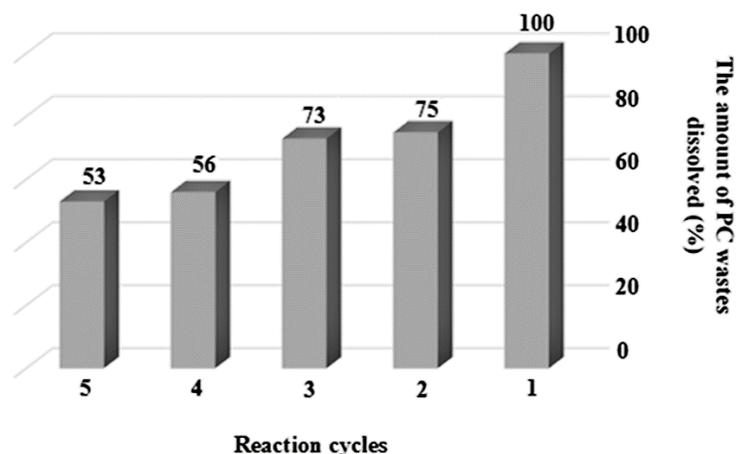


Fig. 4. Reusability of nano-Fe₃O₄@APTES as heterocatalyst.

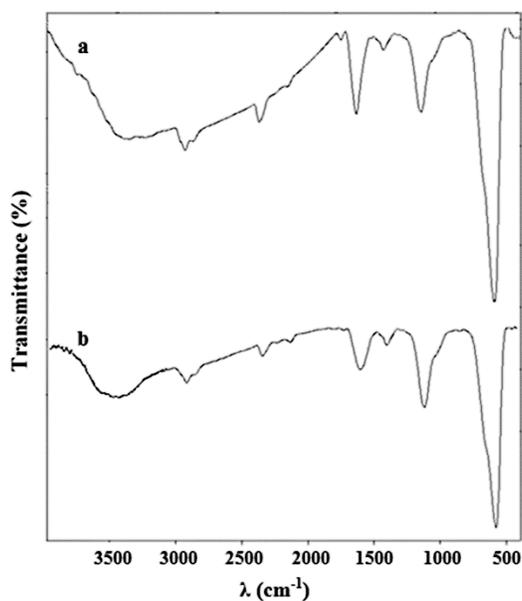


Fig. 5. FT-IR spectrums of nano-Fe₃O₄@APTES as heterocatalyst; (a) virgin heterocatalyst, and (b) heterocatalyst after five times reuse.

Spectroscopy studies of recovered BPA

4,4'-(propane-2,2-diyl)diphenol (BPA). White powder: mp 158°C; ^1H NMR (CDCl_3 , 300 MHz) δ (Fig. 6) 1.60 (6H, s, H_1), 4.50 (2H, s, H_2), 6.70 (4H, d, $J = 8.4$ Hz, H_3), 7.10 (4H, d, $J = 8.4$ Hz, H_4); ^{13}C NMR (CDCl_3 , 300 MHz) δ (Fig. 7) 114.68 (CH_{Ar} , C_3), 127.95 (CH_{Ar} , C_4), 143.33 ($\text{C}_{\text{Ar}}\text{-C-CH}_3$, C_5), 153.22 (C-O , C_6), 31.07 (CH_3 , C_1), 41.69 ($\text{C}(\text{CH}_3)_2$, C_2); FT-IR (KBr pellet) λ (Fig. 8) 1358 cm^{-1} -1506 cm^{-1} ($\sigma\text{C-H}$), 3028 cm^{-1} ($\nu\text{C-H}$ aromatic), 2875 cm^{-1} ($\nu\text{C-H}$ aliphatic), 3200 cm^{-1} to 3500 cm^{-1} ($\nu\text{O-H}$), 1000 cm^{-1} to 1300 cm^{-1} ($\nu\text{C-O}$), 1603 cm^{-1} ($\nu\text{C=C}$).

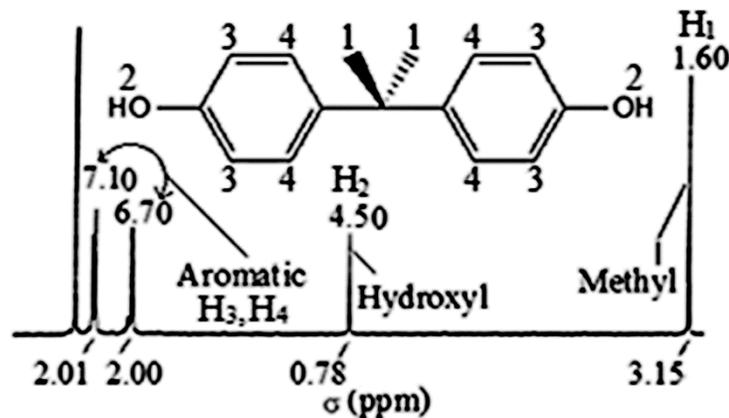


Fig. 6. ^1H NMR spectrum of BPA recovered.

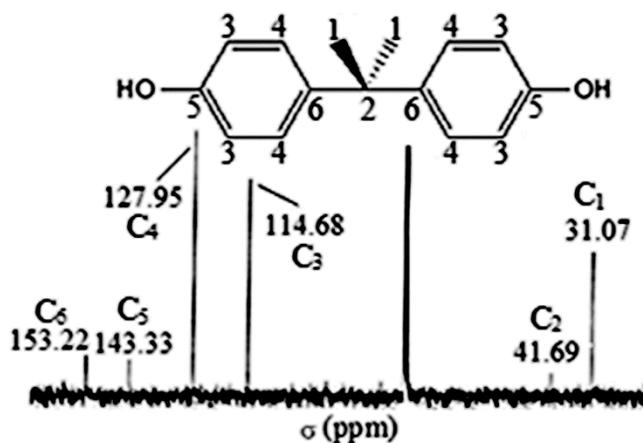


Fig. 7. ^{13}C NMR spectrum of BPA recovered.

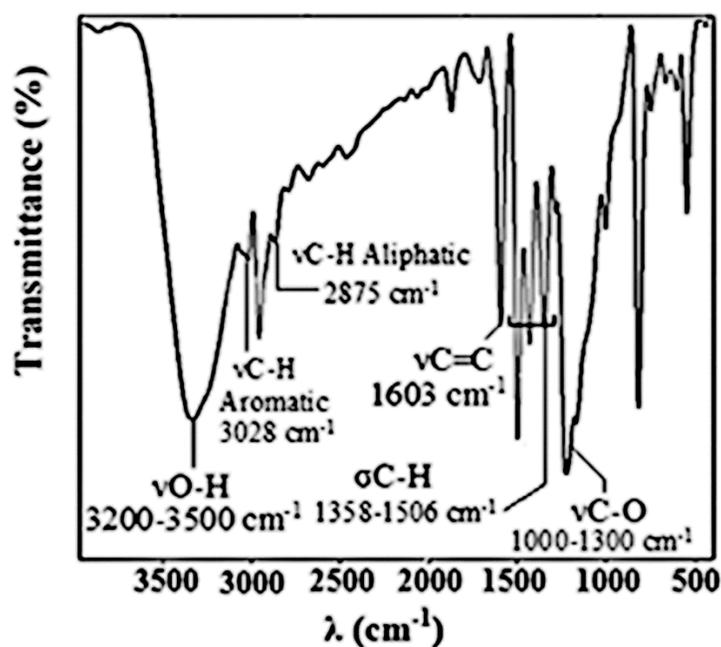


Fig. 8. FT-IR spectrum of BPA recovered.

Conclusions

In conclusion, we evaluated the nano- $\text{Fe}_3\text{O}_4@\text{APTES}$ performance as the heterocatalyst in recovering of pure BPA from hydrolysis of PC wastes under atmospheric pressure in the presence of water and DEG as the green solvent composition. Under the optimal condition heterocatalyst/PC wastes and water/PC wastes where mass ratio of 0.053 and 0.66, reaction time of 135 min, pure BPA as the valuable material were recovered in 100% yield. Moreover, the $\text{Fe}_3\text{O}_4@\text{APTES}$ nanomaterials as the heterocatalyst can be recovered for five cycles and reused in next reactions. Moreover, by comparing the results of the reactions, it was observed that in the presence of water (10 up 40 pbw based on total solvent weight) as the main solvent, the reaction speed and recovery of BPA increased, this corresponds to the principles of green chemistry.

Acknowledgements

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