Recovery of Terephthalic Acid by employing magnetic nanoparticles as a solid support

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Abstract

The aim of this research work is focused on the improvement of Terephthalic acid recovery from PET wastes by using organically modified nano-Fe_3O_4@Cyanuric Chloride as the solid support. The performance of organically modified nano magnetic was examined in detail and the obtained results were compared with the unsupported reaction data. Required reaction time for complete glycolysis of the wastes, consumption of the solvent as well as catalyst decreases up 99%, 37.5% and 40% respectively. Result showed that nano-Fe_3O_4@Cyanuric Chloride delivered good performance as solid support in depolymerizing of PET to the terephthalic acid.

Keywords: *poly (ethylene terephthalate), recycling, solid support, terephthalic acid.*

1. Introduction

The use of polymer in various application are expanded daily and PET is one of the most consumed polymers as its excellent thermal and mechanical properties. This polymer used in the manufacture of high strength fibers, soft drink bottles and photographic films and at the end of the last century its consumption increased to more than 3,000,000 tons per year[1]. In 2009 the global consumption of PET packaging was almost 15.5 Mt while the estimate is to growth to almost 19 Mt by 2017- a 5.2% increase per annum. By increasing in PET production and since this polymer is not biodegradable, big waste stream create a serious environmental problem each year. Chemical recycling of PET has been attracting attention for both environmental and economic reasons[2].

In this case, Nikje and Nazari[3] and his coworker reported glycolyzing of PET by using methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol in the presence of different simple basic catalysts, namely, potassium hydroxide, sodium hydroxide and etc, under microwave irradiation. Pingale and Shukla[4] research group had been used zinc acetate, sodium carbonate, sodium bicarbonate and barium hydroxide as catalyst for glycolysis PET by using microwave as energy source. In our previously reported data, we glycolized PET by using DEG as the solvent and NaOH as the catalysts under microwave irradiation[5]. Parab et al.[6] used ethanolamine for aminolytic depolymerization of PET bottles wastes with heterogeneous, recyclable acid catalysts such as beta zeolite and montmorillonite KSF under microwave irradiation. Siddiqui [2] reported the using of microwave irradiation as a convenient energy source for recycling of poly (ethylene terephthalate) waste through methanolic pyrolysis. Chen et al.[7] glycolized PET by using excess ethylene glycol (EG) in the presence of zinc acetate as catalysts under microwave irradiation. The glycolysis of PET has been reported by using monoetylene glycol (MEG),

diethylen glycol (DEG), monopropylene glycol (MPG) and dipropylene glycol (DPG) in present zinc acetate as catalyst under microwave irradiation[8]. Chaudhary et al.[9] glycolized PET and produced BHET for preparation of polyester polyols under microwave irradiation. Chemical depolymerization of PET complex was done by Liu et al.[10]. Waste depolymerization of PET was done by using bransted acidic ionic liquid under microwave irradiation[11] and in another report PET was glycolized by using several ionic liquids and basic ionic liquids as catalysts[12]. In addition the efficiency of Metal-Containing Ionic Liquids as a highly Effective Catalysts for Degradation of Poly (Ethylene Terephthalate) has been surveyed[13]. All the mentioned catalysts such as alkalies, metal acetate, zeolites, ionic liquids and etc, in the PET glycolysis reactions required long reaction times and contributed low BHET and TPA yields. In order to resolve these drawbacks and improve reaction conditions Imran et al.[14,15] used thermally stable and highly selective silica nanoparticle-supported metal (Mn, Zn, Ce) oxides as the catalysts for PET depolymerization. After that, Park et al.[16] outstretch graphene oxide and manganese oxide as the catalysts for PET glycolysis. Bartolome et al.[17] used nano-γ-Fe_2O_3 as an easily recoverable catalyst for the recycling of PET. The number of active sites in nanoscale catalysts increase and also changing inherent properties of the catalysts in nanoscale usually leads to better catalytic performance.

In continuation of our previous work on PET chemical recycling[3,5] we decided to examine the performance of nano-Fe_3O_4@Cyanuric Chloride as the reagent-solid support in order to recovery TPA from the bottles wastes. By using of this reagent-solid support required time to access to high recovery yield significantly decreases so that is comparable with microwave method.

2. Experimental

2.1 Preparation of nano-Fe_3O_4@Cyanuric Chloride

The magnetic nanoparticles (Fe_3O_4, 0.5 g) were dispersed in the Acetonitrile (100 mL) with sonication (20 min). Then Cyanuric Chloride (0.4 g) was added to the mixture and mechanically stirred at room temperature (7 h). Finally, the core-shell nanoparticles were separated from the reaction medium, and washed with Acetonitrile for two times and then dried at 45 °C in oven overnight and characterized[18].

2.2 PET glycolysis using nano- Fe_3O_4@Cyanuric Chloride and NaOH

For depolymerization, in a three-necked flask, 100 mL round-bottom glass equipped with a condenser, thermometer and magnetic stirrer PET flakes (1 g) was treated with diethylene glycol using different PET: DEG molar ratios (1:4 to 1:8) at 160 °C. The used NaOH and Fe_3O_4@Cyanuric Chloride were (0.1-0.5 g) and (0.01-0.3 g), respectively. At the end of the reaction, distilled water (70 mL) was added to the reaction mixture with vigorous agitation. Then the TPA in the mixture was precipitated by bringing the pH to 2-3 by addition of HCl and dried at 80 °C in the oven (1 h), characterized and data compared with an authentic sample.

3. Results and discussion

3.1 Nano- Fe_3O_4@Cyanuric Chloride solid support characterization

The FE-SEM image of synthesized magnetite nanoparticles is shown in the Figure 1. From the figure, Fe_3O_4 nanoparticles and nano-Fe_3O_4@Cyanuric Chloride have spherical shape with average size of 30-40 and 40-60 nm, respectively.

Figure 2 shows the thermal gravimetry analysis curves (TGA) of Fe_3O_4 and nano-Fe_3O_4@Cyanuric Chloride, respectively. In samples there is an insignificant weight loss stage (below 130 °C) that can be imputed to the evaporation of water and ethanol. In addition in modified sample, weight loss started at 200 to 700 °C and correspondent to the thermal decomposition of (Cyanuric Chloride) coating on magnetite nanoparticles. Actually weight loss, the coated Cyanuric Chloride on the surface Fe_3O_4 NPs is calculated as 12%.

Modification of magnetite nanoparticle with Cyanuric Chloride was confirmed by FT-IR spectroscopy (Figure 3). The vibrations at 400 cm^{-1} and 580 cm^{-1} are attributed to the Fe-O functional groups of magnetite nanoparticle. The vibrations at 810 cm^{-1}, 1066 cm^{-1} and 1634 cm^{-1} refer to C-Cl, C-N and C=N respectively. The vibrations at 3400-3600 cm^{-1} are attributed to adsorbed O-H by Fe_3O_4.

3.2 Depolymerization reaction

Figure 4 shows the reaction scheme of TPA recovery. In this scheme, waste PET flakes received from used bottles were glycolysis in the present nano-Fe_3O_4@Cyanuric Chloride as the solid support and NaOH as the reagent, by the formation of highly reactive PET- Iron Oxide complex. Further neutralization of unreacted sodium hydroxides and disodium-TPA salts by hydrochloric acid, TPA crystals was obtained.
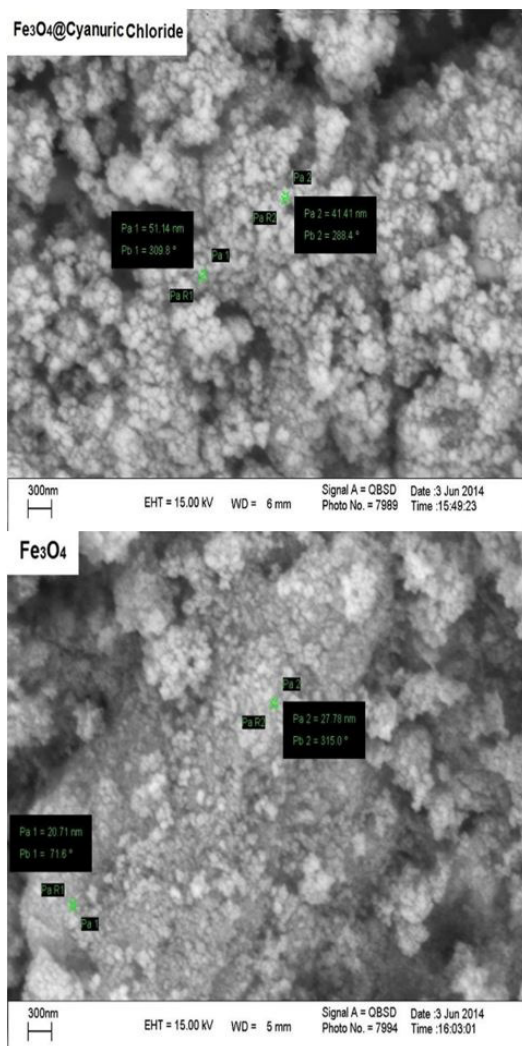

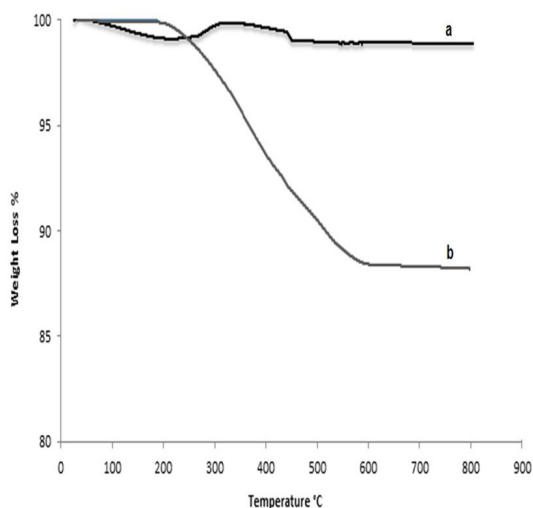**Figure 1.** FE-SEM image of synthesized Fe_3O_4 and nano-Fe_3O_4@ Cyanuric Chloride.

Figure 2. TGA curves for a: Fe_3O_4 and b: Fe_3O_4@Cyanuric Chloride nanoparticles.
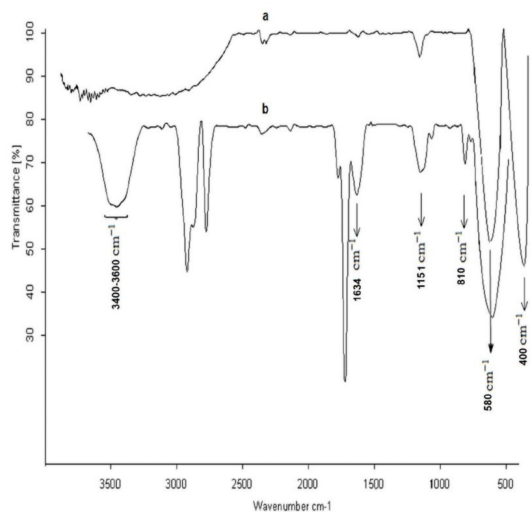
Figure 3. FT-IR spectra of a: Fe_3O_4 and b:nano-Fe_3O_4@Cyanuric Chloride.
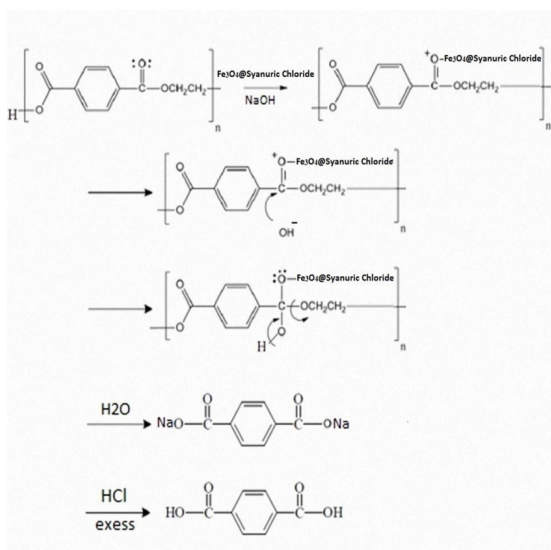

Figure 4. Proposed mechanism for PET glycolysis reaction in the presence of NaOH as the catalyst and nano-Fe_3O_4@Cyanuric Chloride as the solid support.

3.3 The role of reagent-solid support on TPA recovery

The results of performance of nano-Fe_3O_4@Cyanuric Chloride as solid support in recovering of TPA collected in Figure 5 and Tables 1-3, respectively and data were compared with our previously reported data without using this solid support[5]. In the present of nano-Fe_3O_4@Cyanuric Chloride (0.02 g) the required recovery time to access high recovery yield decreases up 99% which is comparable with microwave conducted reaction (Table 1). This can be related to the nano-Fe_3O_4@Cyanuric Chloride capability to increase surface area rendering more active sites and thermal stability.
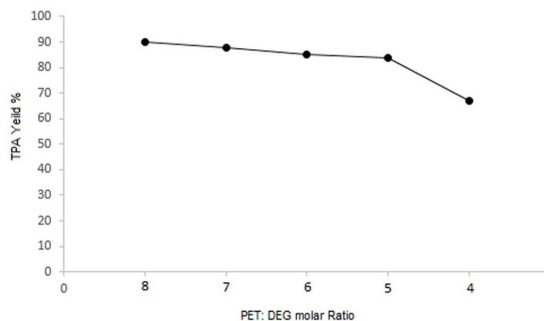

Figure 5. The effect of PET: DEG molar ratios on the glycolysis of PET in the present of Fe_3O_4@Cyanoric Chloride (0. 02 g) and NaOH (0.30 g).

Table 1. The effect of time on the glycolysis of PET in the present of Fe_3O_4@Cyanoric Chloride.

Entry	Fe_3O_4@Cyanoric Chloride (g)	Time (min)	Unreacted PET (g)	TPA yield %
1	0.00	101	0.00	90
2	0.02	101	0.00	95
3	0.02	50	0.00	94
4	0.02	30	0.00	90
5	0.02	20	0.00	90
6	0.02	15	0.00	92
7	0.02	10	0.00	91
8	0.02	5	0.00	90
9	0.02	2	0.00	89
10	0.02	1	0.00	87
11	0.02	0.5	0.32	54

Table 2. The effect of solid supported catalyst concentration on the glycolysis of PET (1 g) in the present of NaOH (0.5 g) and DEG (7 mL).
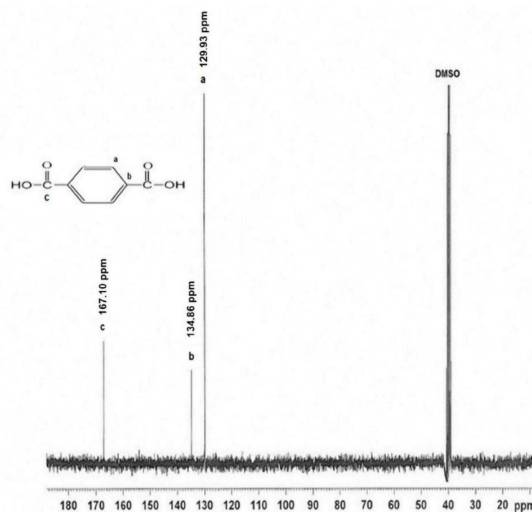
Entry	Fe_3O_4@Cyanoric Chloride (g)	TPA yield %
1	0.01	77
2	0.02	87
3	0.03	88
4	0.05	87
5	0.08	88
6	0.10	84
7	0.20	82
8	0.30	79

The results of changing concentration of nano-Fe_3O_4@Cyanuric Chloride are collected in Table 2. In entry 2 maximum amount of terephthalic acid yield (87%) was obtained, that is related to presence of nano-Fe_3O_4@Cyanuric Chloride (0.02 g) in the reaction mixture.

In order to studying of catalyst role, six sets of reactions were handled in the same reaction times and data collected in the Table 3. As shown on entry 4 of Table 3, by decreasing NaOH concentration to 40% sightly value of reaction (entry 1), the TPA recovery yield will remain constant.

Table 3. The effect of catalyst concentration on the glycolysis of PET (1 g).

Entry	Fe$_3$O$_4$@ Cyanoric Chloride (g)	NaOH (g)	Unreacted PET (g)	TPA yield %
1	0.00	0.50	0.00	90
2	0.02	0.50	0.00	95
3	0.02	0.40	0.00	89
4	0.02	0.30	0.00	87
5	0.02	0.20	0.21	53
6	0.02	0.10	0.52	34
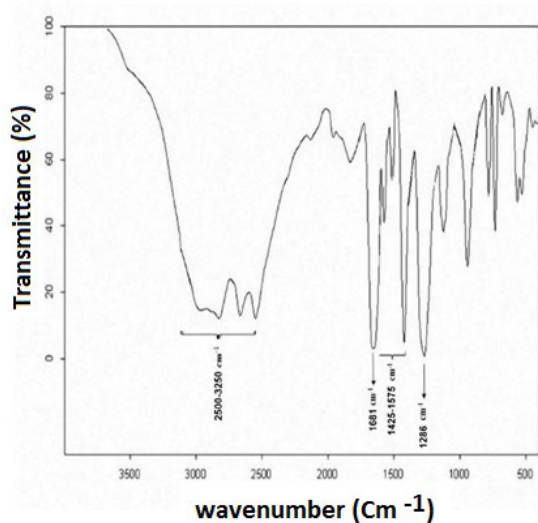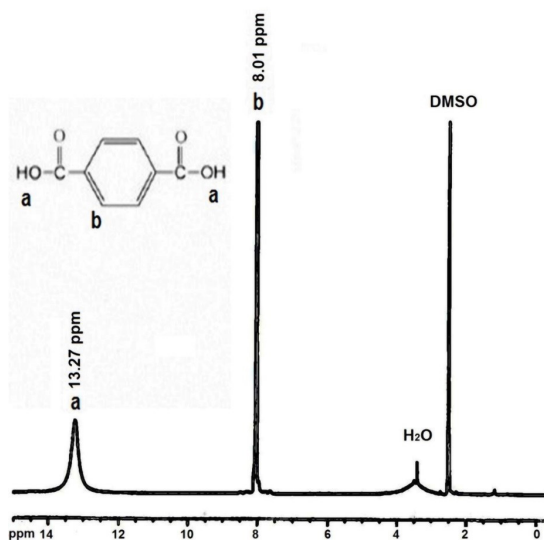
Figure 8. ^{13}CNMR spectra of obtained TPA from Glycolysis.

In order to finding the optimum PET: DEG molar ratios, we decrease this ratio (Figure 5). As shown in this figure, in present of nano-Fe$_3$O$_4$@Cyanuric Chloride (0.02 g) and by altering PET: DEG molar ratios from 1:8 to 1:5, the slight decrements in TPA recovery yield are observed and suddenly drop in 1:4 molar ratio. And this means we have 37.5% saving energy.

3.4 IR spectroscopy analysis of obtained TPA

Figure 6 shows IR Spectroscopy of obtained TPA from glycolysis reaction. Specifications bond at 2500-3250 cm^{-1} are related to carboxylic group, 1685 cm^{-1} are related to carbonyl group and 1574-1425 cm^{-1} are related to aromatic ring. These results have a good match with the reference data related to virgin TPA showing that the purity of the product in this method is passable.

3.5 ^{1}HNMR analysis

Figure 7 shows ^{1}HNMR spectrum of obtained TPA. The revealed bands at 8.01 ppm and 13.27 ppm are related to protons of aromatic ring and acidic proton respectively and spectrum is similar to the authentic sample one.

3.6 ^{13}CNMR analysis

Figure 8 shows ^{13}CNMR spectrum of obtained TPA. The revealed band at 167.10 ppm are related to carbon of carbonyl group and 129.93 ppm and 134.86 ppm are related to carbons of aromatic ring and all signals math with an authentic sample spectrum signal.

4. Conclusion

In conclusion, nano-Fe$_3$O$_4$@Cyanuric Chloride can be used as the effective supported catalyst in recovering of terephthalic acid from PET wastes in combination with sodium hydroxide. The obtained results from the glycolysis of PET wastes by using DEG as the solvent, sodium hydroxide as the reagent and nano-Fe$_3$O$_4$@Cyanuric Chloride as the reagent-solid support led to successful recovering of TPA

Figure 6. FT-IR spectra of obtained TPA from Glycolysis.

Figure 7. ^{1}HNMR spectra of obtained TPA from Glycolysis.

in high yields. In the presences of nano-Fe$_3$O$_4$@Cyanuric Chloride, the required reaction time for TPA recovery, DEG and NaOH consumptions decrease about 99, 37.5 and 40%, respectively.

5. Acknowledgements

6. References

1. Nikje, M. M. A., Nazari, F., Imanieh, H., Garmarudi, A. B., & Haghshenas, M. (2007). PET recycling by diethylene glycol-diethanol amine binary mixture and application of product in rigid polyurethane foam formulation. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, *44*(7), 753-758. http://dx.doi.org/10.1080/10601320701353231.

2. Siddiqui, M. N., Redhwi, H. H., & Achilias, D. S. (2012). Recycling of poly(ethylene terephthalate) waste through methanolic pyrolysis in a microwave reactor. *Journal of Analytical and Applied Pyrolysis*, *98*, 214-220. http://dx.doi.org/10.1016/j.jaap.2012.09.007.

3. Nikje, M. M. A., & Nazari, F. (2006). Microwave-assisted depolymerization of Poly(ethylene terephthalate) [PET] at atmospheric pressure. *Advances in Polymer Technology*, *25*(4), 242-246. http://dx.doi.org/10.1002/adv.20080.

4. Pingale, N. D., & Shukla, S. R. (2008). Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste. *European Polymer Journal*, *44*(12), 4151-4156. http://dx.doi.org/10.1016/j.eurpolymj.2008.09.019.

5. Nikje, M. M. A., & Nazari, F. (2009). Simple and convenient method of chemical recycling of poly (ethylene terephthalate) by using microwave radiation. *Polimery*, *54*(9), 635-639. Retrieved in 2015, July 07, from http://www.ichp.pl/attach.php?id=244

6. Parab, Y. S., Shah, R. V., & Shukla, S. R. (2012). Microwave irradiated synthesis and characterization of 1, 4-phenylene bis-oxazoline form bis-(2-hydroxyethyl) terephthalamide obtained by depolymerization of poly (ethylene terephthalate) (PET) bottle wastes. *Current Chemistry Letters*, *1*(2), 81-90. http://dx.doi.org/10.5267/j.ccl.2012.3.003.

7. Chen, F., Wang, G., Shi, Ch., Zhang, Y., Zhang, L., Li, W., & Yang, F. (2013). Kinetics of glycolysis of poly (ethylene terephthalate) under microwave irradiation. *Journal of Applied Polymer Science*, *127*(4), 2809-2815. http://dx.doi.org/10.1002/app.37608.

8. Rusen, E., Mocanu, A., Rizea, F., Diacon, A., Calinescu, I., Mititeanu, L., Dumitrescu, D., & Popa, A.-M. (2013). Post-consumer PET Bottles Recycling II. PET depolymerization using microwaves. *Materiale Plastice*, *50*(3), 201-207. Retrieved in 2015, July 07, from http://www.revmaterialeplastice.ro/pdf/RUSEN%20E.pdf%203%2013.pdf

9. Chaudhary, S., Surekha, P., Kumar, D., Rajagopal, C., & Roy, P. K. (2013). Microwave assisted glycolysis of poly(ethylene terephthalate) for preparation of polyester polyols. *Journal of Applied Polymer Science*, *129*(5), 2779-2788. http://dx.doi.org/10.1002/app.38970.

10. Liu, N., Ma, Y., Shu, K., Wu, B., & Zhang, D. (2014). Catalysis investigation of PET depolymerization with bransted acidic ionic liquid under microwave irradiation. *Advanced Materials Research*, *893*, 23-29. http://dx.doi.org/10.4028/www.scientific.net/AMR.893.23.

11. Yue, F. Q., Yang, H. G., Zhang, L. M., & Bai, X. F. (2014). Metal-Containing ionic liquids: highly effective catalysts for degradation of poly(Ethylene Terephthalate). *Advances in Materials Science and Engineering*, *2014*, 1-6. http://dx.doi.org/10.1155/2014/454756.

12. Yue, Q. F., Wang, C. X., Zhang, L. N., Ni, Y., & Jin, Y. X. (2011). Glycolysis of poly(ethylene terephthalate) (PET) using basic ionic liquids as catalysts. *Polymer Degradation & Stability*, *96*(4), 399-403. http://dx.doi.org/10.1016/j.polymdegradstab.2010.12.020.

13. Aguado, A., Martínez, L., Becerra, L., Arieta-araunabena, M., Arnaiz, S., Asueta, A., & Robertson, I. (2014). Chemical depolymerization of PET complex waste: hydrolysis vs. glycolysis. *Journal of Material Cycles and Waste Management*, *16*(2), 201-210. http://dx.doi.org/10.1007/s10163-013-0177-y.

14. Imran, M., Lee, K. G., Imtiaz, Q., Kim, Q. B., Han, M., Cho, B. G., & Kim, D. (2011). Metal-oxide-doped silica nanoparticles for the catalytic glycolysis of polyethylene terephthalate. *Journal of Nanoscience and Nanotechnology*, *11*(1), 824-828. PMid:21446554. http://dx.doi.org/10.1166/jnn.2011.3201.

15. Wi, R., Imran, M., Lee, K. G., Yoon, S. H., Cho, B. G., & Kim, D. H. (2011). Effect of support size on the catalytic activity of metal-oxide-doped silica particles in the glycolysis of polyethylene terephthalate. *Journal of Nanoscience and Nanotechnology*, *11*(7), 6544-6549. PMid:22121753. http://dx.doi.org/10.1166/jnn.2011.4393.

16. Park, G., Bartolome, L., Lee, K. G., Lee, S. J., Kim, D. H., & Park, T. J. (2012). One-step sonochemical synthesis of a graphene oxide-manganese oxide nanocomposite for catalytic glycolysis of poly(ethylene terephthalate). *Nanoscale*, *4*(13), 3879-3885. PMid:22592889. http://dx.doi.org/10.1039/c2nr30168g.

17. Bartolome, L., Imran, M., Lee, G. K., Sangalang, A., Ahn, K. J., & Kim, D. H. (2013). Superparamagnetic γ-Fe$_2$O$_3$ nanoparticles as an easily recoverable catalyst for the chemical recycling of PET. *Green Chemistry*, *16*(1), 279-286. http://dx.doi.org/10.1039/C3GC41834K.

18. Balacianu, F. D., Nechifor, A. C., Bartos, R., Voicu, S. I., & Nechifor, G. (2009). Synthesis and characterization of Fe$_3$O$_4$ magnetic particles-multiwalled carbon nanotubes by covalent functionalization. *Optoelectronics and Advanced Materials Rapid Communications*, *3*(3), 219-222. Retrieved in 2015, July 07, from https://oam-rc.inoe.ro/download.php?idu=665