



SYNTHESIS OF BIO-NANOMAGNETITE AND ITS OPTIMIZED CONDITIONS FOR PHTHALATE ABSORPTION

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ABSTRACT

Motivation/Background: Magnetic polymeric nanoparticles have vast range of applications in various fields. Coating or encapsulating of magnetic particles with polymers is one of the most useful methods of modifying magnetic nanoparticles. As these coated particles have magnetic characteristics, they can be easily collected with a single magnet instead of burdensome and time-consuming methods such as centrifugation.

Method: In this work, nano magnetite particles were synthesized using co-precipitation method and then they were firstly coated with a single biodegradable co-polymer, i.e. poly(butylene adipate-co-terephthalate) (PBAT), and secondly with a mixture of two biodegradable polymers of PBAT and poly(butylene adipate) (PBA).

Results: Fourier Transform Infrared (FTIR) spectrum of these two bio-nanoparticles showed their characteristics. They were also used to absorb dibutyle phthalate and dioctyle phthalate from aqueous solutions. UV-Vis was used to characterize optimization of particle mass, time and stirring speed during absorption. XRD spectrum was also taken. Volume, time and stirring speed of desorption were also optimized. In addition, calibration was performed, and the isotherm was plotted for two particles.

Conclusions: According to XRD spectrum, particles were in nano range. They had acceptable biodegradation characteristics. They also were efficient in absorbing and desorbing phthalates and were collected easily through magnet.

1. INTRODUCTION

Magnetic materials have various applications in different fields such as magnetic storage media [1], Ferro fluids [2], magnetic resonance imaging (MRI) [3], magnetically guided drug delivery [4] magnetic bio-separation [5], heavy metal removal [6], and cancer therapy [7]. They have been used extensively as they have various properties such as magnetism, catalytic features, conduction and biological acceptance [8]. The production method of nanomagnetite particles can be divided generally into two approaches, physical and chemical methods [9]. One example of physical method is evaporating particulate materials in tube furnace containing ultra-pure nitrogen. However, physical methods suffer from poor size and shape. Chemical methods are simpler and more efficient [10]. Various methods such as reverse micelle, copolymer gels, solvothermal reduction, ion exchange resin and co-precipitation are used

[11]. Among these, co-precipitation method is probably the most promising one due to its simplicity, productivity, and low cost in the production process [9].

Surface modification and functionalization of magnetite nanoparticles are performed using coating materials. Easy aggregation and instability of bare nanomagnetite particles in aqueous solution, high surface energy, and susceptibility to oxidation lead to the stabilization of iron oxide particles by surface modification so that they can be used in various potential fields [12] [13]. Surface modification is easily performed through the creation of few atomic layers of organic (polymer) or inorganic (metal or oxide) surfaces [14][15]. This coating can be comprised of several materials such as organic, inorganic, polymeric and non-polymeric ones [16]. For example, Lee and Harris (2006) attached oleic acid to the surface of magnetite by ozonolysis and made it more lyophobic [17]. Yantasee et al. (2007) used surface modification of dimercaptosuccinic acid (DMAS) to synthesize superparamagnetic iron oxide (Fe_3O_4) and employed them as a useful sorbent material for toxic soft metals such as Hg(II), Ag(I), Pb(II), Cd(II) and Tl(I) ions which actively bind to the DMSA ligand and for As(III) which binds to the iron oxide lattice [18]. Zhang et al. (2011) reported that the application of starch as a stabilizer in preparation of the Fe_3O_4 particles can effectively reduce particle aggregation and lead to the formation of more effective adsorbing sites on magnetite particle surfaces [19]. Another investigation [20] described the formation of magnetite in the presence of 1 wt.% poly(vinyl alcohol). Low dispersed chitosan-bound Fe_3O_4 nanoparticles were utilized as a unique nano-adsorbent for the removal of heavy metal ions [21].

Rapid industrialization and urbanization have created various pollutants particularly those entering aquatic systems so development of efficient and cost-effective methods for environmental treatment is critical. Nanomagnetites are ideal candidates for pollutant removal and toxicity mitigation due to extremely small size, high ratio of surface area to volume and more importantly the magnetism [22]. Methods of pollutants adsorption to the surface of these nanoparticles include physical adsorption, ion-exchange, chemical bonding, hydrogen bonds, and van der Waal forces. For example, composite of $\text{Fe}_3\text{O}_4/\text{ZrO}_2$ /chitosan was synthesized and employed for the removal of amaranth and tartazine dyes [23].

Phthalates have been used extensively as plastifying agent to make polyvinyl chloride supple and flexible. They exist in the environment, food samples, medical devices, perfume and cosmetics [24]. Phthalates tend to bioaccumulate in the environment and they are poorly degradable and toxic [25]; so monitoring phthalates is of significant importance due to their wide use and toxicity [26]. In this work, it has been tried to absorb phthalate from aqueous solution by nanomagnetite particles. Then, absorbance and desorption conditions were optimized.

2. MATERIALS AND METHODS

2.1. MATERIALS

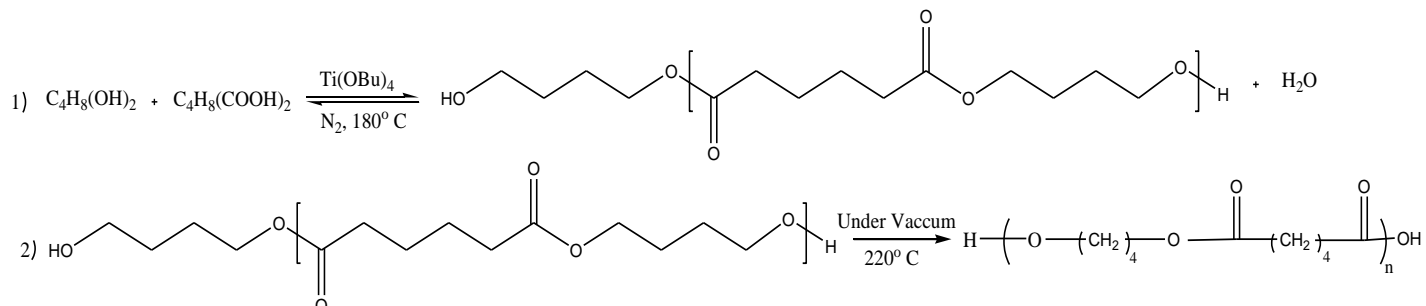
1,4-butanediol (BD; Merck, 99%), adipic acid (ADA; Merck, 99%), terephthalic acid (TA; Merck, 98%), and titanium (IV)tetra-n-butyl orthotitanate (TBT; Merck, 98%) were purchased and used for synthesizing polymers. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ () and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ () along with NaOH () and HCl (Merck, 37%) were used to synthesize the nanoparticle. Dibutyl phthalate (Merck, > 99%) and dioctyl phthalate (Merck, 98%) were purchased and used as received. All solvents were at analytical degree.

2.2. METHODS

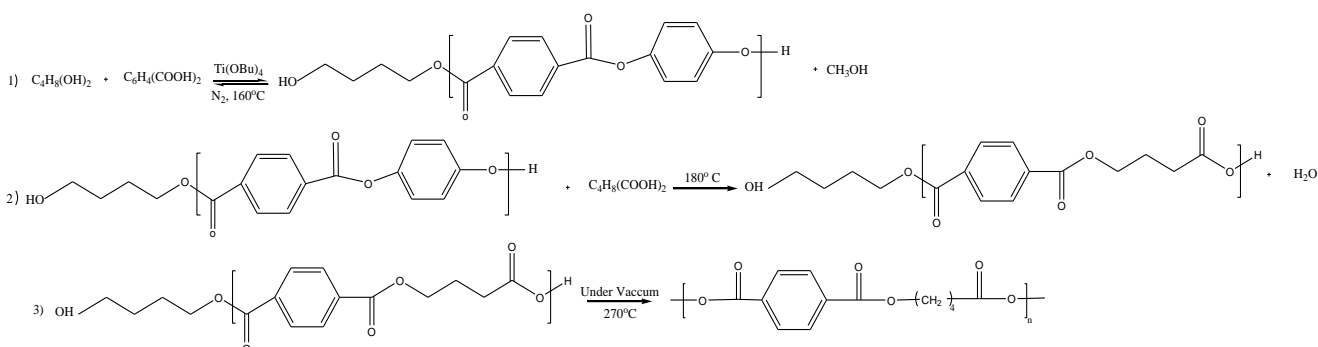
Polymers and nanoparticles were synthesized according to our previous work [27]. So, a brief description is given. Preparing solutions and optimization methods will explain next.

2.2.1. POLYMER SYNTHESIS

PBA was synthesized through two-stage melt polycondensation (first esterification and then polycondensation) using BD and ADA with TBT as catalyst (molar ratio of 1:1:0.1, respectively). Nitrogen atmosphere and vigorous stirring were applied. The reaction is as follows:



PBAT was also synthesized through three-stage melt polycondensation (two stages of esterification and then polycondensation) using BA, ADA, TA with TBT as catalyst (molar ratio of 1:1:1:0.1, respectively). Nitrogen atmosphere and vigorous stirring were applied. The reaction is as follows:



2.2.2. BIO-NANOMAGNETITE SYNTHESIS

Co-precipitation method was used based on similar previous works [28][29][30]. For first nanoparticle (PBAT), PBAT (dissolved in DMSO) were added to a round-bottom flask containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, FeCl_2 (molar ratio of 10^{-4} : 2:1, respectively), HCl 12 M (0.85 ml) and distilled water (25 ml). After partial dissolving, NaOH 1.5 M (250 ml) was added drop wisely while stirring vigorously and nitrogen passing. When adding NaOH was completed, a black precipitation was obtained which was washed three times with distilled water and dried in vacuum oven for 24h at 50°C .

Another nanoparticle (PBA+PBAT) was also synthesized through the same procedure except that in addition to PBAT, PBA (dissolved in CHCl_3) was also added (PBA:PBAT: FeCl_3 : $\text{FeCl}_2 \rightarrow 10^{-4}$: 10^{-4} : 2:1). This precipitation was washed (three times) and dried at the same condition.

2.2.3. SOLUTIONS OF PHTHALATES

As nanoparticles are used to absorb phthalates from aqueous medium, first aqueous solution of them should be prepared. As they are insoluble in water, a 1000-ppm stock solution of each phthalate (dibutyl phthalate (DBPh) and dioctyl phthalate (DOPh) in methanol was prepared. Then, a 20-ppm solution was provided in methanol from 1000-ppm stock solution of each one. Finally, 5-ppm aqueous solution was prepared from solutions of 20 ppm. These 5 ppm solutions were used for optimization process.

2.2.4. OPTIMIZATION PROCESS

Optimization was performed for solution derived from absorption and desorption. First, weight of each nanoparticle was optimized for the absorption of each phthalate. Considered weights included 0.001 gr, 0.005 gr, 0.01 gr, and 0.02 gr. Then, time intervals of 10 min, 20 min, 30 min, 45 min, and 60 min was used for DBPh and 10 min, 20 min, 30 min, 45 min, 60 min, and 75 min for DOPh. Finally, stirring speed was optimized for the absorption of each phthalate solution (250 rpm, 500 rpm, and 750 rpm).

Afterwards, desorption was optimized. First, volume of methanol was optimized (1.5 cc, 2 cc, 2.5 cc and 3 cc). Second, time intervals of 10 min, 30 min, 20 min, and 40 min were considered. Finally, stirring speed was investigated (250 rpm, 500 rpm, and 750 rpm).

3. RESULTS AND DISCUSSIONS

3.1. ¹³CNMR SPECTRA

¹³CNMR spectra of polymers were taken (Browker, 400 MHz). Figs 1 and 2 show these spectra and their corresponding tables indicate their characterizing peaks.

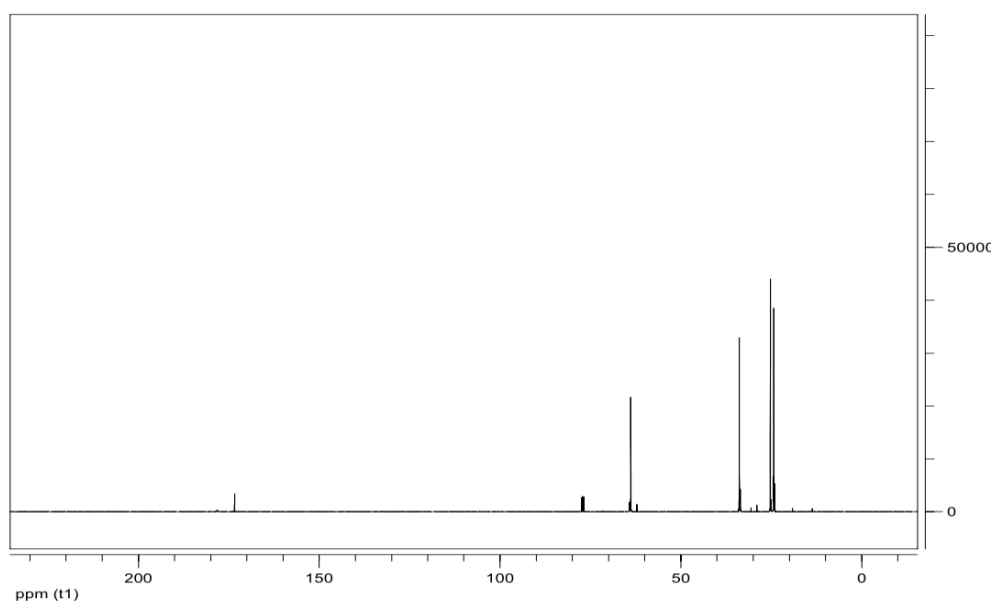


Figure 1: ¹³CNMR spectrum of PBA

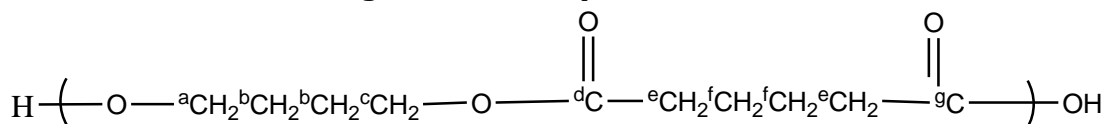


Table 1: Leading peaks of PBA ¹³CNMR spectrum

Carbon type	Chemical shift (ppm)	Carbon type	Chemical shift (ppm)
f	24.26	c	76.80
b	25.24	d	173.32
e	33.80	g	180
a	63.80		

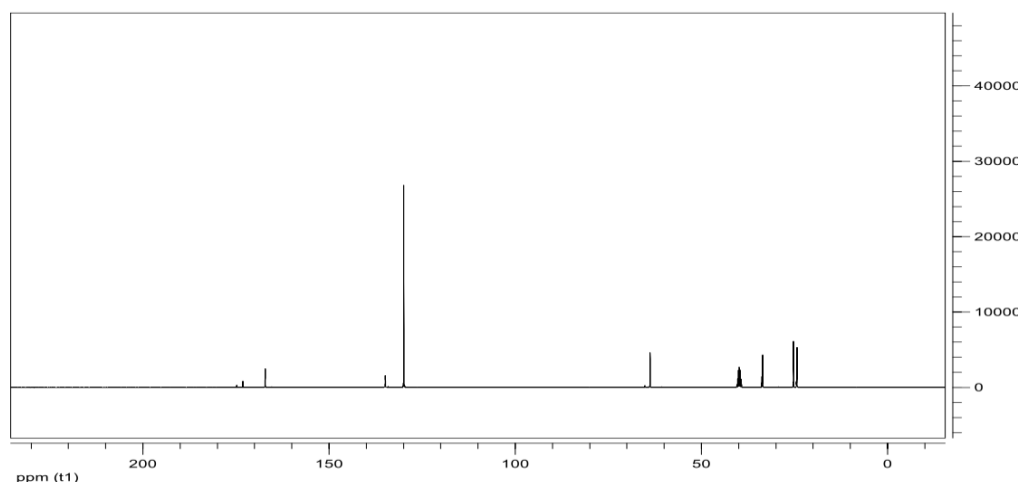


Figure 2: ^{13}C NMR spectrum of PBAT

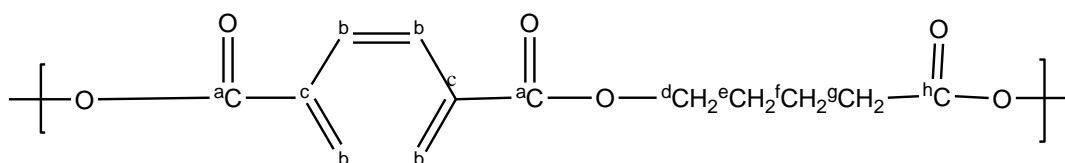


Table 2: Leading peaks of PBAT ^{13}C NMR spectrum

Carbon type	Chemical shift (ppm)	Carbon type	Chemical shift (ppm)
b	129.88	e	25.29
c	134.86	f	33.70
h	176.09	g	39.80
a	173.09	d	63.74

3.2. FTIR SPECTRUM

Fourier Transform Infrared spectrum (FTIR) shows the characterizing peaks (Thermo Nicolet, AVATAR 370, USA). Fig. 3 shows the FTIR result of PBAT nanoparticles. Stretching Fe-O peaks at 440.06 cm^{-1} and 601.11 cm^{-1} , OOP peaks of para substituents at 877.35 cm^{-1} , aromatic stretching C=C at the range of $1475\text{--}1630\text{ cm}^{-1}$, C-O stretching peaks at $1000\text{--}1300\text{ cm}^{-1}$ and broad peak at about 3395 cm^{-1} for stretching O-H are observed which confirmed polymer coating structure. Peaks at 1008.2 and 629.31 can be of esteric characteristic peaks but they are shifted backward due to Fe bounding.

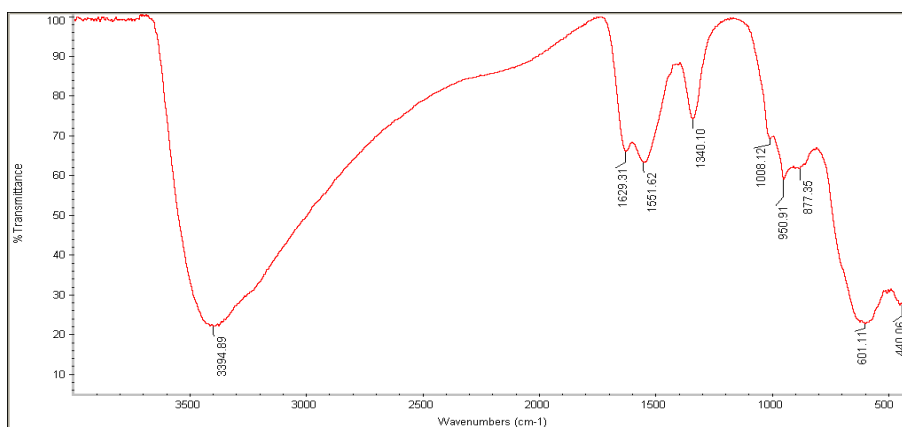


Figure 3: FTIR spectrum of PBAT nanoparticles

Also FTIR spectrum of PBA+PBAT nanoparticles is shown in Fig. 4 which disclosed characteristic peaks of stretching Fe-O (432.69 cm^{-1} and 588.24 cm^{-1}), C-H chain bending (1413.39 cm^{-1}), and O-H stretching band (3373.06 cm^{-1}). Peaks at 1634.05 and 1020.21 can point to ester characteristics peaks but they are shifted backwards which can be due to the iron bounding with the oxygen atom of esoteric group.

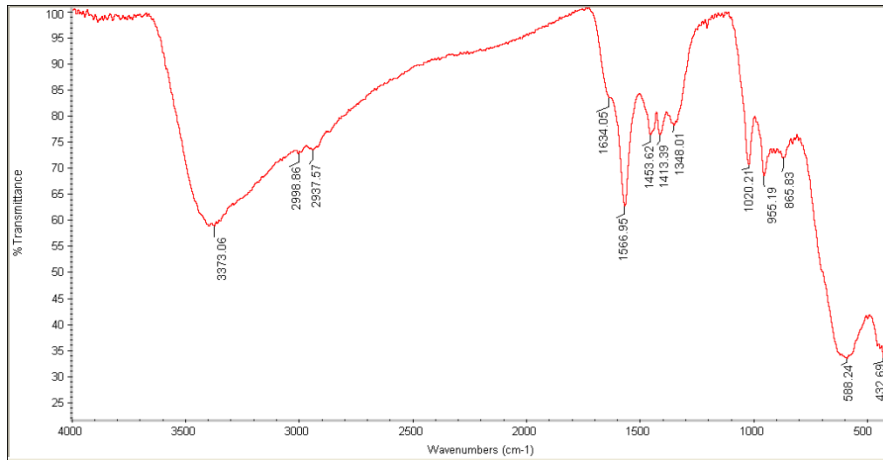


Figure 4: FTIR spectrum of PBA+PBAT nanoparticles

3.3. XRD TEST

Results of X-ray diffraction spectrum can be observed in Fig. 5. This test was performed from 20° to 80° and $\text{CuK}\alpha$ was used. According to this spectrum, crystalline structure of iron is maintained after coating as characteristic peaks of iron can be recognized in the spectrum. In addition, relative size of the particles based on Debye-Scherrer relation was obtained (9.12 nm).

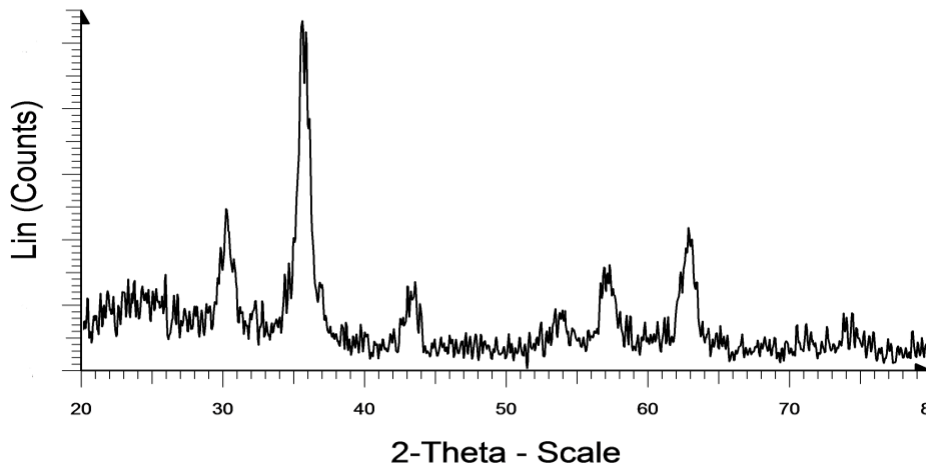


Figure 5: XRD spectrum of nanoparticle

3.4. OPTIMIZATION

First, wavelength for phthalates absorption should be determined. So, 20-ppm methanol solutions of both DBPh and DOPh were obtained with UV-Vis spectroscopy. It was found that the wavelength was 247 nm . To determine whether the nanoparticles had the capacity to absorb phthalates, aqueous solutions of dibutyl phthalate were obtained and PBAT and PBAT+PBA nanoparticles were added. Then, UV spectrum of desorption was taken while methanol was considered as blank. Results are as follows.

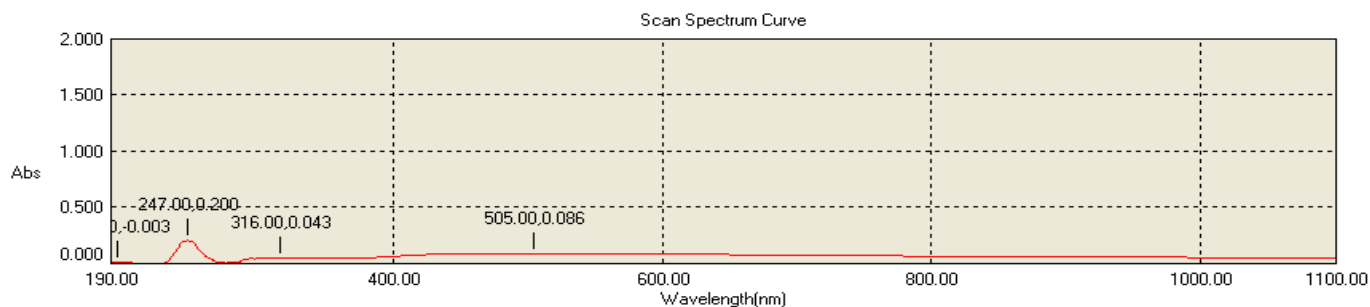


Figure 6: Desorption of DBPh by PBAT nanoparticles

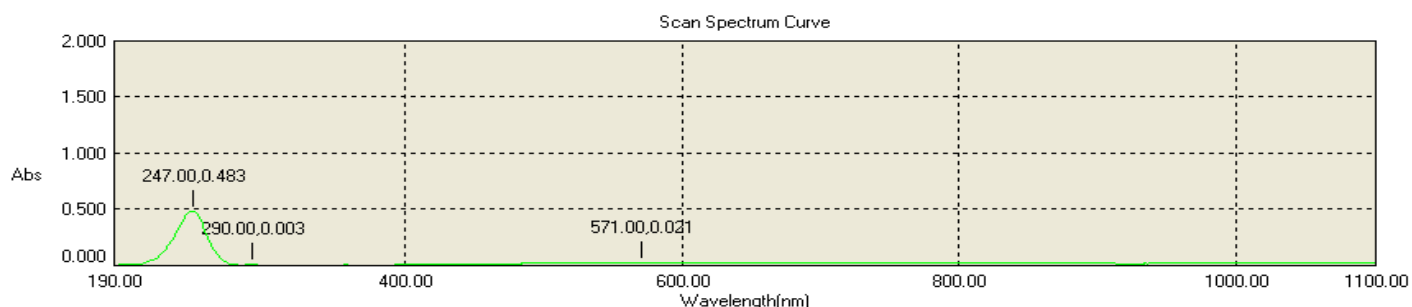


Figure 7: Desorption of DBPh by PBAT+PBA nanoparticles

As it was mentioned that time, nanoparticle weight and stirring speed were optimized for absorption of DBPh and DOPh from aqueous solution.

Optimum desorption conditions were also obtained. Nanoparticles obtained from optimum absorption were put in methanol and then UV-Vis spectrum was taken. Volume, time and stirring speed were optimized and results are given in table 3.

Table 3: Optimum conditions for absorption and desorption of phthalates by bio-nanoparticles

Absorption						
Material	PBAT nanoparticles			PBAT+PBAT nanoparticles		
	Weight (gr)	Time (min)	Stirring speed (rpm)	Weight (gr)	Time (min)	Stirring speed (rpm)
DBPh	0.01	20	500	0.01	45	500
DOPh	0.005	30	500	0.005	60	500
Desorption						
Material	PBAT nanoparticles			PBAT+PBAT nanoparticles		
	Volume (ml)	Time (min)	Stirring speed (rpm)	Volume (ml)	Time (min)	Stirring speed (rpm)
DBPh	2.5	30	500	2.5	20	500
DOPh	2.5	30	500	2.5	20	500

3.5. CALIBRATION

Generally, calibration is a kind of operation in which an output quantity is related to an input quantity for a measuring system under given conditions (IUPAC). Linear regression is used to determine the equation which best explains the linear relationship between the response (y) and analyte level (x) (in this work, y is the absorbance level and x is the concentration). This relation is described by the equation of the line, i.e., $y = mx + c$ in which m is the gradient of the line and c is the intercept with the y-axis. The correlation coefficient, r (and the related parameter r^2) shows the strength of correlation between the y and x values. It can take any value from +1 to -1 and the closer it is to 1, the stronger the correlation. This correlation coefficient is commonly used in analytical measurement. The

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particular value of r can indicate a statistically significant correlation between y and x depends on the number of data points used to calculate it (calibration curve guide).

In order to plot calibration graphs, different aqueous concentrations of DBPh and DOPh were prepared (0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm, 5 ppm, 10 ppm, and 15 ppm) and then, nanoparticles were added. In each case, four or five suitable points were selected to plot the graphs. Results are shown in the following Figs (8-11).

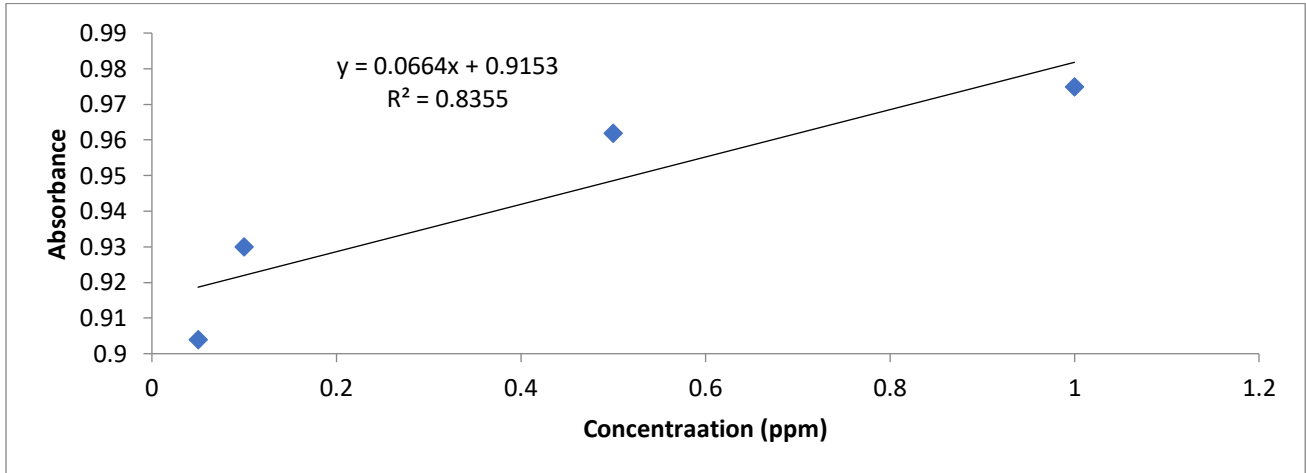


Figure 8: Calibration graph of DBPh desorption from PBAT nanoparticles

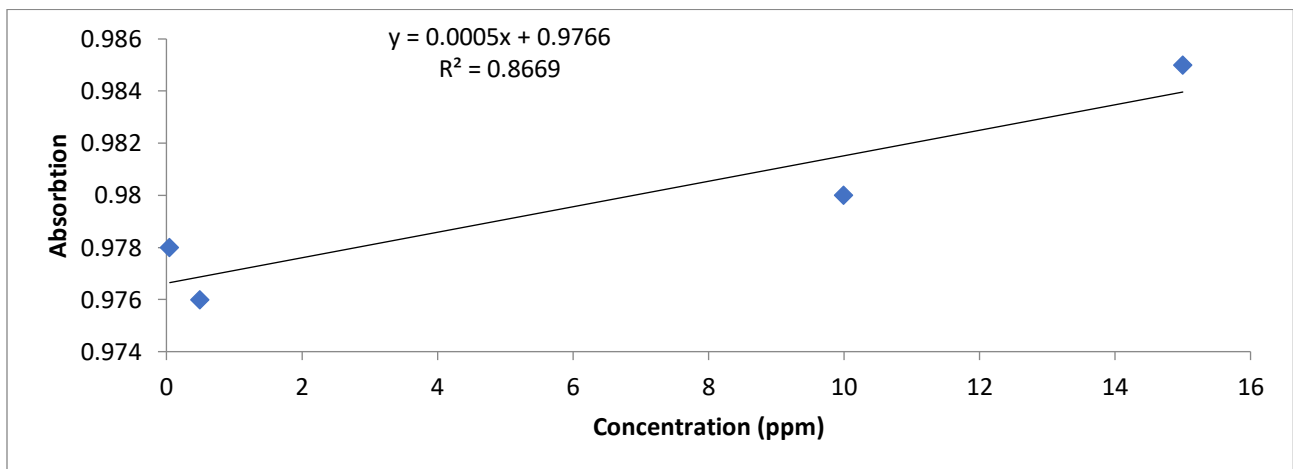


Figure 9: Calibration graph of DBPh desorption from PBA+PBAT nanoparticles

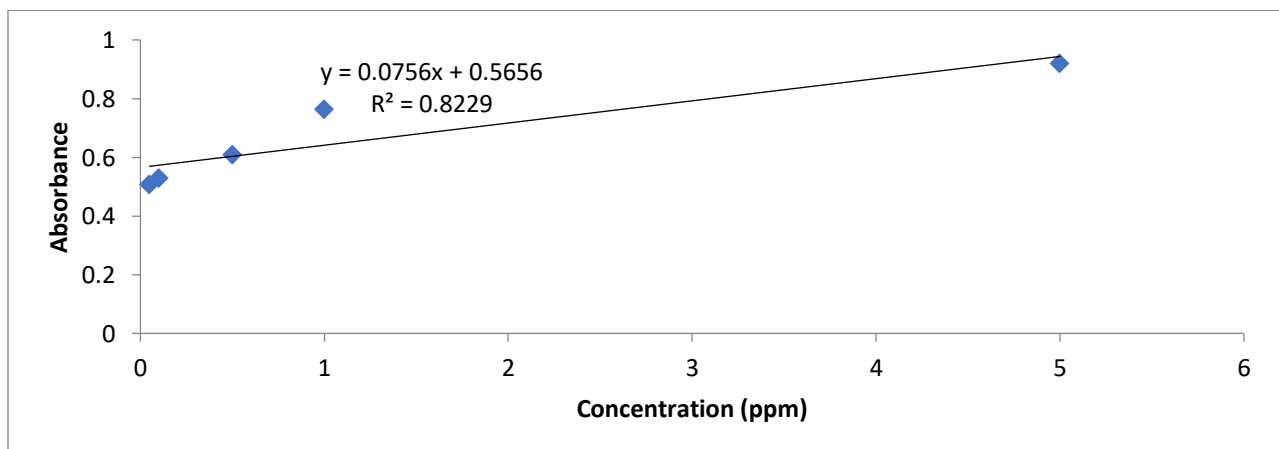


Figure 10: Calibration graph of DOPh desorption from PBAT nanoparticles

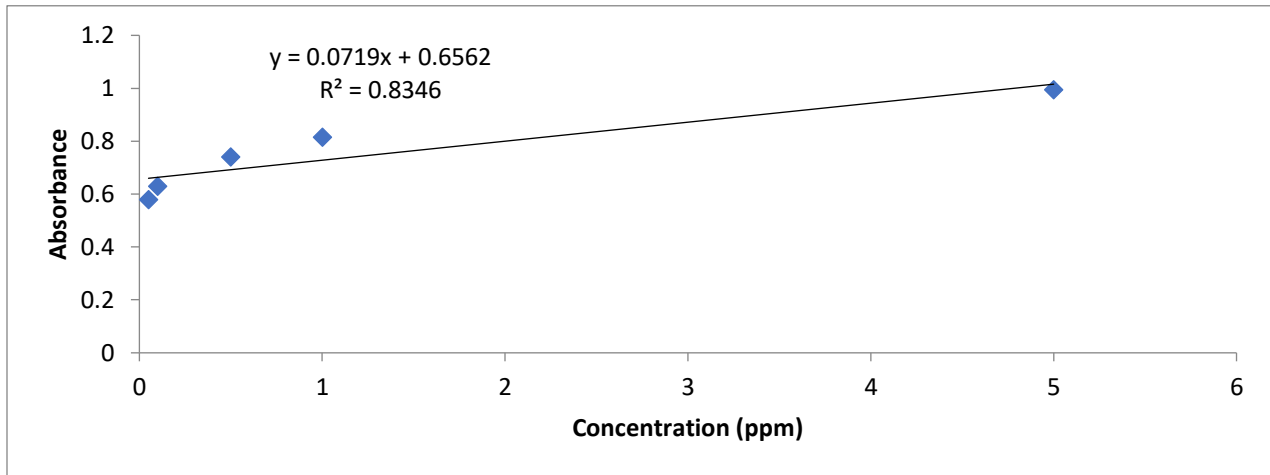


Figure 11: Calibration graph of DOPh desorption from PBA+PBAT nanoparticles

As it can be seen from the Figs, there seems to be good correlations between absorbance and concentration (values of R^2 are close to one). In each case, the equation may be used to estimate the amount of absorbance in any concentration. There are some fluctuations in absorbance amount of different concentrations which can be attributed to the instrument error tolerance and slight differences during preparing different concentrations of the stock solution.

3.6. ISOTHERMS

Isotherms were also plotted for these solutions at five different temperatures (15°, 20°, 25°, 30° and 35°C). Four prepared isotherms are illustrated below.

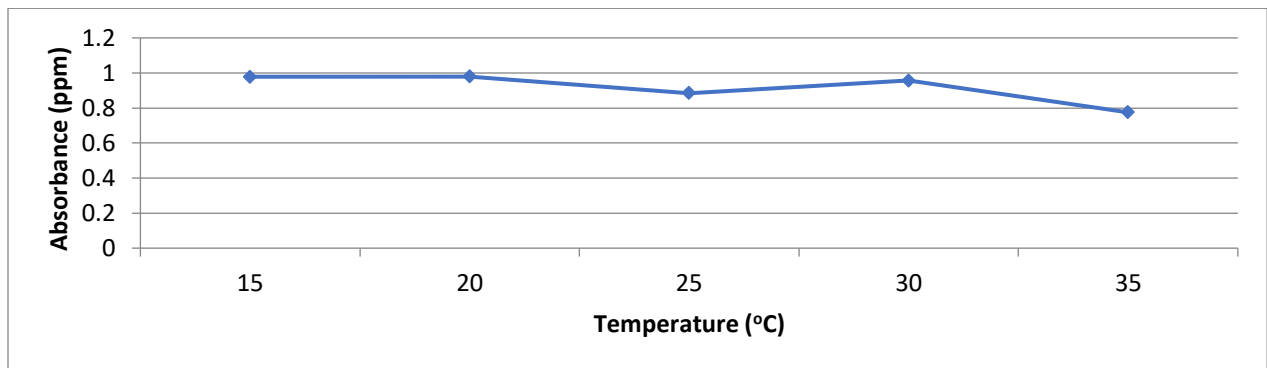


Figure 12: Isotherm of DBPh absorbance by PBAT nanoparticles in different temperatures

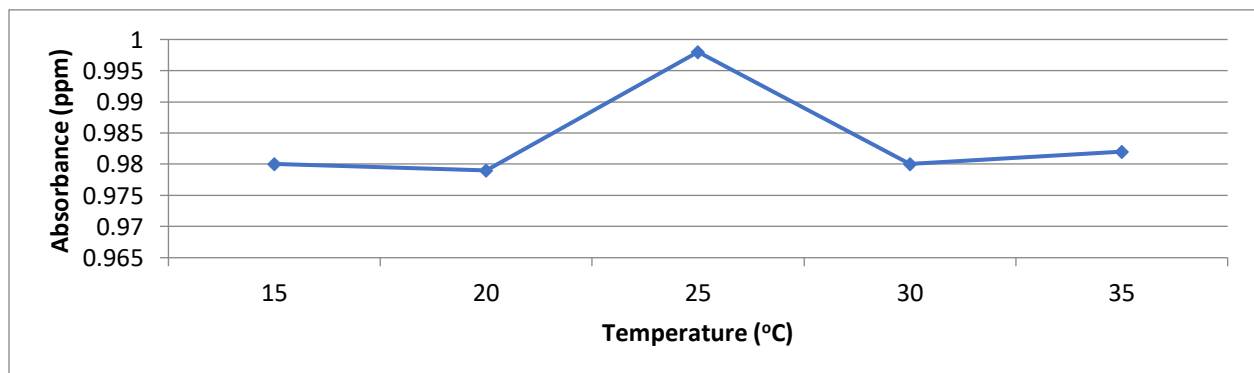


Figure 13: Isotherm of DBPh absorbance by PBA+PBAT nanoparticles in different temperatures

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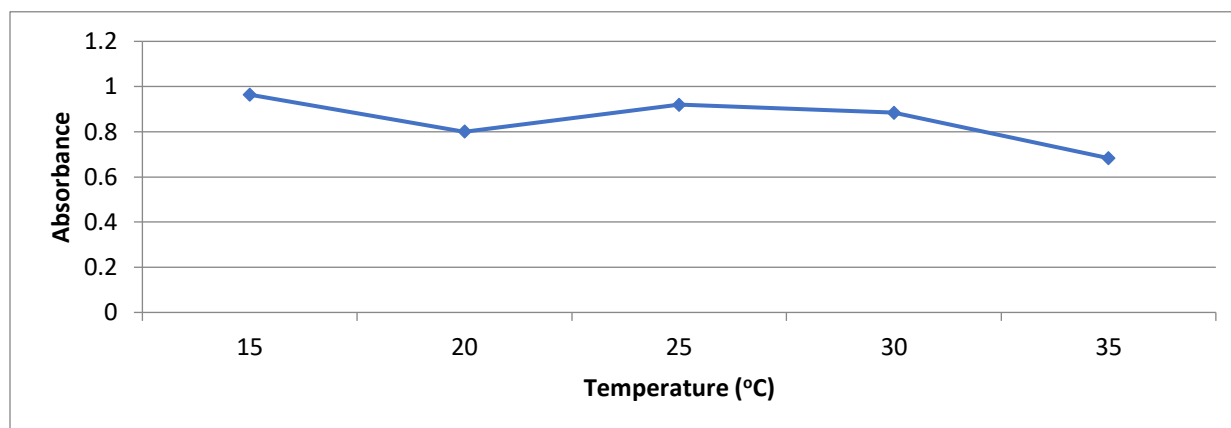


Figure 14: Isotherm of DOPh absorbance by PBAT nanoparticles in different temperatures

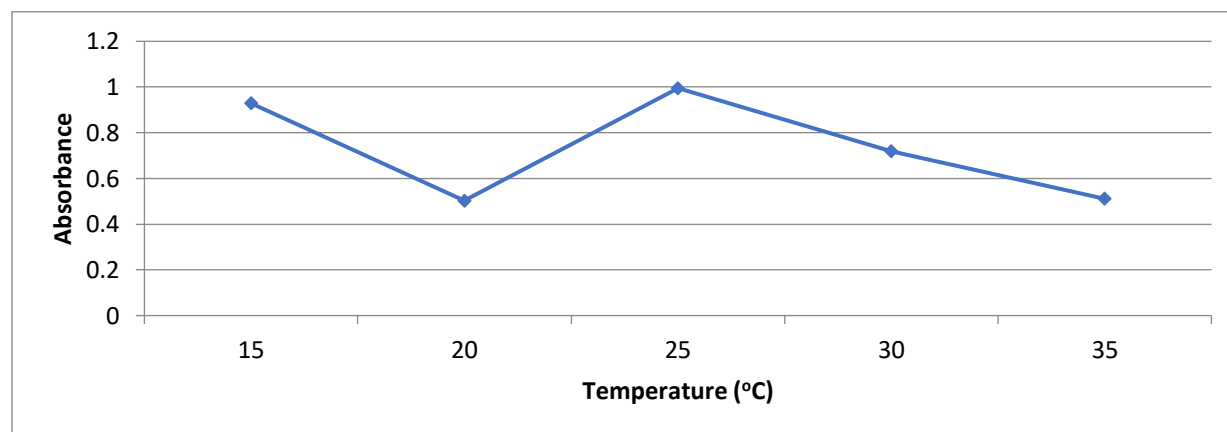


Figure 15: Isotherm of DOPh absorbance by PBA+PBAT nanoparticles in different temperatures

4. CONCLUSIONS

Bio-nanomagnetite particles were synthesized in this work. First, two biodegradable polymers of PBA and PBAT were produced using two- and three-stage melt polycondensation. Their characteristics were studied using ^{13}C NMR spectra. Next, two different bio-nanomagnetites were synthesized using FeCl_3 and FeCl_2 through co-precipitation method. Nanomagnetite particles were coated with PBAT and PBA + PBAT. FTIR and XRD spectra of bio-nanomagnetites were obtained. These coated particles were used to absorb DOPh and DBPh from aqueous medium and their performance were optimized regarding particle weight, absorption and desorption duration, volume of desorption solvent, and stirring speed.

Findings show that PBA+PBAT NP was better in absorbing phthalates from aqueous solution than PBAT NP which may be because combined NP has more functional group and reaction site on its surface than PBAT NP. ^{13}C NMR spectra show peaks may be assigned to functional groups of the polymers. In addition, FTIR spectra of bio-nanoparticles illustrate peaks related to both polymers and iron salts. X-ray diffraction spectrum indicates the relative size of the particles based on Debye-Scherrer relation (9.12 nm). Calibration graphs show a good correlation between absorbance and concentration with values of R^2 approaching one. Optimum features were also obtained and summarized in table 3.

These nanoparticles can be used to absorb phthalates from aqueous solution under optimized conditions which multiplies their efficiency. They are biodegradable and also reusable. Therefore, they can be used with the least trace on the environment.

SOURCES OF FUNDING

None.

CONFLICT OF INTEREST

None.

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