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# HYBRID MAGNETIC NANOPARTICLE-FUNCTIONALIZED POLYTHIOPHENES AND ITS POTENTIAL AS A SORBENT TO EXTRACT PHTHALATES

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**Abstract**

Magnetic polythiophene and poly-3-hexylthiophene was successfully synthesized. FTIR data suggested the presence of functionalized polythiophenes in the nanocomposites. XRD peaks confirmed the entire characteristic peak for $Fe_3O_4$ presence in all prepared nanocomposites. From the vibrating sample magnetometry hysterisis loop P3Th-coated MNPs (MNP@P3Th) established great magnetization than other nanocomposites. BET results showed decreasing trend of pore size due to addition of polymer coating. The thermograms of nanocomposite indicated that all the nanocomposites were stable up to 210 °C. The synthesized material was screened for the extraction of commercially available phthalates namely di-n-octyl phthalate (DNOP) butyl phthalate (DBP), and butyl benzyl phthalate (BBP) and P3Th-coated MNPs (MNP@P3Th) showed highest extraction concentration for all tested phthalates.

**Keywords:** Functionalized polythiophene; $Fe_3O_4$ magnetic nanoparticles, phthalates

## 1.0 INTRODUCTION

Iron oxides nanoparticles or known as magnetic nanoparticles (MNP) have become one of the most valuable species in countless applications (Farrukh et al., 2013; Li, Wei, Gao & Lei, 2005; Lin et al., 2012). High surface area to volume ratio for nano-sized particles enhances adsorption ability and efficacy especially for the elimination of contaminants from the environment (Baharin et al. 2016; Shen, Laibinis & Hatton, 1999). The unique characteristic of MNPs is their apt reaction to a magnetic field, which is superparamagnetism;

which release magnetism after the removal of an external field. Thus, it helps to detached the extractor from an supernatant solution in an intricate matrix easily (Li, Lam, Wu & Jiang, 2010; Xie, Jiang, Zhu, Liu & Ouyang, 2014). Due to the ease of the method, considerable amount of research article available on exploiting $Fe_3O_4$ as the adsorbent for extraction of organic and inorganic analyte (Aguilar-Arteaga, Rodriguez, Miranda, Medina & Barrado, 2010); (Ibarra, Miranda, Rodriguez, Nebot & Cepeda, 2014); (Fayazi, Taher, Afzali & Mostafavi, 2016); (Mehdinia, Rouhani & Mozaffari, 2016). However, nano-sized particle normally not stable and easily accumulated. Besides, metal oxide can be corroded easily which reduced its magnetism. Therefore, a proper surface adjustment can be done, to shield the magnetic core from corrosion and can be personalized agreeing to the definite analyte. Recently,many research articles reported excellent extraction ability on the exploitation of conducting polymers as a shielding agent of the magnetic nanoparticles (Gao, Luo, Bai, Chen, & Feng, 2011); (Tahmasebi, Yamini, Mehdinia, & Rouhi, 2012); (Zhao, Lu, & Feng, 2013). These materials have diverse functionalities and various properties, which may develop the surface modification and shield the magnetic nuclei from perturbation. Besides, it may lessen amassing and increase dissemination of the particles inside the media (Shin & Jang, 2007).

Increasing contamination caused by phthalates is due to widespread use as plasticizers for PVC's resin, cellulose coating and epoxy resin. They are ideal because of their competencies of refining the flexibility of plastics. Up to now, most of the plasticizers are phthalates. Enormous consumption of phthalates by many manufacturers, such as in therapeutic procedures, kid's toys, bottles, fabrics, and etc. eventually enters into the environment. Lipophilic properties of pthalates, make it certainly deposited in fatty tissues (Baharin, Muhamad Sarih & Mohamad, 2016). Contact to phthalates over continuing periods could cause serious health complications such as cancer and infertile. High molecular weight of phthalate such as di-n-butyl phthalate (DBP), butyl benzyl phthalate and di-n-octyl phthalate (DNOP) may cause serious health concerns and is alleged to be cancer-causing and toxic to vital organs (SM, 2014).

In this study, we studied extraction abilities of phthalates by iron oxide nanoparticles, iron oxide coated polythiophene and iron oxide coated poly-3-hexylthiophene as to study the possible active site within the molecular design that can extracts phthalates**.**

## 2.0 METHODLOGY

### 2.1 Materials

A.R grade iron (III) chloride ($FeCl_3.6H_2O$), iron (II) chloride ($FeCl_2.4H_2O$), ammonia solution (25 wt. %), thiophene, acetonitrile, methanol and hydrochloric acid were bought from Merck (Belgium). 3-hexylthiophene, DBP, BBP, DNOP were acquired from Sigma Aldrich (USA). Ethanol and hexane were gotten from Friedemann Schmidt (Australia). The double deionized water was done by a model Aqua Max-Ultra ultra-pure water purification system (United State).

### 2.2 Synthesis of Iron Oxide Coated Functionalized Polythiophene Nanocomposites

$Fe_3O_4$ produced by co-precipitation technique denoted to preceding study (Baharin et al. 2016). The surface of $Fe_3O_4$ nanoparticles was modified by coating with thiophene and 3- hexylthiophene monomers via oxidation polymerisation (Baharin et al., 2016). Later, thiphene (10 mmol) was poured with dynamic

swirling. Later, 0.03 L of HCl (0.5 mol $L^{-1}$) solution was added. Then the gained solutiont was desiccated in an oven at 70 ◦C for 12 h.

### 2.3 Extraction Study

Iron oxide and all the produced products were tested to define optimal sorbent for the extraction of phthalates. Selection experiments were performed with addition of 10 mg MNP, MNP@PTh and MNP@P3Th each to the 0.02 L of phthalate solution at neutral pH. Orbital shaker was used to shake the samples for 0.5 h. Then, the particulates was separated from the fluid via magnetic decantor. Subsequently, the particulates were washed with 0.5 mL ethyl acetate. The washed solution was collected and dried out with purified nitrogen before analysis using GC-FID. Parting and recognition of phthalates were achieved by a Shimadzu 2010 gas chromatograph. DB-5 Agilent fused-silica capillary column (30 m × 320 µm i.d. × 250 nm film thickness) was utilized for partitioned of analytes. Carrier gas used was helium at a continuous flow rate of 400 µL $min^{-1}$. Chromatographic programme were organized as; the temperatures of the detector at 280 °C and injector at 260 °C. The samples injection area was functioned at splitless mode. Oven was detained at 150 °C for 60 s and amplified to 280 °C at 8 °C $min^{-1}$ for 180 s.

## 3.0 RESULT AND DISCUSSION

### 3.1 Fourier Transform Infra Red

Figure 2 validates extra bands in the FT-IR of nanocomposites, relational to the $Fe_3O_4$ spectrum, which caused by the exterior enhancement. The prominent absorption bands at 3400 $cm^{-1}$ for iron oxide nanoparticle and all nanocomposites nominated the occurrence of hydroxyl stretching, while the peak at 530–632 $cm^{-1}$ matches to O-Fe stretching (Aydın et al., 2011).

2980 $cm^{-1}$ indicated =C–H $sp^2$ aromatic stretching band in thiophene was observed MNP@PTh and MNP@P3Th nanocomposite. C–H $sp^3$ stretching for beta aliphatic presence at 2934 $cm^{-1}$. Meanwhile, symmetric and asymmetric absorption peaks of C=C aromatic established in the range of 1573–1461 $cm^{-1}$ for MNP@PTh and 1565-1473 $cm^{-1}$ for MNP@P3Th. Therefore, from IR spectra, it can be concluded that the modification have done.

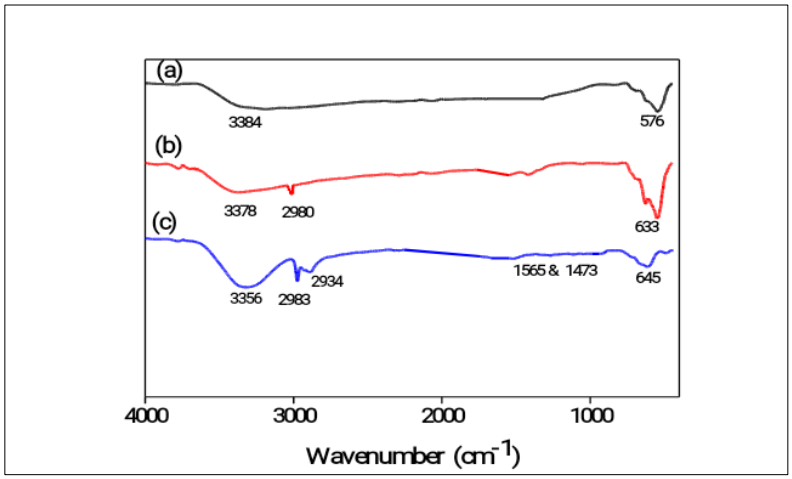


**Figure 2 IR spectra of (a) iron oxide nanoparticle, (b) MNP@PTh and (c) MNP@P3Th**

### 3.2 X-ray Diffractometer

Figure 3 shows the characteristic peaks detected for iron oxide, MNP@PTh and MNP@P3Th. Polymeric and amorphous properties existed in the nanocomposites broaden its peak compare to iron oxide nanoparticle (Cótica, Santos, Girotto, Ferri & Coelho, 2010). From the Figure 3 peaks for all samples were found at 2Θ = 30°, 35.7°, 43°, 53.4°, 57.0°. This unveiled that crystalline phase of the nanocomposites remains unalter even surface modification was done.

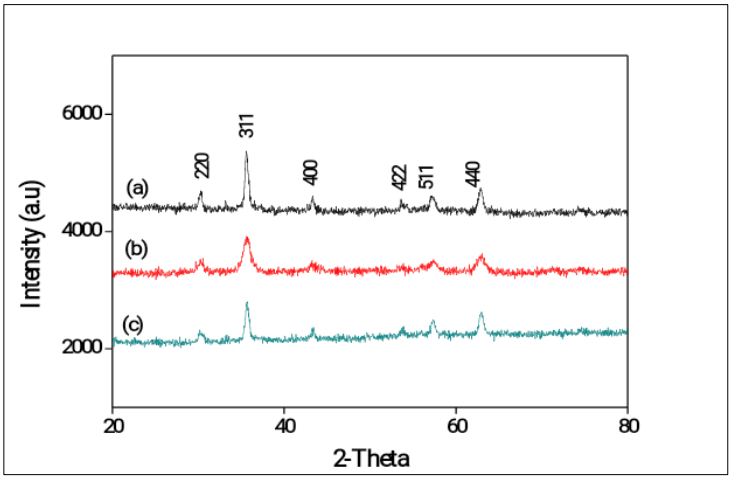


**Figure 3 XRD study of (a) iron oxide nanoparticles, (b) MNP@PTh and (c) MNP@P3Th nanocomposites**

### 3.3 Porosity and Surface Area Analysis

Surface area and pore size were examined by Brunauer-Emmet-Teller surface area analyzer. Results of of iron oxide nanoparticles and nanocomposites surface area and pore size are presented in Table 1. The pore size of nanocomposites decreased because of the amassing of polymeric material on the surface. Surface area for nanocomposites both increased suggested by the segregation of nanoparticles that caused increases the expanses among the nanoparticles (Darab, Linehan & Matson, 1994); (Wang, Chen, Yang, Wu & Tian, 2008).

**Table 1 Surface area and pore size analysis**

| Material | Porosity (nm) | Surface Area ($m^2$ $g^{-1}$) |
|---|---|---|
| Iron oxide nanoparticle | 20.20 | 37.370 |
| MNP@PTh | 18.30 | 95.60 |
| MNP@P3Th | 12.60 | 96.50 |

### 3.4 Thermogravimetry Analysis

Figure 4 displays thermal stability analysis for iron oxide nanoparticles and nanocomposites. Under 200 °C, minor weight loss was observed in all samples, originate to be due to decomposition of water molecules that trapped in the surface of the samples. After 200 °C, for iron oxide nanoparticles, absence of any mass loss is spotted. This can be due to the property of Fe-O that is thermally steady in temperature range of 280 °C - 850 °C (Mahdavi, 2013). Meanwhile, for nanocomposite at temperature above 210 °C the decomposition was increased statically. Prompt weight loss was observed in the temperature range 240 °C-450 °C for all nanocomposites and this is because of the disintegration of polymer coating.

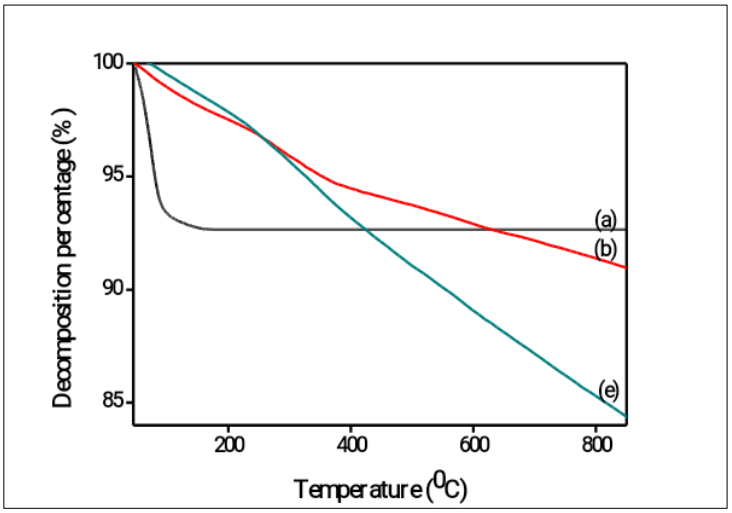


**Figure 4 Thermal analysis of (a) Iron oxide nanoparticles, (b) MNP@PTh and (c) MNP@P3Th nanocomposites**

### 3.5 Vibrating Sample Magnetometer (VSM)

Ability of the samples to give prompt response to an external magnetic field were tested using VSM. Magnetization curves of iron oxide nanoparticles, MNP@PTh and MNP@P3Th are shows in Figure 5. Prominent magnetic variable, which is permeation magnetization ($M_S$), was examined. From the graph in Figure 5 it was found that all the samples exhibited superparamagnetic properties (Jayabharathi, Ramanathan, Thanikachalam & Karunakaran, 2015). Reduction in magnetization showed the incidence of a significant magnetic film on the surface of the composite samples (Aydin et al., 2011). Although magnetic property decreased in nanocomposite, yet still the value of magnetization is still in the permitable range, which propose that they can be isolated appropriately by magnetic decantation technique (Ma, Guan & Liu, 2005).

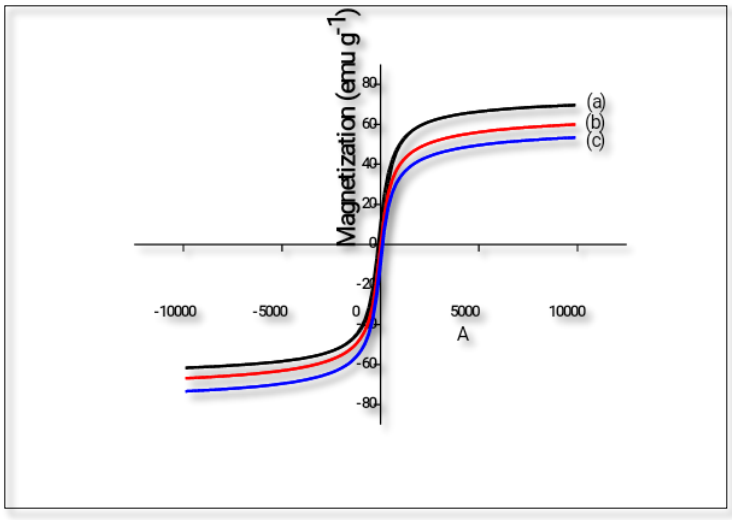


**Figure 5 Magnetic properties analysis of (a) Iron oxide nanoparticles, (b) MNP@PTh and (c) MNP@P3Th nanocomposites**

### 3.6 Extraction Studies

In concept, the interaction of phthalates with adsorbent is recognized on the its unlikelihood to water and pi-pi interactions (Moreno-Castilla, 2004). To validate that the structure design can affect the extraction of phthalates, iron oxide nanoparticles (MNP), MNP@PTh and MNP@P3Th, were verified. As shown in Figure 6, iron oxide produced low peak area for DBP, BBP and DNOP. Peak area of phthalates increased after the occurrences of polythiophene on the surface of iron oxide nanoparticles.

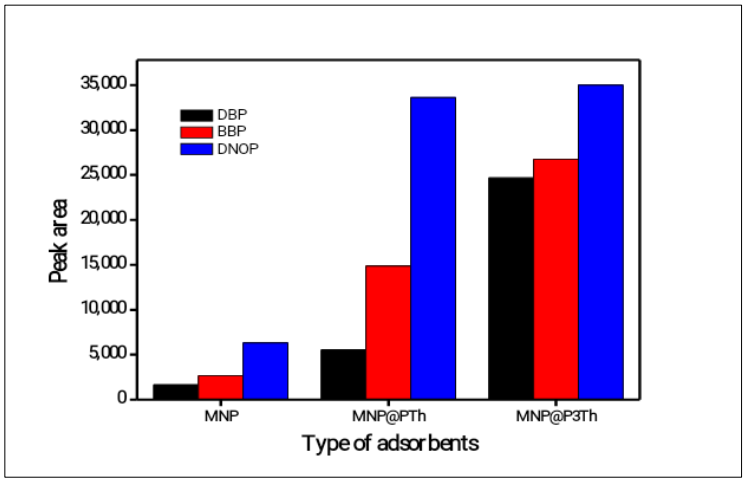


**Figure 6 Screening studies of phthalates with MNP, MNP@Pth and MNP@P3Th**

## 4.0 CONCLUSION AND FUTURE WORKS

Iron oxide nanoparticles, MNP@PTh and MNP@P3Th were effectively produced. The pysico-chemical properties of the samples were analyzed by FTIR, XRD, BET surface area, VSM and TEM. FT-IR results, discovered the presence of distinctive peaks of the polythiophene and poly-3-hexylthiophene. X-ray diffraction preserve crystalline phase in iron oxide nanoparticles after functionalized. TGA results demonstrated the breakdown of polymer coating happened in the 240 °C to 450 °C. Magnetization saturation by VSM showed magnetization of all nanocomposites lies in the satisfactory level, which ascertain that it can be secluded appropriately from a solution with an external magnetic field. Among nanocomposites, MNP@P3Th exhibited high BET surface area.

As for the future works, it is recommended to improve the extraction of phthalates in terms of pH, contact time, initial concentration, effect of eluent etc. Besides, it is also suggested to coat MNP with different type of conducting polymer for comparable results.

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