Removal of 2,4-dinitrophenol (2,4-DNP) by using magnetic nanoparticles (MNPs) coated with polypyrrole (PPy)

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Abstract. The research represented here is oriented towards developing a new approach to functionalise a surface of Magnetic Nanoparticles with Polypyrrole (MNPs-PPy). This development will then applied to remove 2,4 dinitrophenol (2,4-DNP) in aqueous solution. A various analytical technique such as Fourier Transform Infrared Spectroscopy (FTIR) analysis, Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) was employed for complete characterisation of MNPs-PPy. FT-IR spectra have shown the peak of Fe-O at 580 cm\(^{-1}\) while; the SEM images illustrated the globular structure of the surface of MNPs-PPy. Also, XRD result has shown the MNPs-PPy is in the crystalline form. The ultimate aims would then be the optimisation of the superlative condition of several parameters such as effect pH, temperature and concentration, contact time, amount of adsorbent, interfering ions and reusability for the removal of (2,4-DNP) in an aqueous solution by MNPs-PPy. The optimum conditions were observed at pH 6, 318 K, 10 ppm of analyte, 75 minutes and 50 mg of adsorbents which shown 98.67 % removal of analyte.

1. Introduction
According to the US Environmental Agency (EPA) and the European Union, phenol and its derivative become the main importance and apprehension which are comprised of their list of the aquatic environment. The manufactured of plastic, dyes, drugs, pesticides, antioxidants and paper in the petrochemical industries are created from the phenolic compound. The mutual disposal of all these above production products such as 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-
trichlorophenol (2,4,6-TCP) are formed in water sources. Thus, the removal of phenol groups is crucial compared to the determination in water samples [1].

Since the discovery of magnetic nanoparticles (MNPs), specifically iron oxides, it becomes one of the advantageous resources in various uses such as magnetic fluids catalysis and magnetic resonance imaging. MNPs have high surface area because it is in nano-sized particles. So, the adsorption size and performance is increasing [2].

Tahmasebi et al., [3] claim that polymer coating is another way to enhance the stability of the particles and permit the alteration of the useful surface for well-sensitivity and selectivity. One of the most explored coating polymers is Polypyrrole (PPy) that displays advantageous characteristics such as ability to coat on a unique element such as MNPs, simply prepared in liquid and solid medium whether chemical and electrochemical process, high porosity (quick ion exchange with circumstances), high electrical conductivity, good stability, harmless and inexpensive.

Therefore, preparation of MNPs functionalised with PPy will be synthesised to analyse its performance towards removal of 2,4-dinitrophenol in water samples with different pH, temperature and concentration, contact time, amount of adsorbents, the effect of interfering ions and its reusability.

2. Experimental

2.1. Materials.
All experiments were carried out in the air, and the products obtained appear indefinitely stable towards the atmosphere, whether in solution or the solid state. Reagents and solvents were used as received from commercial sources. Magnetic nanoparticles and 2,4-dinitrophenol that act as analyte was purchased from Bendosen company, Selangor. High purity solvent (99%) of hydrochloric acid, ethanol and acetonitrile was supplied by R&M, Shah Alam. Potassium PeroxydiSulfate (KPS) and pyrrole (99%) were bought from Merck, Shah Alam.

2.2. Characterization Technique.
Magnetic nanoparticle (MNP) and magnetic nanoparticle-Polypyrrole (MNPs-PPy) were analysed using the various analytical technique. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Phase identification of crystalline material was analysed using X-Ray Diffraction (XRD). The surface topography and composition of nanoparticles were obtained using Scanning Electron Microscopy (SEM) at high-resolution (80-200 kV), Ultra Violet Visible (UV-Vis) spectrophotometer analysis was conducted using PG-instrument T80/T80+ type equipped with 1 cm quartz cell.

2.3. Synthesis of magnetic nanoparticle coated with Polypyrrole (MNPs-PPy).
A solution of Potassium Peroxydisulfate (KPS) (5.0 g) in a hydrochloric acid solution (50 mL, 0.1 M) was treated with magnetic nanoparticles (1.25 g) in pyrrole (1ml, 0.01 mol). The solution was stirred continuously at 250 ppm for approximately 2h. The solution then was left for 24 hours. The resulting solid product was washed several times with ethanol, methanol and deionised water to remove any impurities [4] and dried in the oven for 24 hours at 45 °C. The dried product was transferred into a clean vial and kept in a desiccator and away from any external sources of the magnetic field.

2.4. Removal and Determination of Phenolic Compound.
MNPs-PPy were weighed (20 mg) in three separate glass vials. A stock solution of 2,4-dinitrophenol (10 mL of 10 ppm) was pipetted into the glass vials. The mixture was shaken for 75 minutes using at 250 rpm at room temperature. The supernatant solution was then filtered and transferred to the centrifuge tubes with the aid of an external magnet. The effect of varying different parameter pH (2-12), temperature (10 – 50 °C), concentration (10 – 100 ppm), amount of adsorbent (5 - 50 mg) and interfering ions were investigated. The reusability of the synthesised MNPs-PPy was used to measure the concentration of the analyte by using UV-Vis Spectrophotometer.
2.5. Effect of pH.
The concentration of analyte was adjusted using HCl (0.1 M) and of NaOH (0.1 M). The determination of phenolic compound was done by transferring the solution into the glass vials containing MNPs-PPy.

2.6. Effect of Temperature and Concentration.
Different concentration of analyte (10, 20, 40, 60, 80 and 100 ppm) was prepared and analyse at a different temperature (25, 35 and 45 °C).

2.7. Effect of Interfering Ions.
There could be some other ions present in the water sample that will interrupt the adsorption of phenolic compound towards the MNPs-PPy. Some of the interfering ions were Cl-, NO3- and SO42-. About 10 ppm of the analyte was added with 10% w/v of the Cl- solution. Next, determination of the phenol anion was continued. All the steps were repeated using NO3- and SO42- solution and its triplicate measurements.

2.8. Reusabilities.
The residue of the adsorbent was washed three times with deionized water and dried in the oven. Then, the overall steps were repeated more than three times to check for the adsorbent performance. The percentage of removal, removal percentage (% R) will be calculated.

3. Result and Discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR).
The spectrum in figure 1, shows both MNPs and MNPs-PPy shows peak at 580 cm\(^{-1}\) indicate the Fe-O bond while the peak at 772.58 cm\(^{-1}\) indicate the C-H out of plane ring deformation bond. C-H pyrrole in rings has observed in the spectrum at 1034.30 cm\(^{-1}\) and C-N stretching band was observed at 1314 cm\(^{-1}\). Both peak at 1537.20 cm\(^{-1}\) and 1451.70 cm\(^{-1}\) were assigned to the C-C asymmetric and symmetric stretching vibrations of pyrrole rings [5]. Most of the spectrum for MNPs-PPy indicated the peak for polypyrrole which indicates that the MNP has been successfully coated with polypyrrole.

![Figure 1. FTIR spectrum for (A) MNP and (B) MNPs-PPy](image)

3.2. X-Ray Diffraction (XRD)
The result obtained as in figure 2 for XRD diffractogram has proven that the MNPs-PPy was in crystal structure. This is due to the highest peak observed at 2θ=35° which indicated to the degree of
crystallinity of PPy. Therefore, the XRD results has shown that the amorphous PPy present on the surface of MNPs [6]. This is because the intensity of MNPs-PPy is lower than MNPs because the crystallinity of MNPs has been decreased due to the existing amorphous surface of PPy.

Figure 2. X-ray Diffraction (XRD) diffractogram of MNP and MNPs-PPy

3.3. Scanning Electron Microscopy (SEM)
Figure 3, the surface of the MNPs is not uniform. The results obtained for the MNPs-PPy has the smooth and uniform surface which has been proven that the PPy has successfully coated the MNPs surface. The MNPs-PPy also has a globular structure. The results was compared with the studies of Shanehsaz et al., [7] and Tahmasebi [3]. MNPs-PPy has the porosity surface so that it can absorb more analyte compared to MNPs that has less porosity surface.

Figure 3. Morphology structure of MNP and MNPs-PPy

3.4. Scanning Analyte
Ultraviolet Visible Spectrophotometer (UV-Vis) was used to check the $\lambda_{\text{max}}$ of the analyte which is 2,4-dinitrophenol (2,4-DNP). The highest absorbance for the 2,4-DNP is 360 nm. The value 360 nm was chosen due to the molar absorptivity of the analyte where it shows the highest peak at 360 nm as shown in figure 4.
3.5. Effect of pH
Based on the figure 5, the best PH results obtained for the removal of 2,4-dinitrophenol (2,4-DNP) was at PH 6 which is in an acidic medium. The percentage removal almost achieved 95 %. Studies from Shaneshaz et al., [7] states that in an acidic condition, the nanoparticles have a positive surface charge which can act one upon another with anion dye molecules. The positive charge density on the surface of adsorbent can be formed under lower PH. So, the adsorbent can attract more of the negative charged analyte and causing the removal efficiency is high. Meanwhile the adsorption process between adsorbent and analytes are affected by the PH of the solution.

3.6. Effect of Temperature and Concentration
Based on the figure 6, the results obtained for the effect of temperature and concentration, the best removal achieved at temperature 318.15 K and concentration of analyte is 10 ppm. The removal is done at the acidic condition which is at pH 4 at all temperatures. The results is backup by the studies from which states that higher temperature will increase the removal of 2,4-DNP because of better diffusion rate. So, it will increase the tendency for the analyte to be absorbed by the adsorbent. Moreover, as the temperature higher, the adsorbent may increase its number of active surface centre for the absorption process.
Figure 6. Removal percentage of 2,4-DNP based on Concentration and Temperature

3.7 Contact in Time

Figure 7 shows the effect of contact time on the removal of 2,4-DNP by the MNPs-PPy. The MNPs-PPy showed high percentage removal (95.77%) at 75th minutes. After 75 minutes, the percentage remained around 95%. The increasing of contact time until 2 hours give the result of removal percentage analyte reached 93.1% up until 95.6% which it has reached equilibrium. When the contact time is extend after 2 hours, the percentage of removal is remained because there is no available adsorption site on the MNPs-PPy surface [8].

Figure 7. Removal percentage of 2,4-DNP based on Contact Time

3.8. Effect on amount of adsorbent

Based on the figure 8, the best amount of adsorbent to remove 10 ppm of 2,4-DNP is 50 mg with the percentage removal is 98.67% at 318.15 K and 75 minutes. Shahneshaz et al., [7] stated in their studies that as the amount of adsorbent increase, the surface area also increase and there will be more adsorption surface exists to absorb the analyte.

Figure 8. Removal percentage of 2,4-DNP based on Contact Time
3.9. Effect of Interfering Ions

From the result obtained on figure 9, it shows that the addition of salt will decrease the percentage removal of 2,4-DNP in the presence of respective interfering ions when the %w/v of ions increase, the removal efficiency also decrease. The ions that had been investigated were from salt which were Cl\(^-\) from NaCl, NO\(_3\)\(^-\) from KNO\(_3\) and SO\(_4\)\(^2-\) from Na\(_2\)SO\(_4\). This condition can be described as the salting out effect where the addition of salt may change the physical properties of the analyte, reduce the diffusion rates of analytes towards the adsorbent and thus decrease the removal ability [9]. Besides, studies from Thavanugul [10] stated that when the concentration of ionic strength increases, the solubility of analyte decreased. This is due to the increasing viscosity of the solution. Therefore, diffusion rate of analyte towards the adsorbent decreases and hence, the removal efficiency also decrease.

3.10 Reusability

Based on the figure 10, it shows that the more the adsorbent is used, the efficiency of the adsorbent will decrease. The MNPs-PPy can be used up until 5 times only. The more it reused, the lower its efficiency. The reusability of adsorbent becomes less efficient because the surface area has been reduced due to the surface alteration of the adsorbent until the fifth times.

![Figure 9. Removal percentage of 2,4-DNP based on amount of Adsorbent.](image)

![Figure 10. Removal percentage of 2,4-DNP by the effect of Interfering Ions](image)

4. Conclusions

As a conclusion, the magnetic nanoparticles coated with polypyrrole was successfully removed the 2,4-Dinitrophenol (2,4-DNP) by using several parameters. The best condition for the 2,4-DNP to be remove by MNPs-PPy were at pH 6, temperature at 318.15 K and concentration at 10 ppm, 75 minutes for the time removal and 50 mg amount of adsorbent. The MNPs-PPy can be used five times only. FTIR spectrum has proved that the MNP has been successfully coated with polypyrrole where the major peak for Fe-O bond at 580 cm\(^{-1}\). The XRD result had shown the MNPs-PPy was in crystal form where the highest peak exist at \(2\theta=35^\circ\). The MNPs-PPy has globular structure which has been proven by using SEM.

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References

[1] Amirah Ahmad, Mohd Hasmizam Razali, Mazidah Mamat, Faizatul Shimal Binti Mehamod and Khairul Anuar Mat Amin (2017). Adsorption of methyl orange by synthesized and functionalized-CNTswith 3-aminopropyltriethoxysilane loaded TiO2 nanocomposites. Chemosphere. Volume 168, 474 – 482.

[2] Baharin, S. N. A., Muhamad Sarih, N., Mohamad, S., Shahabuddin, S., Sulaiman, K., and Ma’Amor, A. (2016). Removal of endocrine disruptor di-(2-ethylhexyl) phthalate by
modified polythiophene-coated magnetic nanoparticles: Characterization, adsorption isotherm, kinetic study, thermodynamics. RSC Advances, 6(50), 44655–44667.

[3] Tahmasebi, E., Yamini, Y., Seidi, S., and Rezazadeh, M. (2013). Extraction of three nitrophenols using polypyrrole-coated magnetic nanoparticles based on anion exchange process. Journal of Chromatography A, 1314, 15–23.

[4] Muliwa, A. M., Leswiff, T. Y., Onyango, M. S., and Maity, A. (2016). Magnetic adsorption separation (MAS) process: An alternative method of extracting Cr (VI) from aqueous solution using polypyrrole coated Fe₃O₄ nanocomposites. Separation and Purification Technology, 158, 250–258.

[5] Bagher, M., Yamini, Y., Dayeni, M., and Seidi, S. (2015). Journal of Environmental Chemical Engineering Adsorptive removal of alizarin red-S and alizarin yellow GG from aqueous solutions using polypyrrole-coated magnetic nanoparticles. Biochemical Pharmacology, 3(1), 529–540.

[6] Jiao, Z., Zhang, Y., and Fan, H. (2016). Ultrasonic-microwave method in preparation of polypyrrole-coated magnetic particles for vitamin D extraction in milk. Journal of Chromatography A, 1457, 7–13.

[7] Shanehsaz, M., Mohammad, S., Shoja, R., and Poursaberi, T. (2016). Removal of Reactive Red195 Synthetic Textile Dye using Polypyrrole-coated Magnetic Nanoparticles as an Efficient Adsorbent, 96, 85–96.

[8] Fan, L., Wei, C., Xu, Q., and Xu, J. (2017). Polypyrrole-coated cotton fabrics used for removal of methylene blue from aqueous solution, 5000(March).

[9] Ebrahimpour, B., Yamini, Y., Seidi, S., and Tajik, M. (2015). Analytica Chimica Acta Nano polypyrrole-coated magnetic solid phase extraction followed by dispersive liquid phase microextraction for trace determination of megestrol acetate and levonorgestrel. Analytica Chimica Acta.

[10] Thavarungkul, P. (n.d.). Polypyrrole / silica / magnetite nanoparticles as a sorbent for the extraction of sulfonamides from water samples.