Fabrication of magnetic nanoparticles coated with polyaniline for removal of 2, 4-dinitrophenol

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Abstract. Magnetic nanoparticles (MNPs) coated polyaniline (PANI) was successfully synthesized and further used for removal of 2, 4-dinitrophenol. The presence of PANI coatings on the surface of MNPs was confirmed by using Fourier Transform Infrared (FT-IR) Spectroscopy and X-ray Diffractometry (XRD) analysis. MNPs coated PANI (MNPs/PANI) showed higher capabilities to remove 2,4-dinitrophenol (2,4-DNP) via spectrophotometry at 358 nm by using Ultraviolet Visible (UV-Vis) Spectrophotometer. Different parameters such as pH, contact time, initial concentration and temperature, amount of adsorbent, interfering ions were investigated to optimize the performance of MNPs/PANI in removal of 2,4-DNP. In addition, the reusability of MNPs/PANI was also studied to add up its economic value. The best performance of MNPs/PANI to remove 2,4-DNP molecules was found at pH 7, 105 minutes contact time, 10 ppm initial concentration of 2,4-DNP with 298.15 K temperature and 10 mg of adsorbent amount. The removal percentage (%R) of 2,4-DNP was still up to 90% in the presence of chloride (Cl-) ions, nitrate (NO3-) ions and sulfate (SO42-) ions. Lastly MNPs/PANI was used up to five cycles.

1. Introduction

'Phenolic' or 'polyphenol' can be defined as a substance that possesses an aromatic ring with one or more hydroxyl substituents, or other functional derivatives like methyl ethers, esters, glycosides and etc. [1]. Some of phenolic compounds, were naturally occurring and some of them were widely manufactured and accidentally distributed into the environment. Crawford et al., [2] stated that phenols were abundantly found in different daily products including throat lozenges, mouthwashes and antiseptic lotions. Shukla et al., [3] stated in their studies that nitrophenols is one of the phenolic compounds that were recognized as industrial effluents, especially in agricultural and urban waste.
One of the most important dinitrophenyls forms is 2, 4-Dinitrophenol (2, 4-DNP). It was found to be the most hazardous compound to the environment as well as human health. Bagal et al., [4] also reported in their studies that nitrophenols and its related compounds are released from the effluent of mine processing facilities, pesticide application, metal finishing plants, dye manufacturing plants and refineries to the environment. As a result, nitrophenols were abundantly found as pollutants in groundwater, rivers, wastewaters, soil, and in the atmosphere. The accidental consumption of nitrophenols can cause adverse effects such as serious gastrointestinal damage, muscle tremors, walking difficulties and death in animals. The accumulation of phenolic compounds in plants and fish tissues can cause an awful smell and rotten flavor [2].

The treatment of these types of industrial effluents is a challenging topic in environmental science, as the importance of controlling water pollution has become a focus in recent years [5]. The most common methods that have been used in removal of phenolic compounds in water samples includes adsorption by using different adsorbents, membrane separation process, oxidation as well as ozonation [6]. Since adsorption is cost effective and the easiest process, it has been widely used for organic and inorganic micro pollutants removal from the aqueous environment [7]. Certain types of pollutants from the waste water can be removed via these adsorption techniques include dyes, metallic compounds and other toxic compounds.

MNPs were chosen as adsorbate because of its wide availability and unique properties such as large surface area; which is suitable for separation of analytes in larger volume. These MNPs react rapidly in applied magnetic fields at negligible residual magnetism and coercivity, due to their large constant magnetic moment [8]. In addition, polyaniline (PANI) was used to enhance the adsorption properties of MNPs. These type of surface modification is possible and crucial when the surface of MNPs were coated as it provides selectivity to target analytes and improves nanoparticles stability [9]. PANI is much preferred among the conducting polymers due to the ease of synthesis, enhanced conductivity and various color changes depending on its oxidation levels and suitable for making composites with different types of binders [10].

2. Experimental

2.1 Materials
All reagents in this experiment were analytical reagents and were used as supplied. The commercial magnetic nanoparticles were bought from Bendosen Company in Selangor and the analyte, which is 2, 4-dinitrophenol was supplied from AMDI Bertam, Penang. The reagents such as acetonitrile, hydrochloric acid, methanol, ethanol and diethyl ether which have about > 99% of purity, were bought from R&M Chemicals Sdn. Bhd in Shah Alam. Lastly the aniline (99%) and Potassium Peroxydisulfate, KPS was purchased from Merck Sdn Bhd, Malaysia.

2.2 Synthesis of Magnetic nanoparticles coated with Polyaniline (MNPs/PANI)
A 5 g of potassium peroxydisulfate (KPS) was dissolved in 50 ml of 0.1M of hydrochloric acid. The mixture was stirred until a clear solution obtained. Meanwhile in a 250 ml conical flask, about 1 ml of 0.011mol of aniline was added along with 1.25 g of purchased MNPs. The mixture of KPS and HCl was slowly added into the conical flask and continuously stirred at 250 rpm for 2 hours. The mixture was left for 24 hours. The product was filtered washed with ethanol, methanol and deionized water. Next, the product was dried at 45°C for 24 hours. Then the product was sieved and transferred into a glass vial and kept in the desiccator.

2.3 Characterization
The infrared (IR) absorption measurements were done by Fourier Transform Infrared (FTIR) spectrometer model Perkin--Elmer RX1 and the spectra were recorded in range of 400-4000 cm⁻¹. Besides that, XRD analysis was also run to study the crystallographic structures of MNPs and synthesized MNPs/PANI by using X-Ray Diffractometer PANalytical X’Pert Pro MPD System. Lastly, UV-Vis spectrophotometer
with PG-instrument T80/T80+ type equipped with 1 cm quartz cell was used in scanning of wavelength and quantitative analysis of 2,4-DNP.

2.4 Removal and Determination procedures
For removal and determination procedures; in each experiment 10 mg of the synthesized MNPs/PANI was weighed and put together with 10 ppm of 2,4-DNP stock solution into tightly sealed glass vials. After that, the solutions were shaken by using water bath shaker which was set at 250 rpm at room temperature for 120 minutes. Next, the supernatant solution was filtered and transferred into centrifuge tubes with the aid of external magnet. The concentration of the obtained solution was measured by UV-Vis spectrophotometer with PG-instrument T80/T80+ type equipped with 1 cm quartz cells at 358 nm. The percentage of removal, %R will be calculated for each time of removal and determination of nitrophenol anions by using equation (1)

\[
\%R = \frac{C_o - C_e}{C_o} \times 100\% 
\]

Where
\( C_o = \) Initial concentration of analytes (ppm)
\( C_e = \) Final concentration of analytes (ppm)

Optimizations were done on pH, initial concentration and temperature, contact time, amount of adsorbent, effect of interfering ions and reusability.

2.5 Effect of pH
The pH values that were studied in this experiment included pH 3, pH 5, pH 7, pH 9 and pH 11. A stock solution of 0.1M HCl and 0.1M NaOH were prepared to adjust the pH values throughout this experiment. The overall steps were repeated with triplicate measurements for each pH.

2.6 Effect of Contact Time
The effect of contact time studied in this experiment was in the range of 5 - 120 min. About 10 mg of MNPs/PANI with 10 ppm concentration, fixed at pH 7, was transferred in the glass vials. Time for shaking in the water bath shaker was varied at room temperature.

2.7 Effect of Initial Concentration and Temperature
The different temperature, which is 298.15 K, 318.15 and 338.15 K were studied with a range concentration of 2, 4- DNP (10-100 ppm), at fixed pH 7 for 75 minutes.

2.8 Effect of amount of adsorbent (MNPs/PANI)
Different amounts of adsorbents (5 – 60 mg) were used in this study at 10 ppm of 2, 4- DNP, at 25°C and pH 7 were maintained [11]. The solution then was shaken for 75 minutes.

2.9 Effect of interfering ions
The interfering ions that were studied in this experiment includes chloride ions (Cl\(^-\)), sulfate ions (SO\(_4^{2-}\)) and nitrate ions (NO\(_3^-\)). Since industrial water mainly consist of these types of ions, the effect of presence of these ions on the removal efficiency of 2, 4- DNP solutions were studied. About 10% to 50% w/v of solutions consisting of these ions were prepared. The prepared solutions then were added along with 10mg MNPs-PANI, 10ppm of 2, 4-DNP at pH 7. The selectivity of MNPs/PANI towards 2, 4-DNP was studied by using UV-Vis Analysis as well.

2.10 Reusability
The ability of regenerating the synthesized MNPs/PANI was studied so that it can be reused for the adsorption process. MNPs/PANI were desorbed first with 5 ml methanol before they were washed with
deionized water and dried in the oven for 12 hours. The overall steps in removal and determination of 2, 4-DNP was repeated for more than three times [5].

3. Result and Discussion

3.1 Characterization

FTIR spectra of MNPs and MNPs/PANI were shown in Figure 1. By referring to Figure 1 both MNPs and MNPs/PANI have similar frequencies at 570 cm$^{-1}$ and 1230 cm$^{-1}$. The sharp peak at 570 cm$^{-1}$ represent the characteristics of Fe–O bond absorption which confirms the presence of magnetic core in both MNPs and MNPs/PANI [12]. However, peak of MNPs is quite broad due to the purity of the commercial MNPs used compared to the coated MNPs.

Meanwhile the appearance of C-O peaks at 1230 cm$^{-1}$ for both MNPs and MNPs/PANI represent the impurities during analysis. The peaks at 1500 cm$^{-1}$ and 1700 cm$^{-1}$ are related to N-H bending and C=C stretching vibration of the quinoid ring and benzenoid ring of pure PANI respectively. In addition, there were also stretching of C-N bonds at 1230 cm$^{-1}$ and 1270 cm$^{-1}$ for secondary aromatic amine and quinoid ring. Both peaks have confirmed that MNPs were successfully coated with PANI which is similar to the studies by Yu et al., [13]. Tahmasebi et al., [9] also stated in their studies that in the spectrum of MNPs/PANI, there was also a peak that appears at 2900 cm$^{-1}$ due to stretching and bending vibrations of C-H bonds. The peak at 800 cm$^{-1}$ was assigned as out-of-plane bending vibration of C-H in benzene ring of PANI [13].

![Figure 1. FTIR spectra of MNPs and MNPs/PANI](image)

Further evidence for the formation of MNPs/PANI was studied by conducting XRD analysis (Fig. 2). The analysis was carried out to determine the nanocrystalline structure of both MNPs and MNPs/PANI. There were characteristic peaks at 2 values of 35.2°, 41.42°, 50.65° and 63.33° for MNPs; and with marked indices respectively as (220), (311), (400), and (422).The respected values were in a good agreement with the previous study conducted by Mahto and co-workers [10].
3.2 Effect of pH
By referring to Figure 3, the adsorption performance of MNPs/PANI was greatly varied according to the pH values. This was related to the electrostatic interaction exist between MNPs/PANI with nitrophenol anions in its natural acidic form. At higher pH, nitrophenols anions exist in deprotonated forms, therefore there were competition between these anions and hydroxides anions (OH⁻) adsorbed onto the positively charged MNPs/PANI surfaces. Meanwhile, at lower pH values, nitrophenol anions exist in protonated forms. These anions will likely to form hydrogen bonding with the hydrogen ions (H⁺) present in the acidic medium rather than adsorbed onto the MNPs/PANI surfaces. Since pH 7 was found to have the highest percentage of removal, pH 7 was selected as the optimum pH to proceed with the next parameters.

![Figure 3](image)

**Figure 3.** Effect of pH on the percentage of removal, R% (condition: amount of adsorbent: 10 mg; initial concentration: 10 ppm; temperature: 298.15 K)

3.3 Effect of contact time
The effect of contact time was studied in this experiment to determine the optimum time for MNPs/PANI to remove 2,4-DNP. This study of contact time was set between 5 to 105 minutes. Based on Figure 4, as soon as the experiment was started, there was already an increase in percentage of removal of 2,4-DNP. The drastic increase in percentage occurs due to the high number of adsorption sites that available on MNPs/PANI surfaces for 2,4-DNP molecules to be adsorb. However, after 75 minutes, there was a decrease in percentage of removal as it has achieved its equilibrium time, that means 2,4-DNP molecules were completely adsorbed onto the available sites of MNPs/PANI surfaces.
3.4 Effect of Initial Concentration and Temperature

Different initial concentration ranging from 5 to 80 ppm and three different temperatures (298.15 K, 318.15 K, 338.15 K) were studied in this study to select the optimum initial concentration and temperature for MNPs/PANI to remove 2,4-DNP. The effect of initial concentration was investigated to fully utilize the adsorption sites found on MNPs/PANI during adsorption of 2,4-DNP [15]. In Figure 5, 10 ppm of 2,4-DNP at 298.15 K shows the highest percentage of removal, R%. It is very important to identify the point as it will determine the mass transfer resistance between the aqueous phases of 2,4-DNP molecules and solid phases of MNPs/PANI [7].

In addition, the decreasing pattern of %R at three different temperatures suggests that the adsorption is an exothermic process. Haj-kacem et al., [16] found that temperature affects the viscosity properties of fluids. When temperature increases, the viscosity of the solution decreases then stimulates the diffusion process [10]. For instance, in Fig. 5, 10 ppm of 2,4-DNP at 338.15 K shows a sharp decline on percentage of removal, R% as the viscosity of 2,4-DNP at this temperature has been lowered which then lead these molecules to diffuse out rather than adsorbed onto MNPs/PANI surfaces. Bazrafshan et al., [7] also added that the adsorptive forces between 2,4-DNP molecules and the active sites on MNPs/PANI surface weakened at high temperature as well as its adsorption efficiency.

3.5 Effect of adsorbent amount

Different amount of adsorbent, which is MNPs/PANI from 0.005 g to 0.05 g were used in this study to select the optimum dosage of adsorbent to remove 2,4-DNP molecules whilst the other condition were fixed. From Figure 6, by increasing the amount of adsorbent, the percentage of removal also increase up to 0.010 g of MNPs/PANI. However, the percentage of removal shows a decline but remain constant from 0.020 g to 0.050 g. This pattern of graph clearly indicates that the availability of adsorption sites of
MNPs/PANI were fully utilized. Only 0.010 g of MNPs/PANI was needed to remove 10 ppm of 2, 4-DNP which increases its economic value [17].

**Figure 6.** Effect amount of adsorbent on percentage of removal, R% (condition: pH: 7; contact time: 75 minutes; initial concentration: 10 ppm; temperature: 298.15 K)

**3.6 Effect of Interfering ions**

Effect of interfering ions was studied to determine the selectivity of MNPs/PANI in the presence of common interfering species. The interfering ions that were selected in this study include Cl⁻ ions, NO₃⁻ ions and SO₄²⁻ ions. By referring to Figure 7, addition of different concentration of Cl⁻ ions, NO₃⁻ ions and SO₄²⁻ ions show a decreased pattern in percentage removal of 2,4-DNP for the first addition at 10% w/v of these ions respectively. However, further addition of the concentration of these ions shows only a little effect because the synthesized MNPs/PANI does not selectively adsorb Cl⁻ ions, NO₃⁻ ions and SO₄²⁻ ions. The SO₄²⁻ ions were the least ions that give effect on removal of 2,4-DNP as it possess larger steric effect compared to Cl⁻ and NO₃⁻ ions. This small portion of interfering ions might compete with 2,4-DNP anions to bind onto the surface of MNPs/PANI.

**Figure 7.** Effect on the percentage of removal, R% of 2,4-DNP in the presence of Cl⁻, NO₃⁻ and SO₄²⁻ ions (condition: pH:7; contact time: 75 minutes; initial concentration: 10 ppm; temperature: 298.15 K)

**3.7 Reusabilities**

The reusability test was conducted to investigate the probability of reusing and regenerating the adsorbent, MNPs/PANI. In Figure 8, the adsorbent was still active in removing 2, 4-DNP molecules after five repeated experiments, even though a slight decrease in percentage of removal was observed. The decreasing pattern occurred as some of the particles in the adsorbent has accumulated because of the heat treatment applied that decreases its surface area after several cycles [17].
4. Conclusion

In this study, MNPs/PANI was successfully synthesized to remove 2,4-DNP. MNPs/PANI was characterized by using FT-IR spectroscopy and X-Ray Diffractometry analysis. The synthesized MNPs/PANI was found to achieve its optimum condition at; pH 7; contact time about 75 minutes; room temperature with 10 ppm initial concentration; 10 mg of MNPs/PANI. In addition, MNPs/PANI showed excellent selectivity towards 2,4-DNP molecules in the presence of Cl\textsuperscript{-} ions, SO\textsubscript{4}\textsuperscript{2-} ions and NO\textsubscript{3}\textsuperscript{-} ions. MNPs/PANI can be used and recycled up to five times by maintaining its percentage removal of 2,4-DNP about 82.64%.

Acknowledgement

The authors would like to thank UiTM Cawangan Negeri Sembilan for the financial support to attend ICFAS2018.

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