Removal study of Cu(II), Fe(II) and Ni(II) ions from wastewater using polymer-coated cobalt ferrite (CoFe$_2$O$_4$) magnetic nanoparticles adsorbent

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Abstract. Nowadays, heavy metal pollution has become one of the most serious environmental problems. The magnetic nanoparticles (MNPs) have received great attention to solving the problems as adsorbent materials due to their unique physical and chemical properties. CoFe$_2$O$_4$ MNPs was prepared by co-precipitation method, and its application for removal of Cu(II), Fe(II) and Ni(II) ions from wastewater. The various structural as well as morphological properties were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM) analysis. Factor of affecting adsorption including temperature, contact time, particles size, magnetic properties and additional Polyethylene glycol (PEG-4000) as coating agent of adsorbent were further investigated. The results show that maximum Fe(II) was adsorbed at all of various parameters. Adsorption process of heavy metal ions from wastewater was known as increase as temperature range from RT to 60°C, but decrease at 120°C for Cu(II) and Ni(II). The maximum adsorption of Cu(II) and Ni(II) also occurs at the smallest particle size, 4nm. On the other hand, percentage of removing metal ions using PEG-coated MNPs decrease comparing to Co-MNPs without coating, for Cu(II), Fe(II), and Ni(II) is 97.1%, 100%, and 99.6%, respectively. The ability of Co-MNPs for removing metal ions decrease after coated using PEG-4000 maybe due to the small surface area and existence of polymer as nonmagnetic. Furthermore, the result of this experiment revealed that CoFe$_2$O$_4$ MNPs can be used as the effective adsorbent to remove metal ions in the wastewater.

1. Introduction
The presence of heavy metals as contaminant in our environment poses a serious problem due to human activity. Among these heavy metals are such as Hg [1], Pb[1-3,22], Cu and Zn [3-5], Cr [6], Sr[2], As [7], and Ni [4] which were released into the environment, and are now becoming a worldwide concern due to its toxic and bioaccumulation. In order to solve the problems, many experimental techniques have been applied to remove the contaminant as the colour, odour, organic and inorganic pollutant. There are several methods which have been developed such as ion
exchange[4], nanofiltration [8], solvent extraction, electrowinning, electrocoagulation and adsorption method [3,5]. Compared with the other methods, the adsorption method is highly efficient, easy in application and is inexpensive [3].

Adsorption method depend on the ability of the surface of adsorbent to adsorb contaminants. The commonly employed adsorbents used for heavy metal removal are graphene oxide [2,9], active carbon [10], Chitosan modified [11], magnetite [12], etc. More recently, much attention has been paid to nanoparticles adsorbent, such as Fe₂O₃, MnFe₂O₄, etc., due to their basic properties, extremely small size, high surface area to volume ratio, and unique morphology, which provide better kinetics for the adsorption of metal ions from wastewater [13].

The one of magnetic nanoadsorbent which has attracted attention is a ferrite which chemical formula is MeFe₂O₄ (Me = Co, Ni, Zn, Mg, etc.). Among ferrites, CoFe₂O₄ is an interesting magnetic material due to its moderate saturation magnetization, excellent chemical stability, and mechanical hardness [14]. Compared with the other ferrites of the same size, cobalt ferrite exhibits better magnetic response [15]. In order to further improve the dispersion of nanoparticles as well as to prevent their agglomeration, polyethylene glycol (PEG) is widely used as the coating agent. In addition to these applications, PEG can also support magnetic nanoparticles due to its pore forming ability and its hydrophilic characteristic which can improve the adsorption capacity rate [16].

In this study, CoFe₂O₄ magnetic adsorbent are used for Cu(II), Fe(II) and Ni(II) metal ions removal. We focus on various study under control parameters such as temperature, contact time, particles size, magnetic properties, and modification of CoFe₂O₄ using PEG as a coating agent.

2. Material and methods

2.1. Preparation of magnetic nanoparticles CoFe₂O₄

CoFe₂O₄ nanoparticles were prepared by the co-precipitation of an aqueous solution of FeCl₂·6H₂O (2 mol; 14.35 mL) and CoCl₂·6H₂O (1mol; 7.9 mL). The mixture of the solution is then dispersed into a NaOH solution drop by drop at a temperature of 80°C. The solution is stirred with a 450 rpm stirring speed for 3 hours. The synthesized materials were rinsed and repeated for ten times to remove salt and impurities particles. In producing nanoscale, subsequent furnace at 80°C for 4 h was needed.

2.2. Characterization

The characterization of magnetic nanoparticles was carried out using the X-ray diffraction (XRD) (Shimadzu model XD-3H) method for crystal identification. The instrument was equipped with a copper anode generating Cu-Kα radiation (λ = 1.5406 Å). A bright field TEM apparatus (JEOL JEM-1400) was used for size investigation and morphology of magnetic nanoparticles and the VSM method (Riken Denshi Co., Ltd) was used for magnetic behavior analysis.

2.3. Adsorption studies Batch

A batch of experiments have been conducted to examine heavy metal removal from artificial wastewater by CoFe₂O₄. The process of making artificial waste using basic materials CuSO₄·5H₂O, FeSO₄·H₂O, and NiSO₄·6H₂O, respectively, in which 1.5 grams of material is dissolved in 1000mL of distilled water. The solution was stirred by a magnetic stirrer (room temperature) for 4 hours and then HCl (chloride acid) was added drop wise into the solution for as many as 20 drops.

The adsorption process in wastewater is carried out with the mixture 0.4 g of CoFe₂O₄ in 80 mL waste water solution, blended thoroughly using a magnetic stirrer. NH₄OH added to the solution in order to control the pH level of the solution at level 9. The mixture solution is then shaken for 3 hours at room temperature. The solution was separated with the pollutant subsequent filtering. The authors then carried out similar process for various parameters, such as temperature (room temperature, 60, 90, 120)°C, contact time (60, 180, 300) min, particles size (4, 8, 9, 10) nm, magnetic properties (8,18, 37) emu/g and adding polymer PEG-4000 (polyethylene glycol) as coating agent with mass ratio 1 : 1.
The amount of adsorbed Cu(II), Fe(II) and Ni(II) ions was calculated according to the following equations:

\[
\text{metal ion removal efficiency } Re = \left(\frac{C_0 - C_f}{C_0}\right) \times 100\% (0.1)
\]

where \(C_0\) and \(C_f\) are the initial and the final concentration of Cu(II)/Fe(II)/Ni(II) ions in the solutions, respectively.

3. Result and discussion

3.1. Characterization of magnetic nanoparticles

The XRD spectra of CoFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\)+PEG-4000 are shown in figure 1, and CoFe\(_2\)O\(_4\) sample for various particles are shown in figure 2. It indicates that the CoFe\(_2\)O\(_4\) phase has been formed in the sample. The indication is based upon the main reflection peak (311) which appears at the 2θ diffraction angle of 35.379\(^\circ\), which is consistent with the typical characteristic of CoFe\(_2\)O\(_4\). The other reflection peaks (220), (400), (511) and (440) for CoFe\(_2\)O\(_4\) (JCPDS 22-1086) are also clearly observed. The obtained lattice parameter is (8.408±0.040 Å). This result is close to the literature value for the lattice bulk of CoFe\(_2\)O\(_4\) (8.395±0.005 Å) [17]. The addition of PEG as coating agent into CoFe\(_2\)O\(_4\) samples has resulted in the formation of impurities; α-Fe\(_2\)O\(_3\) (hematite), α–FeO(OH), and γ-FeO(OH). The particles size values were obtained by using the Scherrer formula 8.8 nm for CoFe\(_2\)O\(_4\) and 10.6 nm CoFe\(_2\)O\(_4\)+PEG-4000, respectively.

\[\text{Figure 1. XRD spectrum; (a) CoFe}_2\text{O}_4, \quad \text{(b)CoFe}_2\text{O}_4+\text{PEG-4000}}\]

\[\text{Figure 2. XRD spectrum of CoFe}_2\text{O}_4 \text{ at various particles size; (a) 10 nm, (b) 9 nm, (c) 8nm and (d) 4nm.}\]

The TEM images of the prepared CoFe\(_2\)O\(_4\) particles were obtained as shown in figure 3(a). CoFe\(_2\)O\(_4\) surface morphology analysis showed the agglomeration of many ultrafine particles with a diameter of
about 8.4 nm. This is consistent with Scherrer analysis on the XRD diagram, which is about 8.8 nm. The pattern of dash ring showed the diffraction of particles samples and the Miller indices that could be identified were (220), (311), (400), (511), and (440).

![Figure 3](image_url) The result of TEM analysis of sample (a) CoFe₂O₄ and (b) CoFe₂O₄ coated by PEG-4000

![Figure 4](image_url) Magnetic moment vs. applied magnetic field for various sample of CoFe₂O₄ adsorbent.

CoFe₂O₄+PEG sample has spherical form and is homogeneous as shown in figure 3(b). The particle size after PEG coating is larger than that of pure CoFe₂O₄. Miller indices from this sample can be identified as (111), (220), (311), (400), (511), and (440). The particles size distribution obtained from TEM analysis is around 10nm.

It is known that magnetic particles which less than 30 nm diameter size will exhibit superparamagnetism[6]. Therefore, in this experimental work, the authors would like to claim that the CoFe₂O₄ sample has superparamagnetic properties. It has been verified by the magnetization curve measured by VSM method, as shown in figure 4. The magnetic samples are expected to respond well to the magnetic field without any permanent magnetization.

3.2. Adsorption Studies

3.2.1. Effect of temperature

To investigate the effect of temperature on the adsorption capacity, the experiment was carried out for initial metal uptake concentration of 5 g/L at four different temperature of 30°C, 60°C, 90°C and 120°C, respectively. It has been observed that for the increasing temperature, the percentage of metal uptake would decrease. It arises due to the weakness of bonding energy between the adsorbent and pollutant [18].

Table 1 shows the adsorption of Fe(II) maximum, below 0.02 ppm (limit detection). In this case, temperature did not have any significant effect on the adsorption. The sorption of Ni(II) increases proportional to the increasing temperature. On the other hand, the sorption of Cu(II) reaches a maximum at 60°C, and decreases at 120°C. The decreases of metal uptake due to binding of Cu(II) and adsorbent have desorption at the temperature [19].
Table 1. The effect of temperature on removal efficiency.

| Parameter | Raw material | Removal efficiency | Temperature (°C) |
|-----------|--------------|---------------------|------------------|
|           |              |                     | 30              | 60      | 90   | 120  |
| Cu        | 292.144 (ppm)| 2.73                | 0.87            | 1.19           | 6.17          |
|           |              | (%) 99.07           | 99.70           | 99.59           | 98.28          |
| Fe        | 306.240 (ppm)| no detection        | no detection    | no detection    | no detection   |
|           |              | (%) 100             | 100             | 100             | 100            |
| Ni        | 358.940 (ppm)| 0.34                | 0.23            | 0.19            | 2.45           |
|           |              | (%) 99.91           | 99.94           | 99.95           | 99.34          |

Table 2. The effect of contact time on removal efficiency.

| Parameter | Raw material | Removal efficiency | Contact time (min) |
|-----------|--------------|---------------------|--------------------|
|           |              |                     | 60                | 180         | 300  |
| Cu        | 292.144 (ppm)| 1.64                | 2.73              | 1.30         |
|           |              | (%) 99.44           | 99.07             | 99.55        |
| Fe        | 306.240 (ppm)| no detection        | no detection      | no detection |
|           |              | (%) 100             | 100               | 100          |
| Ni        | 358.940 (ppm)| 2.13                | 0.34              | 0.52         |
|           |              | (%) 99.41           | 99.91             | 99.85        |

The adsorption by the system is of the physics adsorption typeso the temperature is a major contributor to the major effect on exothermic process of pollutants. The adsorption occurs due to the Van der Waals interaction at the exothermic condition.Van der Waals interaction is the weak interaction between molecules and it releases low energy. It means that at low temperatures, molecules could attract adsorbents. The increase in temperature will affect an increase in the energy and ionic reactivity. As with this increase, ions will be enabled to overcome the energy barrier and to chemically interact with the active sites on the surface. Since the ionic reactivity increases, then the number of diffusing ions at the adsorbent surface also increases. Therefore, ions will be adsorbed more at the surface; and as one could see, the metal Cu(II) removal increases as the temperature increases, from 30°C to 60°C. Equilibrium temperature occurs at 60°C. Above that, ionic reactivity could break the other bond, however due to a very weak Van der Waals interaction,a desorption might occur instead.

3.2.2. Effect of contact time

Contact time is another factor in batch adsorption process. In order to establish an equilibration time for the maximum uptake, the adsorption of heavy metal was studied as a function of contact time. For this purpose 0.4 g of CoFe₂O₄ in 80 mL of wastewater was shaken for a period of 60-, 180- and 300 minutes. Table 2 shows the variation of the removal efficiency of the Cu(II), Fe(II) and Ni(II). The adsorption rate was very fast and adsorption was achieved by Fe(II) within 60 minutes. On the other hand, removal of Cu(II) decreased at the 180 minutes time, and increased when the contact time ran into 300 minutes. The decrease in the of Cu(II) removal is caused by a desorption process. The desorption process occurs at weak interaction between Cu(II) ions and CoFe₂O₄ adsorbent. Reverse phenomenon occurs at adsorption study of Ni(II) ions. The maximum removal of Ni(II) took 180 minutes but it decreased after 300 minutes. In the adsorption process, any interaction and collision
occurs between metal ions and adsorbent. The increase in contact time means an increase in the interaction that resulted in the molecular bond being broken. This provided the chance for the active sites to adsorb each metal ions. In this case, the adsorption is known to be reversible.

| Parameter | Raw material | Removal efficiency | Particle size (nm) |
|-----------|--------------|---------------------|-------------------|
|           |              |                     | 10 nm | 9 nm | 8 nm | 4 nm |
| Cu        | 292.144      | (ppm) 3.49          | 2.73  | 3.16 | 2.30 |
|           |              | (%) 99.08           | 99.28 | 99.17| 99.40|
| Fe        | 306.240      | (ppm) no detection  | no detection | no detection | no detection |
|           |              | (%) 100             | 100   | 100  | 100  |
| Ni        | 358.940      | (ppm) 0.89          | 0.34  | 0.74 | 0.80 |
|           |              | (%) 99.77           | 99.91 | 99.81| 99.80|

Table 4. The effect of magnetic properties on removal efficiency.

| Parameter | Raw material | Removal efficiency | Magnetic properties (emu/g) |
|-----------|--------------|---------------------|-----------------------------|
|           |              |                     | 37  | 18  | 8.0  |
| Cu        | 292.144      | (ppm) 2.73          | 2.19 | 2.30 |
|           |              | (%) 99.28           | 99.42 | 99.40|
| Fe        | 306.240      | (ppm) no detection  | no detection | no detection |
|           |              | (%) 100             | 100   | 100  | 100  |
| Ni        | 358.940      | (ppm) 0.34          | 0.74  | 0.77 |
|           |              | (%) 99.91           | 99.81 | 99.80|

Table 5. The effect of polymer-coated $\text{CoFe_2O_4}$ on removal efficiency.

| Parameter | Raw material | Removal efficiency | Adsorbent | Nanoadsorbent |
|-----------|--------------|---------------------|-----------|---------------|
|           |              |                     | $\text{CoFe_2O_4}$ | $\text{CoFe_2O_4} + \text{PEG}$ |
| Cu        | 292.144      | (ppm) 2.73          | 8.47      |                |
|           |              | (%) 99.07           | 97.10     |                |
| Fe        | 306.240      | (ppm) no detection  | no detection | no detection |
|           |              | (%) 100             | 100       | 100            |
| Ni        | 358.940      | (ppm) 0.34          | 1.31      | 99.63          |
|           |              | (%) 99.91           | 99.81     | 99.80          |

3.2.3. Effect of particle size
The authors prepared $\text{CoFe_2O_4}$ samples, each with a different particles size, and used them as adsorbent to adsorb heavy metal in wastewater. Table 3 shows result of particles size effect on the metal uptake of Cu(II), Fe(II) and Ni(II). The maximum removal occurs with the smallest particles size. The adsorbent of small particles size has large surface area to adsorb the heavier metals [20]. Surface area besides the particles size, depends on the adsorbents morphology. However, in case of the 8 nm
particle size samples, the capacity of adsorption decreased. In addition, the phenomenon occurred due to magnetic properties of metal pollutant (volume of metal ions) and solubility of metal in water.

3.2.4. Effect of magnetic properties
The heavy metal adsorption efficiency by different magnetic properties show some particular trend but not very significant. The maximum adsorption efficiency of Ni(II) by CoFe₂O₄ would occur at the utmost magnetic properties. Moreover, the magnetic properties of Ni(II) pollutant contribute to nano adsorbent CoFe₂O₄. In addition, due to the large saturation magnetization values, they can be separated from the solution with a permanent magnet in a relatively short time [21]. On the other hand, the adsorption efficiency of Cu(II) has reversed from metal uptake of Ni(II), as seen from table 4. The sample of CoFe₂O₄ nano adsorbent with the lowest magnetic properties has the maximum adsorption to Cu(II). The possible explanation of this phenomenon is the role played by some other factors such as surface area, particle morphology, and available active sites [6].

3.2.5. Effect of PEG-coating
PEG (Polyethylene glycol) is used to coat the CoFe₂O₄ nano adsorbent in order to stabilize it against oxidation, corrosion, and spontaneous aggregation to increase their physic-chemical stability and to provide a functionalized surface [21]. Furthermore, the functions of PEG is being nanoparticles template to control the size and pores structures of particles. However, the particle size of nano adsorbent which was coated with PEG is larger than before coating. The particle size of nano adsorbent is related to surface area of the particles. It means that the particles with the small size have larger surface area than the bigger one. The effect of that is the particles have many active sites to adsorb heavy metal in wastewater. Therefore, the PEG coated CoFe₂O₄ nano adsorbent would adsorb the heavy metal Cu(II) and Ni(II) less than CoFe₂O₄ without coating, which can be seen in table 5.

4. Conclusion
CoFe₂O₄ magnetic nanoparticles (MNPs) is effectively used as adsorbent to remove heavy metal Cu(II), Fe(II) and Ni(II) ions from wastewater. A variety of parameters were then introduced in the experiment in order to complete this study. The percentage of metal ions removal is not significantly affected by the change of temperature and contact time. Particles size gives the major contribution on large surface area, so that metal uptake has a maximum value. Magnetic properties of CoFe₂O₄ contributes to the separation of the pollutants within the solution. However, the additional polymer polyethylene glycol as agent of adsorbent coating decrease the ability of CoFe₂O₄ MNPs to remove metal ions. The possible explanation is that the particles size was increased after coating by polymer, and consequently the surface area become small.

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