SYNTHESIS OF EDTA-FUNCTIONALIZED SILICA COATED NANOMAGNETITE AS A COBALT(II) ION ADSORBENT

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Abstract: This research aims to synthesize silica-coated nanomagnetite EDTA functionalized ($Fe_3O_4@SiO_2$-EDTA) to characterize its properties and test its ability to bind Co(II) metal ions. This research was carried out in several steps, including Synthesis of nanomagnetite and characterization via SEM, VSM, XRD, and FTIR; (2) Synthesis of nanomagnetite-coated silica (TEOS) and characterization via SEM, VSM, (3) Synthesis and characterization of silica-coated nanomagnetite with EDTA functionalization ($Fe_3O_4@SiO_2$-EDTA), and characterization was carried out via SEM, VSM, XRD, and FTIR. (4) Adsorption ability test of $Fe_3O_4@SiO_2$-EDTA as a Co(II) metal ion adsorbent. EDTA-functionalized silica-coated nanomagnetite was successfully synthesized. Confirmation and characterization of the synthesized material was performed on the basis of the FTIR spectrum band at wavenumber 687 cm-1, which confirmed the formation of magnetite, whereas the absorption band at wavenumber 1092 cm-1 confirmed the formation of a silica coating, and the peak at wavenumber 1617 cm-1 confirmed EDTA functionalization in the material. The peak of the XRD chromatogram is shown in XRD pattern 2, which confirms nanomagnetite, and in silica-coated nanomagnetite, the resulting characteristic peak is the same as the characteristic peak in Fe_3O_4 except in region 24, which confirms the presence of the silica coating. The magnetization of nanomagnetite before coating was 57 emu/g and that after coating was 48 emu/g. The maximum adsorption ability of the synthesized material for Co(II) ions was 0.1336 mg/g.

Keywords: Nanomagnetite, Silica, EDTA, Cobalt

Abstrak: Penelitian ini bertujuan untuk mensintesis nanomagnetit berlapis silika terfungsionalisasi EDTA ($Fe_3O_4@SiO_2$-EDTA) untuk mengkarakterisasi sifat-sifatnya dan menguji kemampuannya dalam mengikat ion logam Co(II). Penelitian ini dilakukan melalui beberapa tahap yaitu, (1) sintesis nanomagnetit dan karakterisasi menggunakan SEM, VSM, XRD, dan FTIR (2) sintesis nanomagnetit berlapis silika (TEOS) dan karakterisasi menggunakan SEM, VSM, (3) sintesis dan karakterisasi nanomagnetit berlapis silika dengan fungsionalisasi EDTA ($Fe_3O_4@SiO_2$-EDTA) dan karakterisasi dilakukan menggunakan

SEM, VSM, XRD, dan FTIR. (4) uji kemampuan adsorpsi ($Fe_3O_4@SiO_2$-EDTA) sebagai adsorben ion logam Co(II). Nanomagnetit berlapis silika terfungsionalisasi EDTA telah berhasil disintesis. Konfirmasi dan karakterisasi material hasil sintesis telah dianalisis berdasarkan pita spektrum FTIR pada bilangan gelombang 687 cm -1 yang mengonfirmasi terbentuknya magnetit, sedangkan pita serapan pada bilangan gelombang 1092 cm -1 mengonfirmasi pelapisan silika dan puncak pada bilangan gelombang 1617 cm -1 mengonfirmasi fungsionalisasi EDTA dalam material. Puncak kromatogram XRD terlihat dengan pola XRD 2 yang mengonfirmasi nanomagnetit, dan pada nanomagnetit berlapis silika puncak karakteristik yang dihasilkan sama dengan puncak karakteristik pada Fe_3O_4 kecuali pada daerah 24 yang mengonfirmasi adanya pelapisan silika. Magnetisasi nanomagnetit sebelum pelapisan adalah 57 emu/g dan setelah pelapisan adalah 48 emu/g. Kemampuan adsorpsi maksimum material hasil sintesis untuk ion Co(II) adalah 0,1336 mg/g.

Kata kunci: Nanomagnetit, Silika, EDTA, Kobalt

INTRODUCTION

The separation of metal ions needs to be carried out as one of the stages in analysis preparation, waste treatment, metal purification, preconcentration and so on. The adsorption method is a common technique used to separate metal ions from a mixture; the advantage of the adsorption method is the operational simplicity of the separation process. Adsorption of metal ions by adsorbents is carried out physically and chemically (Sudiarta & Sulihningtyas, 2012). The development of adsorbents to obtain superior adsorbents, namely, adsorbents that are inexpensive, have high adsorption power and selectivity, are easily separated from their matrices, support a fast separation process, and increase the efficiency of the separation process, is needed. Various adsorbent materials continue to be explored and developed to obtain superior adsorbents, including zeolites, activated carbon, and nanomagnetites. (Pizarro et al., 2021).

Nanomagnetite (Fe_3O_4) has been developed as an adsorbent. Particles (Fe_3O_4) are magnetic, easy to modify and nontoxic. Magnetite has been modified by coating to obtain the desired properties and performance. Several previous researchers have used various coating materials to obtain coated nanomagnetic metal ion adsorbents. Among them, several synthesis methods and applications of modified nanomagnetite have been studied by previous researchers, including the synthesis of citrate-coated magnetite nanomaterials and their application as gold adsorbents (Susanto et al., 2017), humic acid-coated nanomagnetite as uranium adsorbents (Singhal et al., 2017), and silica-coated nanomagnetite for arsenic adsorption (Jamali-Behnam et al., 2018). Silica-coated nanomagnetite is generally used by researchers as a multimetal ion adsorbent. Nanomagnetic coatings can prevent magnetite clumping while binding certain physicochemical properties. (Machfiro & Munasir, 2015).

Silica is a material commonly used as a magnetite modifier. The silica coating prevents the possibility of hydroxyl bonds forming on the surface so that the polar attraction between magnetite particles is reduced and makes magnetite insoluble under acidic conditions (Ngatijo et al., 2020). Silica-coated magnetite has been developed as an adsorbent of nickel and manganese ions (Mahmudah et al., 2017). Several researchers have functionalized the silica surface by attaching complexes that can bind metal ions so that selective metal ion adsorption can be carried out. One of the complexes used as a surface modifier for silica-coated nanomagnetic adsorbents is ethylene diamine tetraacetate (EDTA). The complex formed by EDTA with metal ions is stable, and EDTA forms an EDTA-metal ion complex with six coordination bonds. Modifying the silica-coated nanomagnetite with EDTA has the potential to improve the performance of nanomagnetite as a selective adsorbent. The selective binding of metal ions with complex formation can be achieved by adjusting the degree of acidity because the stability of the complex is influenced by the degree of acidity (Lailis & Murwani, 2010).

Heavy metal pollution in water can be caused by waste generated by industrial activities, household activities, mining and so on (Ahmad, 2010). Heavy metals that pollute water include Zn, Cu, Fe, Co, Mn, Ni, Pb, Cr, and Cd (Yudo, 2006). Cobalt(II) ions are heavy metal ions that are often found in industrial waste and have the potential to pollute water bodies. The permitted threshold of cobalt(II) ions in water is low, and the analysis method used must have high accuracy at low analyte levels. When low analyte levels are measured, the potential for decreasing the accuracy of the measurement results is greater than when high analyte levels are measured; therefore, the concentration of general samples is increased through preconcentration. Preconcentration of metal ions via adsorption desorption techniques requires ion-selective adsorbents so that the adsorption process can attract one type of targeted ion.

Ethylene diamine tetraacetate (EDTA) is a metal ion complexing agent whose selectivity can be adjusted by adjusting the pH; therefore, previous researchers have used a pH-based complexing method to selectively withdraw metal ions. EDTA forms complexes with the metal ions nickel(II) and cobalt(II) (Kornev et al., 2017). Binding by complex formation has been carried out by previous researchers, namely, the adsorption of Pb(II) and Cu(II) ions (Liu et al., 2016), and Salman has also adsorbed scandium(III) ions (A. D. Salman et al., 2021). This study develops a preconcentration method for samples containing Co(II) metal ions on the basis of the adsorption desorption process using an Fe_3O_4 magnetic adsorbent coated with silica as a selective separation method for Co(II) ions.

METHOD

Material

$FeSO_4.7H_2O$, $FeCl_3.6H_2O$, distilled water, NH_4OH, ethanol, tetraethyl orthosilicate (TEOS), 3amino-propyl triethoxysilane (APTES), glacial acetic acid, ethylenediamine tetraacetic acid (EDTA), HCl, $CoCl_2.6H_2O$, and $NiCl_2.6H_2O$, all of which are pa grade from Merck, are universal pH indicators.

Apparatus

Laboratory glassware, hotplate, reflux set, SEM FEI INSPECT-S50 instrument, XRD AAP Analytical Expert Pro, XRF PANalytical, FTIR Prestige 21 Shimadzu, VSM-20, Visible Genesys 20 spectrophotometer, and AAS Thermo Scientific ICE 3000.

Synthesis and Characterization of Nanomagnetite

A total of 3.372 g of $FeCl_3.6H_2O$ and 1.736 g of $FeSO_4.7H_2O$ were dissolved in 50 mL of distilled water. Fifty milliliters of $FeCl_3.6H_2O$ solution was mixed with 50 mL of $FeSO_4.7H_2O$ solution, heated to 90°C, 20 mL of 0.5 M NH_4OH solution was added, and the mixture was stirred and heated at 90°C for 30 minutes. The resulting precipitate was filtered, washed with distilled water and then dried in an oven at a temperature of 50–60°C for 4 hours. The resulting solid was sieved with 200 mesh and then ground using a mortar. The method used was a modified coprecipitation method (Rahimah, Fadli, Nurfajriani, et al., 2019). The resulting nanomagnetite powder was characterized using XRD, FTIR, SEM, and VSM.

Synthesis and Characterization of Silica-coated Nanomagnetite

One gram of magnetite powder was suspended in a mixture of 35 mL of distilled water, 200 mL of 96% ethanol, 3 mL of tetraethyl orthosilicate (TEOS), and 15 mL of NH_4OH and then stirred for 2 hours. The precipitate formed was collected by attracting an external magnetic field, washed with 96% ethanol three times, and then dried in an oven. The resulting precipitate was coated again, coated three times, washed three times with 96% ethanol, and then dried in an oven for 4 hours. The method used was a modified method (D. Salman et al., 2021). The resulting silica-coated nanomaphnetite deposits were characterized using XRD and FTIR.

Synthesis and Characterization of EDTA Functionalized Silica Coated Nanomagnetite

One hundred milligrams of silica-coated nanomagnetite was dispersed in 40 mL of EtOH/aquadest 85:15, and a few drops of concentrated HCl were added until the pH was 4.5. Then, the mixture was ultrasonicated for 10 minutes. Next, 700 μL of APTES and glacial drops of acetic acid were added to the mixture, which was refluxed for 4 hours at 60°C. The nanoparticles were separated via an external magnet and rinsed once with water and acetone. The nanoparticles were then dispersed in a 0.3 M EDTA solution while sonicating for 30 minutes and refluxed at a temperature of 60°C for 2 hours. The magnetite nanoparticle adsorbent coated with EDTA-functionalized silica was then heated in an oven at a temperature of 50°C for 60 minutes.

Determination of the optimum pH for the formation of the $[Co(EDTA)]^{2-}$ complex

Ten milliliters of 50 ppm Co(II) solution was added to 0.1 M HCl or 0.1 M NaOH to adjust the pH and 2 mL of 0.3 M EDTA solution was added and then diluted to 50 mL. Various Co(II)-EDTA solutions with pH values of 3.5, 6, 7, and 9 were made. The absorbance of the Co(II) solution was then measured using a UV–Vis spectrophotometer at a wavelength of 540 nm.

Cobalt(II) Ion Adsorption Capability Test with an EDTA-Functionalized Silica Coated Nanomagnetite Adsorbent

The synthesized adsorbent with a certain mass was put into 10 mL of 5 ppm Co(II) sample solution, whose acidity was adjusted to pH 5 with HCl, and the mixture was shaken for 20 minutes. then, the adsorbent was withdrawn and collected via an external magnetic field, and the sample liquid was decanted and centrifuged at 3000 rpm for 5 minutes. The Co(II) levels in the samples were determined using an AAS instrument. Adsorbent mass variations of 0.08, 0.1, 0.2, 0.3, and 0.6 g were used in each experiment. The percentage of Co(II) ions adsorbed by the adsorbent was determined.

RESULTS AND DISCUSSION

Synthesis and Characterization of Nanomagnetite

Nanomagnetite synthesis was carried out via the coprecipitation method. A total of 25 mL of $FeCl_3.6H_2O$ 0.25 M solution and 25 mL of $FeSO_4.7H_2O$ 0.125 M solution were mixed and then added dropwise into 100 mL of NH_4OH solution. The reaction equation that occurs is as follows:

$$2Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow 2Fe(OH)_3(s)$$

$$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$$

$$2FeOOH(s) + Fe(OH)_2(s) \longrightarrow Fe_3O_4(s) + 2H_2O(l)$$

The result of nanomagnetite synthesis (Figure 1) is a black powder that can be attracted by an external magnetic field (Rahimah, Fadli, Yelmida, et al., 2019). The powder resulting from the synthesis of nanomagnetite was then characterized using XRD, SEM, FTIR and VSM. FTIR (*Fourier transform infrared*) analysis (Figure 2) was carried out to determine the functional groups present in nanomagnetite. The absorption peak that appears is at 687 cm $^{-1}$, which indicates the presence of the FeO group (Gong & Tang, 2020).

The morphology of nanomagnetite was analyzed using SEM (scanning electron microscopy). Figure 3 shows the morphological structure of Fe_3O_4. Figure 3 shows that the nanomagnetite particle size is in the range of 37.88–46.08 nm, and there are clumps that indicate the occurrence of agglomeration in the nanomagnetite. This can occur because the magnetic properties of the particles cause clumping. (Rahimah, Fadli, Yelmida, et al., 2019).

Figure 1. Nanomagnetite attracted by an external magnetic field

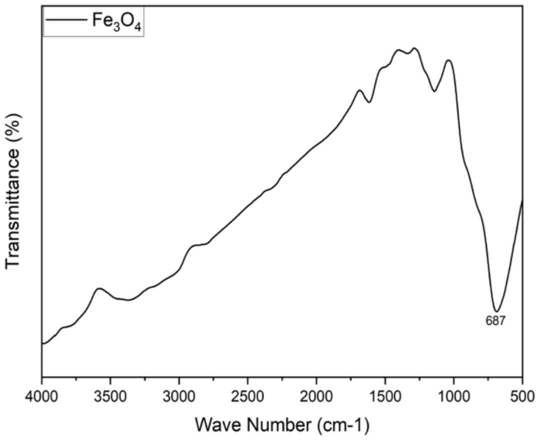

Figure 2. FTIR spectrum of nanomagnetite

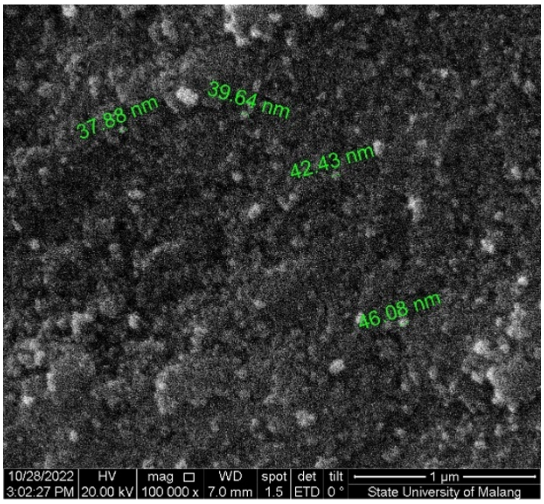

Figure 3. Morphological structure of the Fe_3O_4 nanoparticles

EDTA-Functionalized Silica-Coated Nanomagnetite

Silica contains silanol and siloxane groups, and the chemical properties of the silica surface are determined from the density of silanol per unit mass of silica. On the surface of silica-coated nanomagnetite, the surface structure is covered by either a siloxane group (Si-O-Si) with oxygen or a silanol group (Si-OH). Through hydrolysis, the alkoxide group (OC_2H_5) from aptes will be exchanged with a hydroxyl group (-OH) to form a silanol group that interacts with each other through siloxane bonds (Si-O-Si) to produce a silane polymer. The silane polymer coats magnetite nanoparticles with oh groups on the outer surface (inaloo et al., 2020). Illustration of nanomagnetite coating with silica is presented in Figure 4.

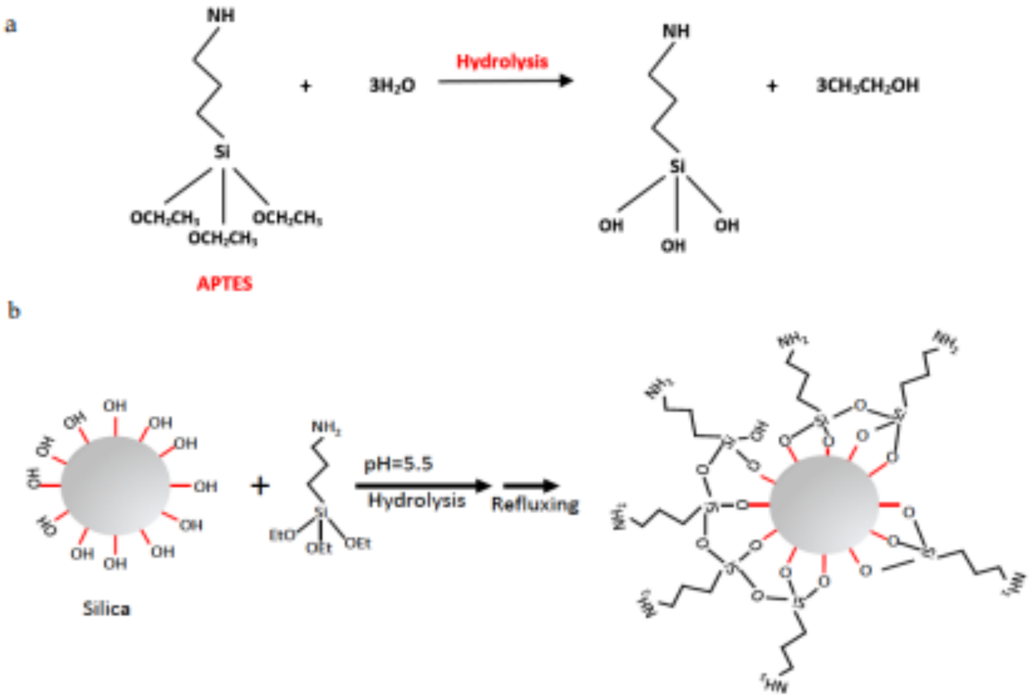

Figure 4. Illustration of nanomagnetite coating with silica

Nanomagnetite is functionalized with EDTA, and EDTA is covalently bound through interactions in the form of amide bonds between the carboxylate group of EDTA and the amino group of APTES. The magnetizations of the magnetite nanoparticles and EDTA-functionalized silica-coated magnetite were measured using a vibrating sample magnetometer (VSM). The measurement results show that the magnetic values of nanomagnetite (Fe_3O_4) and silica-coated nanomagnetite ($Fe_3O_4@SiO_2$) are 57.0 emu/g and 48 emu/g, respectively (Figure 5). There was a decrease in the magnetic value after coating the nanomagnetite with silica. The modifications to the surface of nanomagnetite cause its surface to be covered by a layer of silica. The silica layer covers the surface of nanomagnetite and reduces its saturation magnetization.

Characterization via X-ray diffraction (XRD) was carried out on Fe_3O_4 nanoparticles and silica-coated nanomagnetite ($Fe_3O_4@SiO_2$) to determine the crystalline phase of the material (Figure 6). XRD pattern $2\boxed{\theta}$ can be seen with peaks at 18.2°, 30.2°, 35.6°, 43.2°, 53.9°, 57.3°, 62.9° and 74.2°, which are identical to diffraction [1 1 1], [2 2 0], [3 1 1], [4 0 0], [4 2 2], [5 1 1],[4 4 0] and [5 3 3] crystal planes of the cubic spinel unit cell conform to the standard Fe_3O_4 pattern . For $Fe_3O_4@SiO_2$, the characteristic peak produced is the same as the characteristic peak for Fe_3O_4 except in the 24° region. The peak in the 24° area probably points to the silica layer (Rangelova et al., 2018). The silica formed is amorphous silica, whereas in the 24° area, no sharp peaks are formed.

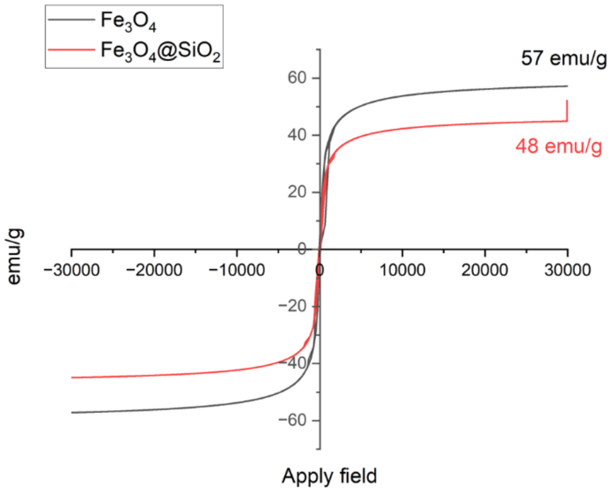

Figure 5. Magnetic curves of (Fe_3O_4) and ($Fe_3O_4@SiO_2$)

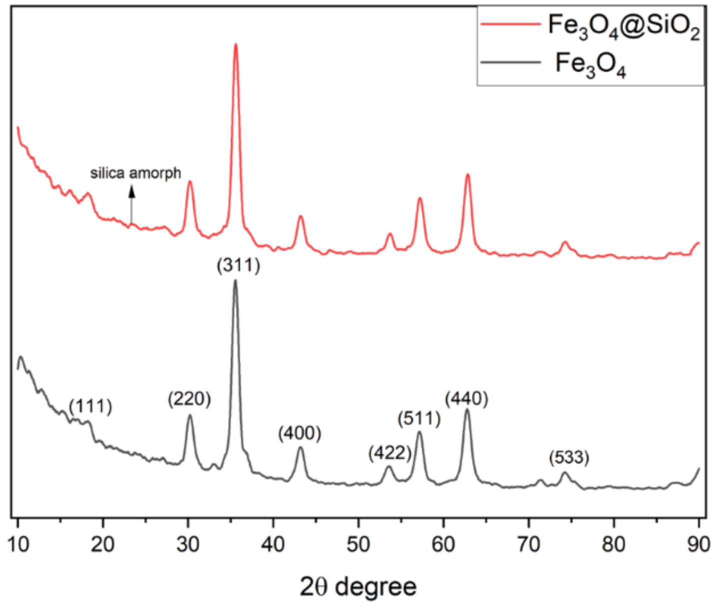

Figure 6. XRD patterns of the Fe_3O_4 and Fe_3O_4 @SiO_2 nanoparticles

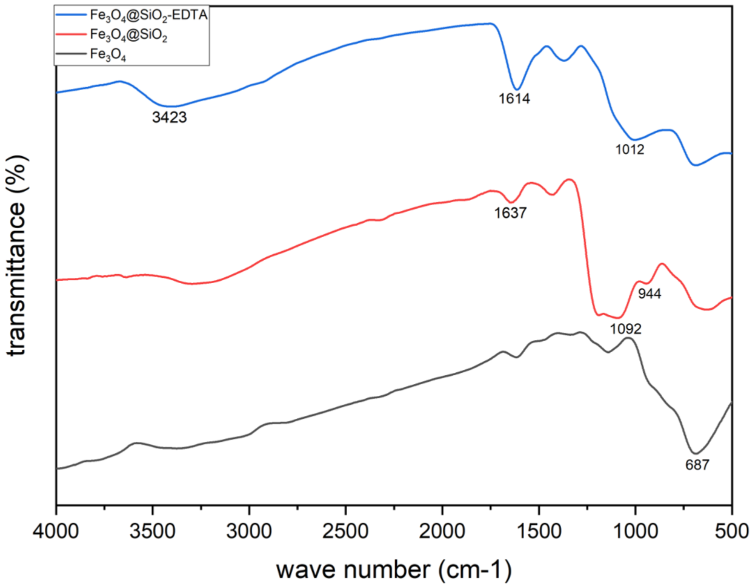

Figure 7. FTIR spectra of the **(A)** Fe_3O_4 (B) Fe_3O_4@SiO_2-NH_2, and (C) Fe_3O_4@SiO_2-EDTA nanoparticles

Characterization using FTIR was carried out on nanomagnetite (Fe_3O_4), silica-coated nanomagnetite (Fe_3O_4@SiO_2-NH_2), and EDTA-functionalized silica-coated nanomagnetite (Fe_3O_4@SiO_2-EDTA). The absorption peak appears at wavenumber 687 cm^{-1}, and the peak at approximately 1617 cm^{-1} and 1637 cm^{-1} is caused by the stretching vibration of the Fe–O bond (Kulpa et al., 2020). The Fe-O peak decreases in Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2 -EDTA, which indicates that coating has been carried out on the

Fe_3O_4 surface. Figure 7 shows peaks at wavenumbers of 794 cm^{-1} and 1092 cm^{-1}, which indicate the occurence of Si-O-Si and Si-OC stretching vibrations (Munasir & Terraningtyas, 2019). The peak at 944 cm^{-1} corresponds to the Si-OH stretching vibration. The peak at 3423 cm^{-1} is caused by the stretching of the -OH band on the surface of the silanol group. The FTIR spectrum of the $Fe_3O_4@SiO_2$-EDTA nanoparticles shows a peak at 1617 cm^{-1}, which corresponds to the vibration of the carboxylic group (C=O) (Gong & Tang, 2020). This is correlated with the silica coating and functionalization of the surface of the Fe_3O_4 nanoparticles with EDTA.

Determination of the optimum pH for the formation of the $[Co(EDTA)]^{2-}$ complex and testing the adsorption ability of EDTA-functionalized silica-coated nanomagnetite as a Cobalt(II) ion adsorbent

The formation of complex compounds is strongly influenced by pH. On the basis of research conducted by previous researchers, the complex compound $[Co(EDTA)]^{2-}$ can occur optimally at pH 5 (Hameed et al., 2021). At this pH, the concentration of the complex compound $[Co(EDTA)]^{2-}$ is the greatest. The structure of the $Fe_3O_4@SiO_2$-EDTA adsorbent in the binding of Co(II) metal ions is shown in the Figure 8.

The absorbance values of $[Co(EDTA)]^{2-}$ formed at several different pH values obtained from measurements via a spectrophotometer are shown in Figure 9. The maximum absorbance value was obtained at pH 5, with an absorbance value of 0.104. The resulting graph shows the formation of the best complex compound at pH 5 so that the adsorption of Co(II) metal ions was carried out at pH 5.

After the optimum pH for the formation of the $[Co(EDTA)]^{2-}$ complex was determined, the adsorption of Co(II) metal ions was carried out via a nanomagnetite adsorbent coated with EDTA-functionalized silica ($Fe_3O_4@SiO_2$ -EDTA). Adsorption of Co(II) metal ions was carried out at the optimum pH for the formation of the $[Co(EDTA)]^{2-}$ complex. The adsorption process is carried out by varying the mass of the adsorbent to determine the mass of the adsorbent with the maximum absorption capacity. Figure 10 shows the stable adsorption level of Co(II) metal ions by the adsorbent ($Fe_3O_4@SiO_2$ -EDTA) at a mass of 0.3 g with an adsorption value of 86.4%. The maximum adsorption capacity reached 0.1336 mg Co(II)/g adsorbent.

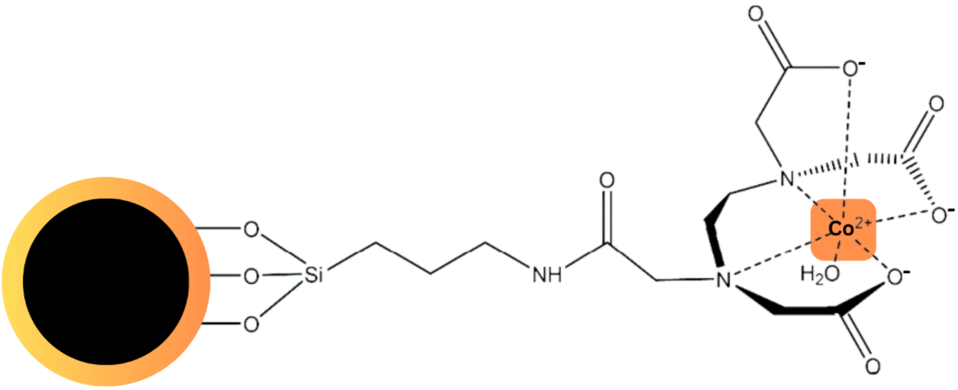

Figure 8 . Binding of Co (II) metal ions by Fe_3O_4@SiO_2 -EDTA

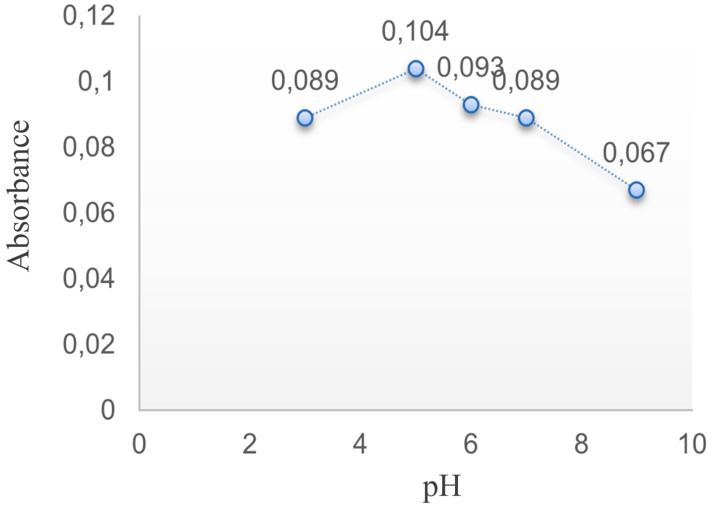

Figure 9. Absorbance curves of the $[Co(EDTA)]^{2-}$ complex at various pH values

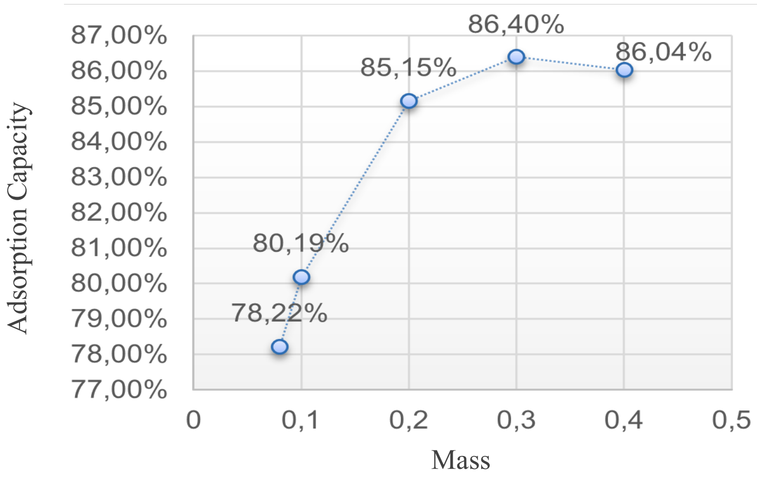

Figure 10. Curve of the percentage of Co(II) ions adsorbed on several adsorbents

CONCLUSION

The synthesis of EDTA-functionalized silica-coated nanomagnetite can be carried out via the coprecipitation method. SEM characterization revealed that the nanomagnetite adsorbent particles were 37.88–46.08 nm in size. The magnetization value of the Fe_3O_4 nanoparticles decreased from 57 emu/g to 48 emu/g after being coated with silica. The chromatographic peak pattern shown by XRD is identical to the nanomagnetite crystal structure, except in area 24°, which has a silica layer. The functionalization of $Fe_3O_4@SiO_2$ by EDTA was confirmed by the FTIR peak at 1614 cm-1. Through mass variations, the maximum absorption level of Co(II) metal ions was obtained with an adsorbent mass of 0.3 g and an adsorption capacity of 0.1336 mg Co(II)/g adsorbent.

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