Jurnal
Riset Kimia

ISSN (print) : 1978-628X
ISSN (online) : 2476-8960

Synthesis and Characterization of Adsorbent Materials Magnetite Mercaptosilicate Ion Imprinted Polymer as Cadmium Ion Adsorbent

Nabela Viviana[1], Ngatijo[1], Restina Bemis[1], and Diah Riski Gusti [1*]
[1]Chemistry Study Program, Faculty of Science and Technology, Universitas Jambi

Corresponding Author:
Diah Riski Gusti
diahgusti@unja.ac.id

Received: July 2023
Accepted: September 2023
Published: September 2023

Abstract

Cadmium (Cd) is a toxic heavy metal with the active property of reacting with other components so that cadmium residues can quickly enter the food chain and cause cardiovascular, kidney, and cancer diseases. The purpose was to synthesize the magnetite mercaptosilicate ion imprinted polymer adsorbent material by forming Ion-Imprinted Polymer as a template, to analyze the characterization results using XRD and SEM-EDS, and to determine the adsorption test results for Cd metal ions. The results of the characterization of XRD show that there is a broad peak at a diffraction angle of 2θ= 20-220 with an amorphous structure, which is silica, and there is a high peak at a diffraction angle of 2θ= 35.55140 which indicates magnetite. The results of SEM analysis with magnifications of 500x, 1000x, and 5000x showed that the surface morphology of the particles was not uniform. For the EDS results, it can be seen that the components of the magnetite mercaptosilicate ion imprinted polymer material are elements C, O, Si, S, and Fe, with a mass percentage of 25.0%; 41.2%; 29.9%; 3.28% and 0.8%. The results of the adsorption test for the Magnetite-IIP-Mercaptosilika Material were able to adsorb Cd ions with the highest adsorption capacity of 10.536 mg/g at a concentration of 100 mg/L. Then the selectivity coefficient value of the Ion Cd metal ion is 2.32 greater than 1, indicating that the selectivity of the magnetite mercaptosilicate ion imprinted polymer material is much higher for Ion Cd metal ions than for Cu and Cr ions with a selectivity coefficient of 0.1 and 0.26.

Keywords: *ion-imprinted polymer, cadmium, adsorbent, selective.*

Introduction

Environmental pollution is a negative impact caused by the rapid development of industrial technology; one of the dangerous pollutant materials is heavy metals. Cadmium (Cd) is a toxic heavy metal that occurs naturally in ecosystems, and its presence is increased by anthropogenic activities that threaten animal and human life. Cadmium has the active property of reacting with other components so that cadmium residues can quickly enter the food chain by consuming contaminated vegetables and fish[1],[2]. Cadmium that enters food is capable of contaminating the human body so that it can cause cardiovascular, kidney, and cancer diseases [3].

Various methods are used to reduce the concentration of contaminants such as cadmium in wastewater. The most selective and efficient is the adsorbent [4]. The adsorbent to be developed is magnetite-mercapto silicate nanoparticles (Fe_3O_4-MS). Magnetite is a type of iron oxide with good magnetic properties and is very effective as an adsorbent for removing various heavy metal cations in wastewater [5]. However, magnetite is unstable because it is easily oxidized. Magnetite must be coated with silica from rice husk ash, with as much as 86.90-90.30% SiO_2 content. Silica is a porous material with a flexible structure, large surface area, good mechanical stability, and heat resistance [6]. In addition, on the silica surface, there are active sites in the form of silanol groups (Si-OH) and siloxane (Si-O-Si), and the presence of -OH groups can be modified into other active functional groups such as -CH, -SH and NH_2 [7]. The disadvantage of using silica gel as an adsorbent is the low adsorption effectiveness of metal ions.

Adsorption efficacy can be increased by modifying the silica surface. The silica surface can be modified by adding -SH groups produced from 2-mercaptoethanol, resulting in mercapto silicate (MS). When mercapto silicate (MS) is mixed with magnetite to generate Fe3O4-MS material, regular pores form and surface expansion occurs. The ability of Fe_3O_4-MS needs to be improved to be more selective in adsorbing cadmium ions. Increasing the selectivity of Fe_3O_4-MS can be increased by forming an Ion Imprinted Polymer (IIP).

IIP is a method to produce adsorbents that have high selectivity properties and are very suitable for the adsorption of heavy metal ions. IIP has high selectivity because it includes metal ions as mold formers. Previous research has reported the synthesis of Ion Imprinted Polymer material using 3-ammonium propyl triethoxysilane (APTES) as a functional monomer and tetraethylorthosilicate (TEOS) as a crosslinker with an adsorption capacity of 7.34 mg/g while the Un-Ionic Imprinted Polymer material has an adsorption capacity of 5.59 mg/g against ion cadmium [8]. Combining Fe3O4-MS with the formation of ion imprinted polymer so that it becomes magnetite mercaptosilicate ion imprinted polymer (Magnetit-IIP-MS), which can produce a material adsorbent that is efficient, selective, has high adsorption capacity and thermal stability. This material is also resistant and can be used repeatedly, so its application costs relatively little[9],[10].

Experimental

Materials

The materials used in this study were Kerinci rice husk, Jambi Province, HNO_3 69% (Merck), HCl 37% (Merck), APTMS 95% (Sigma-Aldrich), 2-mercaptoethanol 98% (Merck), H_2SO_4 98% (Merck), cadmium sulfate hydrate (Merck), NaOH, $FeSO_4.7H_2O$, $FeCl_3.8H_2O$, ethanol, NH_4OH, distilled water, tissue, filter paper, Whatman paper, and universal pH.

Instruments

The tools used in this study were a set of standard glassware (Erlenmeyer flask, volume pipette, baking glass, funnel (Pyrex), analytical balance, oven, furnace, sample bottle, filter paper, hotplate, magnetic stirrer, volumetric flask, stir bar, spatula, mortal and pestle as well as X-Ray Diffraction (XRD XPERT PRO PANalytical PW3040/60), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS Type Prisma E 16.0 Thermo Scientific) and Atomic Absorption Spectrophotometer (AAS).

Methods

Synthesis of Sodium Silicate and Synthesis of Silica from Rice Husk Ash

Destruction of sodium silicate from rice husk ash was carried out using the sol-gel method. Rice husk is burned to become charcoal, then heated at 700 ^{0}C. Then crushed until smooth and sieved at 270 mesh. Take 100 grams of rice husk ash, add 80 grams of crystal NaOH, and add 500 mL of distilled water. Then heated and stirred using a stirrer for 2 hours at room temperature. After the stirrer is cooled and filtered, the filtrate is taken. The filtrate is Sodium Silicate (Na_2SiO_3).

Continuing with the synthesis of silica, 2M HCl was added drop by drop into the Na_2SiO_3 solution to a pH of 9, and a sol was formed.

Then let stand for 3x24 hours until a gel forms, then washed with distilled water until the pH is neutral, filtered and dried in an oven at 80 ^{0}C for 2 hours, then crushed until smooth. Silica was obtained and characterized using XRD.

Magnetite Synthesis (Fe_3O_4)

The synthesis of magnetite (Fe_3O_4) was carried out using the coprecipitation method. As much as 8 grams $FeCl_3.6H_2O$ and 4 grams $FeSO_4.7H_2O$ each dissolved in 30 mL of distilled water until homogeneous and the two solutions were mixed. After mixing, the solution was heated to 60 ^{0}C and stirred with a stirrer, and slowly added 10% NH_4OH solution to produce a black precipitate, carried out for 90 minutes. The precipitate was separated from the solution by filtration, then rinsed with distilled water until the ammonia smell disappeared and dried in an oven at 80 ^{0}C for 3 hours, then crushed until smooth. Obtained precipitate which is Fe_3O_4 and characterized using XRD.

Mercaptosilicate Coated Magnetite Material (Fe_3O_4-MS)

Coating of magnetite with mercapto silica was carried out using the sol-gel method. As much as 2 grams of Fe_3O_4 was dissolved with 4 mL of 1 M HCl solution, then added 5 mL of sodium silicate (Na_2SiO_3) and 10 mL of 2-mercaptoethanol and stirred using a stirrer for 2 hours. After mixing, distilled water was added until the volume of the mixture was 24 mL and 1 M HCl was added drop by drop until it reached pH 7. The resulting precipitate was separated with an external magnet, then washed with distilled water and dried at 80 ^{0}C for 2 hours, then crushed until smooth. Magnetite-MS was obtained and characterized using XRD.

Synthesis of Magnetite Mercaptosilicate Ion Imprinted Polymer

Magnetite-IIP-MS synthesis was carried out with 5 mL of APTMS dissolved in 5 mL of 0.5 M cadmium ion and stirred using a stirrer for 3 hours at room temperature. Furthermore, 5 grams of silica and 0.5 grams of Fe_3O_4-MS material were dissolved with 50 mL of ethanol, then stirred for 2 hours at room temperature. Then mix the two solutions until homogeneous and let stand for 24 hours. Then it was leached using 3 M H_2SO_4, then rinsed with distilled water until the pH was neutral, and dried in an oven at 80 ^{0}C for 3 hours. Magnetite-IIP-MS material was obtained and characterized using XRD and SEM-EDS.

Measurement

Adsorption Test with the Effect of Concentration

A total of 20 mL of Cd solution with various concentrations of 10, 15, 20, 25, 50, and 100 mg/L. Then added 0.1 gram of Magnetite-IIP-MS adsorbent material each. Then stirred using a shaker with a variation of contact time of 30 minutes. Then the solution was filtered and the filtrate was analyzed using AAS.

Selectivity test

A total of 10 mL of a solution of Cd ions, Cu ions, and Cr ions with each concentration of 10 mg/L was put into the Erlenmeyer. Then 0.1 gram of Magnetite-IIP-MS adsorbent material was added. Then stirred using a shaker with a variation of contact time of 30 minutes. Then the solution was filtered and the filtrate was analyzed using AAS.

Results and Disscusion

Synthesis of mercapto silicate magnetite-IIP adsorbent material begins with the destruction of sodium silicate from rice husk ash which is a source of silica (SiO_2) which is carried out by adding NaOH as an extractor. As for the reaction of SiO_2 and NaOH.

$$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$

During this process, NaOH which is the extractor will break down the molecule (doctorate) by forming Na^+ and OH^- ions. In the SiO_2 compound the element O has a higher electronegativity than Si so the OH^- ion will affect the Si element which is more electropositive and will form a compound in the form of $[SiO_2OH]^-$ The remaining OH^- ion affects the protonated H^+ ion in the compound

$[SiO_2OH]^-$ so that the H^+ from these compounds are released and form H_2O molecules. The release of H^+ ions causes the formation of SiO_3^{2} compounds which will then bind to two H^+ ions which dissociate from NaOH to form Na_2SiO_3 which is a brownish-red solution.

Next, the preparation of silica was taken from a sodium silicate solution. The process of making silica used the sol-gel method, which was carried out in the following stages:

- acidification of sodium silicate, which acts as a precursor
- forming hydrogels
- washing hydrogels and drying hydrogels to become xerogels

The last step is drying using an oven at 70˚C for 2 hours, then grinding until smooth and getting silica as a white powder.

The synthesis of Fe_3O_4 was carried out using the coprecipitation method, which is based on the deposition of more than one substance together. The precursors used in this process are iron (II) sulfate heptahydrate ($FeSO_4$.7H2O) and iron (III) chloride hexahydrate ($FeCl_3.8H_2O$) as sources of Fe^{2+} and Fe^{3+} in a ratio of 2:1. In the coprecipitation process by dissolving $FeSO_4$.7H2O and $FeCl_3.6H_2O$ in distilled water to produce a solution containing Fe^{2+} and Fe^{3+} ions. At the same time, the water contained in the hydrolyzed solution becomes H^+ dan OH^-. Fe^{3+} ions bind to hydroxyl groups to form $Fe(OH)_3$. $Fe(OH)_3$ is hydrolyzed to FeOOH, which is indicated by a reddish-brown color in the solution. Fe^{2+} ion binds to a hydroxyl group to form $Fe(OH)_2$. Then, a precipitating agent, namely NH_4OH, was added so that FeOOH and $Fe(OH)_2$ reacted to form Fe_3O_4, which was marked by a change in the color of the solution to dark black [11]. Then, it was filtered and rinsed until the smell of NH_4OH disappeared. Then put in the oven at 80 0C for 3 hours. The Fe_3O_4 obtained is black powder, as shown in Figure 1(a).

The synthesis of mercapto silica-coated magnetite material involves the silica gelation process of the Na_2SiO_3 compound followed by the attachment of the mercapto group (-SH) of the 2-Mercaptoethanol compound. The coating of Fe_3O_4 with silica and mercapto groups was carried out in water solvent. Before that, magnetite acidification was first carried out by adding 1 M HCl solution which aims to form active sites on the surface of magnetite, so that it can easily interact with the reagent to be coated. Then, it continued with the formation of mercaptosilika (MS), namely the interaction between mercapto and silicate ions. Furthermore, during the Fe_3O_4-MS coating process, namely by adding 1 M HCl solution until it reaches a pH of 7, the aim is to produce silicate anions from sodium silicate solution so that they can form siloxane bonds.

It is because part of the protonated silicate anion forms the driving force of silicic acid which causes the formation of a silica network (oligomerization) so that condensation occurs between the anion and silicic acid and forms a gel. In addition, the addition of acid leads to the protonation of the oxygen atoms in magnetite thereby reducing the negative charge density on the Fe atoms. This makes Fe easily attracted by the electron pair from the siloxy group ($Si—O^-$) of the silicate anion to form the Fe—O—Si group. The result of making mercapto silicate-coated magnetite is in the form of a gray powder and does not lose its magnetic properties as shown in Figure 1(b).

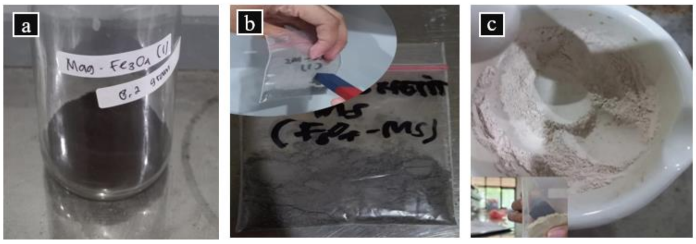

Figure 1. (a) Magnetite, (b) Mercaptosilka-coated Magnetite, and (c) Magnetite-IIP-MS and its Trials

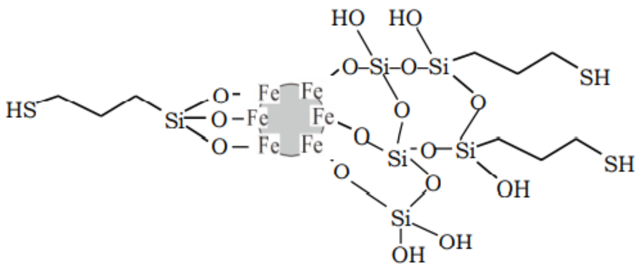

Figure 2. Mercaptosilicate-coated Magnetite Structure

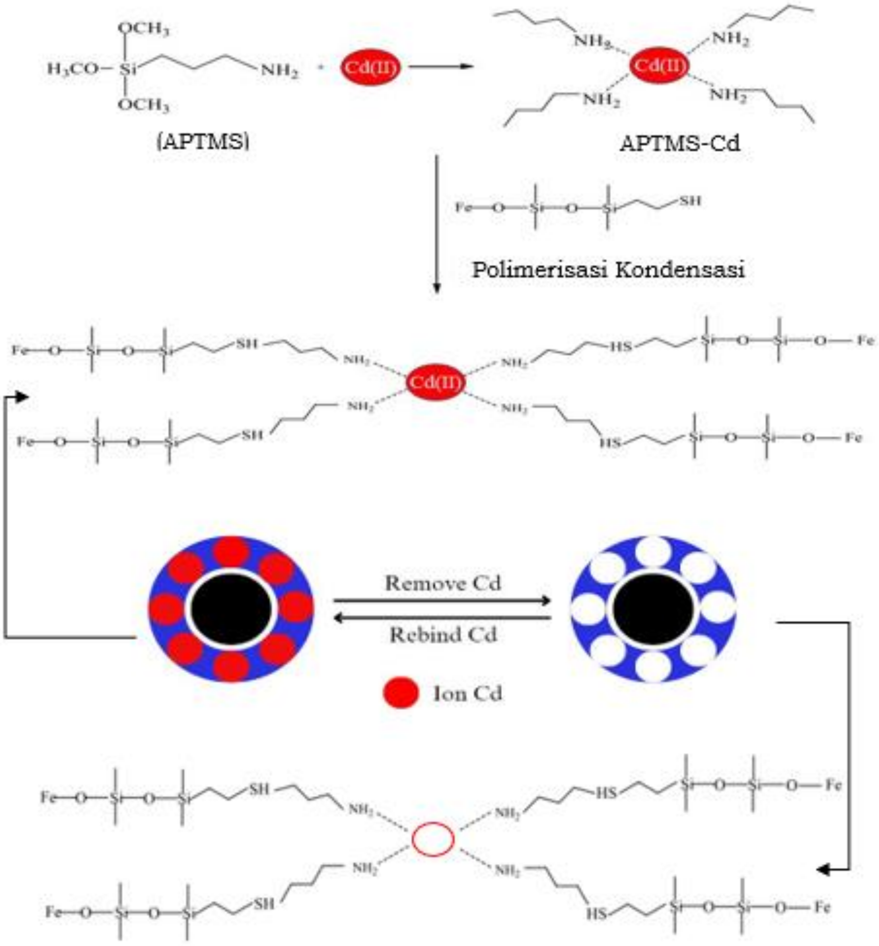

Figure 3. Magnetite Adsorbent Material Reaction Magnetit-IIP-MS

After the process of making mercaptosilicate-coated magnetite (magnetite-MS). Furthermore, a selective synthesis was carried out when carrying out adsorption, namely by using the Ionic Imprinted Polymer method. Using this method will form a mold that matches the target metal. The first stage begins with the formation of a binary complex between the metal and the chelating ligand by mixing a solution of cadmium ion and APTMS which is stirred for 3 hours at room temperature. The cadmium ion solution serves as the template itself while the APTMS compound is used as the functional monomer (chelating ligand). Then in a different place, namely mixing silica material which functions as a cross-linker, and magnetite-MS as the core with ethanol solvent for 2 hours at room temperature.

The next stage of polymerization is by mixing the two solutions and letting them stand for 24 hours. In this process, there is a crosslinker that can bind functional monomers to binary complex ions that will be printed with a combination of compounds. After polymerization has occurred, leaching with a suitable solvent is carried out to separate the metal ions from the polymer. In this synthesis, the leaching solvent used is H_2SO_4 3 M, H^+ ions from the H_2SO_4 solvent will generate energy to bind Cd ions covalently and form polymer templates [12]. When the Cd ions are successfully separated, the polymer will selectively form according to the size and function of the ions that enter the polymer, this is what is known as Ion Imprinted Polymers. Then filtered and rinsed using distilled water until the pH is neutral. The final step is drying using an oven at 80˚C for 2 hours. The results obtained are brownish-gray powder as shown in Figure 1(c).

Characterization

To find out the compounds and structures contained in the synthesized material, the analysis that can be used is the X-Ray Diffraction (XRD) instrument.

In the diffractogram in Figure 4(a), which is the diffraction pattern of Fe_3O_4, there are three main peaks, namely at an angle of $2\theta = 35{,}452^0$; $62{,}728^{0,}$ and $30{,}168^{0,}$ and the highest peak is at the diffraction angle $2\theta = 35{,}452^0$. This is by the JCPDS card database no.39-1340 for magnetite standards. Figure 4(b) is a diffractogram of mercaptosilicate-coated magnetite material (Fe_3O_4-MS). In the diffractogram, there is the highest peak at the diffraction angle of $2\theta = 2\theta = 35{,}3843^0$ which indicates magnetite. In addition, there is a slightly widened peak at a diffraction angle of $2\theta = 20\text{-}22^0$. It is agreed that the broad peaks at the diffraction angle $2\theta = 20\text{-}22^0$ indicate the presence of silica with an amorphous structure that is present due to the addition of mercapto silicate to coat the magnetite [13]. Figure 4(c) is a diffractogram of the main product Magnetite-IIP-MS adsorbent material in this study. From the diffractogram, there is a broad peak at the diffraction angle of $2\theta = 20\text{-}22^0$ with an amorphous structure indicating silica. The diffraction angle of this material has wider peaks than the material that has not yet formed an IIP, namely the Fe_3O_4-MS material. This is due to the addition of silica as a crosslinker. In addition, there is a high peak at a diffraction angle of $2\theta = 35{,}5514^0$ which indicates magnetite. This means that this material does not lose its magnetic properties after the leaching process.

Besides being characterized using XRD, characterization was also carried out using SEM which aims to determine in general the surface morphology, surface homogeneity, and distribution of particles in a material.

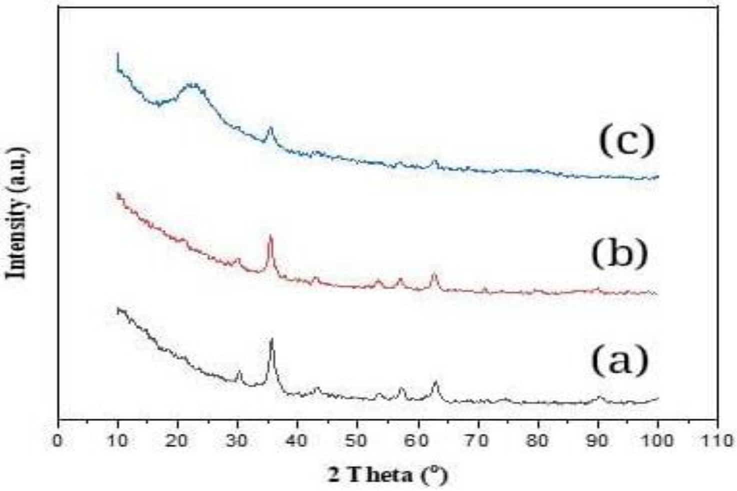

Figure 4. Diffractogram (a) Magnetite, (b) Magnetite-MS dan (c) Magnetite-IIP-MS

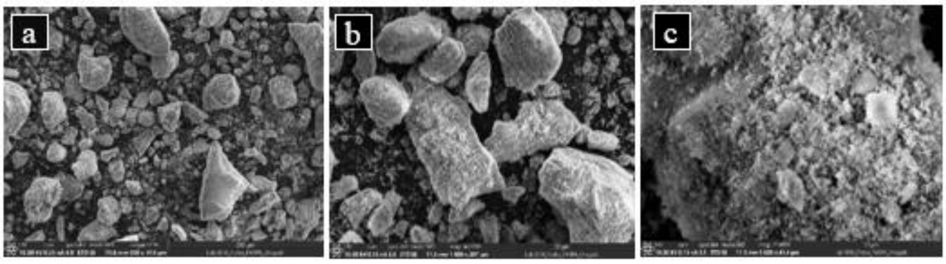

Figure 5. SEM Results of Magnetite-IIP-MS Material Magnifications (a) 500x, (b) 1000x and (c) 5000x

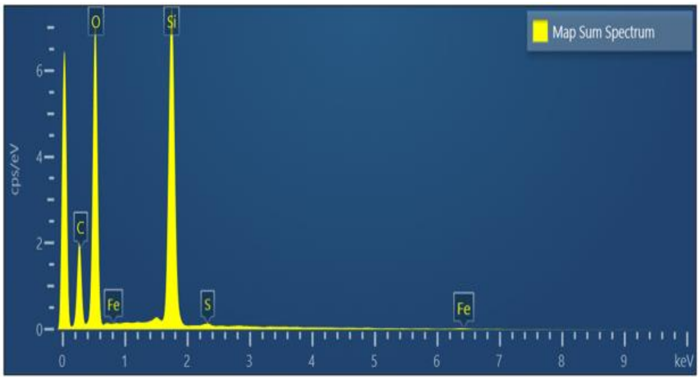

Figure 6. Results of EDS Material Magnetite-IIP-MS

Figures 5 (a), (b), and (c) are SEM results on the Magnetite-IIP-MS adsorbent material with different magnifications. Figure 5(a) with 500x magnification and Figure 5(b) with 1000x magnification shows the non-uniform particle surface morphology.

Based on research [14] magnetite-ion imprinted polymer materials have irregular morphology. This is consistent with the results of research conducted that the material that has formed IIP has a non-uniform particle surface morphology. In addition, at 5000x magnification it shows that there is an overlap between the grayish-white lumps which are indicated as silica, and the gray-black lumps which are indicated as Fe_3O_4, this occurs because of the coating process[15]. From the results of this analysis, the Magnetite-IIP-MS adsorbent material still has magnetic properties after the leaching process.

Furthermore, to see the presence of components contained in a material, EDS analysis can be used. In this study, several components make up the Magnetite-IIP-MS material, namely elements C, O, Si, S, and Fe. The component that has the highest first percentage is element O 41.02% derived from Si-O-Si and Si-OH compounds. The second is the element Si 29.9% derived from mercaptosilika. Then the third is element C 25.0% derived from methyl compounds that are in APTMS. Then there is the 03.28% Fe element which is a compound of Fe_3O_4 and the last is the 0.8% S element derived from the H_2SO_4 compound. From the results of the EDS analysis, the Magnetite-IIP-MS adsorbent material component does not contain Cd, which means that the Cd has been successfully separated so that it can be said to have formed an ion imprinted polymer as a template.

Effect of Adsorbate Concentration on Adsorption of Cd ions

The effect of Adsorbate Concentration on the Adsorption of Cd ions by Magnetite IIP-MS adsorbent material was carried out at various concentrations of 10, 15, 20, 25, 50, and 100 mg/L.

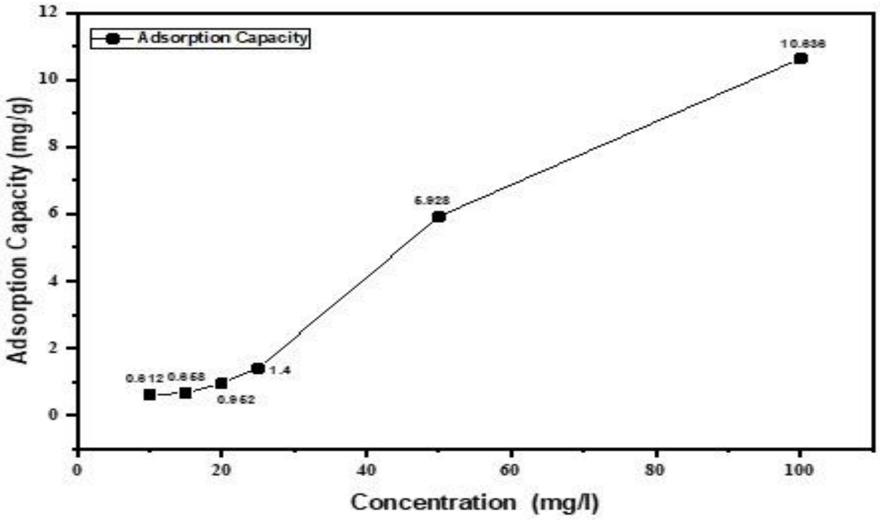

Figure 7. Graph of the Effect of Adsorbate Concentration on the Adsorption Capacity of Cd Ions

Adsorption was carried out for 30 minutes using a 100 rpm shaker with a mass of 0.1 grams of adsorbent. Determination of the concentration was carried out to determine the amount of concentration between the adsorbent and Cd ions so that the ability of the adsorbent material can be known.

In Figure (7) it can be seen that the amount of Cd ion adsorbate was able to be adsorbed by the Magnetite-IIP-MS adsorbent material with the highest adsorption capacity of 10.636 mg/g and still increased to a concentration of 100 mg/L. This shows that the Magnetite-IIP-MS adsorbent material has not reached equilibrium, which means that the ability of the adsorbent to adsorb Cd ions can still be above 100 mg/L. It can also be seen that the amount of adsorbate adsorbed on the adsorbent increases linearly with increasing concentration. The results obtained correspond to the increasing concentration, the more adsorbate and adsorbent molecules that interact with each other in the adsorption process, so that adsorption tends to increase [16].

Selectivity Determination

The competitive metal ions used are Cu and Cr ions with ionic radii of 0.72 Å and 0.87 Å. Cu ions and Cr ions are used as competitive metal ions because these metals belong to the transition metal group, as are Cd ions. The selectivity test is indicated by the magnitude of the distribution coefficient (Kd) and selectivity coefficient (k) which can be calculated using the following equation [17].

$$\text{Kd} = \frac{C_0 - C_1}{C_1} \text{ x } \frac{V}{m} \text{ ......(1)} \quad \text{k} = \frac{Kd\ analyte}{Kd\ competitors} \text{ ......(2)}$$

Information :

Kd = distribution coefficient

V = volume of solution (mL)

C_0 = initial concentration (mg/L)

C_1 = final concentration after adsorption (mg/L)

m = adsorbent mass (g)

k = selectivity coefficient

Kd analyte = analyte distribution coefficient

Kd competitors = competitive distribution coefficient

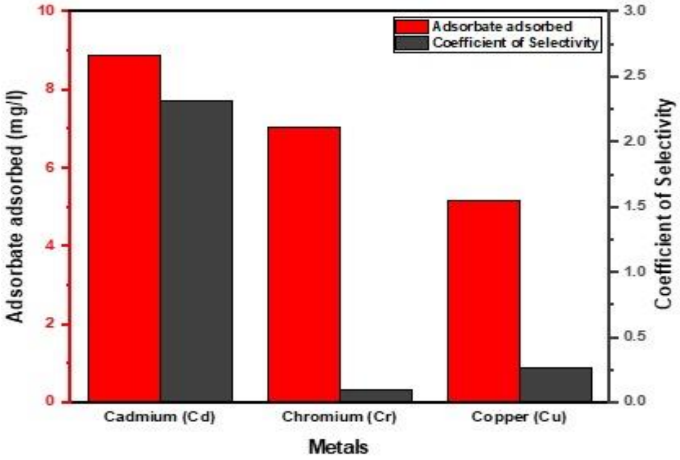

Figure 8. Adsorbate and Selectivity Coefficients of Cd, Cu, and Cr Ions

Figure 8 shows that the magnetite mercaptosilicate ion imprinted polymer material can adsorb more Cd ions compared to Cu ions and Cr ions which have a smaller ionic radius than Cd ions which is 0.97 Å. Then the value of the selectivity coefficient of Cd ions 2.31 is greater than 1, indicating that the selectivity of the Magnetite-IIP-MS material is much higher for Cd ions than for Cu ions and Cr ions which have selectivity coefficient values of 0.1 and 0.26. These ions show that the competitive metal ion affinity of the Magnetite-IIP-MS material can be expressed as follows: Cd ion > Cu ion > Cr ion.

Thus, the magnetite-IIP-MS material showed better adsorption selectivity to Cd ions than solutions containing other metal ions. This is because the IIP-MS magnetite material has a special identification cavity for Cd ions or a mold has formed on its surface so that it can absorb Cd ions specifically.

Conclusions

The magnetite mercaptosilicate ion-imprinted polymer material can adsorb more Cd ions than Cu and Cr ions. The Cd ion selectivity coefficient of 2.32 is greater than 1, indicating that the selectivity of the mercaptosilicate magnetite ion-imprinted polymer material is much higher for Cd ions compared to Cu ions and Cr ions, which have selectivity coefficient values of 0.1 and 0.26.

The results of the characterization of the Magnetite-IIP-Mercaptosilika adsorbent material were analyzed using XRD instrument the results of a wide peak at a diffraction angle of $2\theta = 20\text{-}22^0$ with an amorphous structure indicating silica and there is a high peak at a diffraction angle of $2\theta = 35.5514^0$ which indicates magnetite. For SEM-EDS instruments in the SEM analysis with 500x, 1000x, and 5000x magnification the results of the analysis of the magnetite merkaptosilka ion imprinted polymer adsorbent material showed non-uniform particle surface morphology. Furthermore, for the EDS results, it can be seen that the components of the Magnetite-IIP-Mercaptosilika material are elements C, O, Si, S, and Fe, with a mass percentage of 25.0% respectively; 41.2%; 29.9%; 3.28% and 0.8%.

References

1. Ishak, A. R., Zuhdi, M. S. M. & Aziz, M. Y., Determination of lead and cadmium in tilapia fish (Oreochromis niloticus) from selected areas in Kuala Lumpur. *Egypt. J. Aquat. Res.*, **46(3)**: 221–225 (2020).
2. Huang, R., Shao, N., Hou, L. & Zhu, X., Fabrication of an efficient surface ion-imprinted polymer based on sandwich-like graphene oxide composite materials for fast and selective removal of lead ions. *Colloids Surfaces A Physicochem. Eng. Asp.*, **566(January)**: 218–228 (2019).

3. Young, J. L. & Cai, L., Implications for prenatal cadmium exposure and adverse health outcomes in adulthood. *Toxicol. Appl. Pharmacol.*, **403(May)**: 115161 (2020).
4. Ngatijo, N., Gusmaini, N., Bemis, R. & Basuki, R., Adsorpsi Methylene Blue pada Nanopartikel Magnetit tersalut Asam Humat: Kajian Isoterm dan Kinetika. *CHEESA Chem. Eng. Res. Artic.*, **4(1)**: 51–64 (2021).
5. Rahmayanti, M., Sintesis dan Karakterisasi Magnetit (Fe3O4): Studi Komparasi Metode Konvensional dan Metode Sonokimia. *Al Ulum Sains dan Teknol.*, **6(1)**: 26–31 (2020).
6. Handayani, P. A., Nurjanah, E. & Pita, D., Pemanfaatan Limbah Sekam Padi menjadi Silika Gel. *J. Bahan Alam Terbarukan*, **3**: 20–24 (2014).
7. Fadhilah, A.H., Ngatijo., D. R. G. dan R. K., Adsorben Magnetit Terlapis Dimerkaptosilika untuk Adsorpsi Anion Logam. *J. Ris. Kim.*, 113–120 (2020).
8. Sari Puspita, I. & Amran, M. B., Sintesis dan Karakterisasi SiO_2 @ APTES-IIP Sebagai Material Fungsional Penjerap Ion Kadmium (II). **04(01)**: 18–29 (2021).
9. Sharma, G. & Kandasubramanian, B., Molecularly Imprinted Polymers for Selective Recognition and Extraction of Heavy Metal Ions and Toxic Dyes. *J. Chem. Eng. Data*, **65(2)**: 396–418 (2020).
10. Erdem, özgecan., Saylan, Y., Andaç, M. & Denizli, A., Molecularly imprinted polymers for removal of metal ions: An alternative treatment method. *Biomimetics*, **3(4)**: 1–17 (2018).
11. Lestari, A. S. & Dewi Sartika., Preparasi dan Karakterisasi Nanopartikel Fe_3O_4 menggunakan Metode Kopresipitasi. **11(1)**: 7–10 (2018).
12. Kartika1), H. D., Jorena2)., , Fiber Monado1, 2). & Royani, dan I., Jurnal Penelitian Sains. **24(1)**: 18–23 (2022).
13. Kalapathy, U., An improved method for production of silica from rice hull ash. **85**: 285–289 (2002).
14. Xu, X., Wang, M., Wu, Q., Xu, Z. & Tian, X., Synthesis and Application of Novel Magnetic Ion-Imprinted Polymers for Selective Solid Phase. **(Ii)**: (2017). doi:10.3390/polym9080360
15. Nuryono, N., Rosiati, N. M., Rusdiarso, B., Candra, S., Sakti, W. & Tanaka, S., Coating of magnetite with mercapto modified rice hull ash silica in a one-pot process. 1–12 (2014).
16. Irawan, C., Pengaruh Konsentrasi Adsorbat terhadap Efektivitas Penurunan Logam Fe dengan Menggunakan Fly Ash sebagai Adsorben The. *Seminastika*, 291–293 (2018).
17. Madikizela, L. M., Mdluli, P. S. & Chimuka, L., Experimental and theoretical study of molecular interactions between 2-vinyl pyridine and acidic pharmaceuticals used as multi-template molecules in molecularly imprinted polymer. *React. Funct. Polym.*, **103**: 33–43 (2016).