Functionalization of ZnO Particles with Tetraethyl Orthosilicate (TEOS) and Application as Heavy Metal Adsorbent Cu^{2+}

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Abstract. The increase in Indonesia's population is directly proportional to industrial growth which also has an impact on the industrial waste produced. One type of waste that is mostly generated from the industrial sector is Cu^{2+} heavy metal waste. Research that has been developed to overcome this problem is the use of adsorbents such as TiO_2, SiO_2, Al_2O_3, and zinc oxide (ZnO). The presence of silanol groups aims to control particle size homogeneity and increase the ability of ZnO particles as heavy metal adsorbents. The research was carried out by synthesizing ZnO particles and then functionalizing them with the addition of by adding tetraethyl orthosilicate (TEOS) as a coating on the surface of ZnO particles through the coprecipitation method. The synthesized P- ZnO and S-ZnO particles were tested with Atomic Absorption Spectrophotometer (AAS) to determine the absorption ability of S-ZnO and P-ZnO particles. The test results showed that the adsorption capacity of P-ZnO was 202.11 mg/g and S-ZnO was 202.54 mg/g with an adsorbent mass of 16 mg. The adsorption isotherm model of P-ZnO and S-ZnO particles followed Temkin's model with an adsorption heat on P-ZnO particles of 1.35 x 10^{-3} kJ/mol and S-ZnO particles of 7.67 x 10^{-3} kJ/mol, and a physical interaction between adsorbent and adsorbate. P-ZnO particles had a ΔG value of -14.00 kJ/mol and ΔS of 0.09 kJ/mol.K while S-ZnO particles had a ΔG value of -13.401 kJ/mol and ΔS of 0.07 kJ/mol K which indicated that adsorption occurred spontaneously. The ΔH value of P-ZnO was 12.34 kJ/mol and S-ZnO was 7.21 kJ/mol which indicated that the reaction occurred endothermically.

1 Introduction

The increase in the amount of heavy metal waste is due to the large number of industries that use heavy metals as raw materials or as additives in the manufacture of a product. Several types of heavy metals that can pollute the environment and are toxic are chromium (Cr), silver (Ag), cadmium (Cd), lead (Pb), zinc (Zn), mercury (Hg), copper (Cu), iron (Fe), nickel (Ni), tin (Sn), cobalt (Co), arsenic (As), and aluminum (Al) [1]. Copper metal (Cu) is one type of heavy metal that is commonly found in industrial waste. Copper (Cu) metal is solid with a red-orange color. Copper metal that enters the waters becomes a heavy metal pollutant that is harmful to the environment, such as causing damage to the biodiversity of organisms and microorganisms and health, such as decreased kidney function and brain damage.

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In waters, Cu metal is found as a divalent cation (Cu2+) and in an environment with a low pH value or acidic pH [2]. Related to the problems that occur, technological development is urgently needed to treat heavy metal waste, especially in water. Based on the results of the latest reports that have developed, one way that can be done is to use the adsorption method. Adsorption is a process of absorption by certain solids of certain substances that occurs on the surface of solids because there is an attractive force on the surface of the solid. The advantages of this method are that it is simple and efficient and has a good impact on the environment [3].

Several types of chemical compounds that have been widely applied as adsorbents are titanium dioxide (TiO_2), iron oxide (Fe_3O_4), zinc oxide (ZnO) [1], silicon dioxide (SiO_2) [2], aluminum oxide (Al_2O_3) [4], and so on. ZnO particles are getting more attention because they have properties that can interact with other substances, biocompatibility, good affordability, long-term stability, good surface characteristics, non-toxic, non-toxic, and lower production costs [5]. Based on previous studies, ZnO particles have potential as heavy metal adsorbents [6]. The ability of ZnO particles as adsorbents is due to their large surface area, reactive surface, high diffusivity, and porous surface. The potential of ZnO particles as a heavy metal adsorbent can be functionalized to increase the performance of ZnO particles as an adsorbent for heavy metal waste. The form of functionalization carried out was coating on the surface of ZnO particles with tetraethyl orthosilicate (TEOS) compounds. TEOS is used as a source of silanol groups that act as a capping agent in adsorbent synthesis because it will have an impact on ZnO particles so that they have a large surface area and high metal absorption [7]. Synthesis of ZnO particles uses various methods, namely the sol-gel method [8], hydrothermal [9], solvothermal [10], spray pyrolysis [11], microwave-assisted [12], and coprecipitation [13]. In the research conducted by the author, the synthesis method used is the coprecipitation method. The coprecipitation method is a method of synthesizing inorganic compounds based on the precipitation of more than one substance together. The advantages of the coprecipitation method are that it has an easy process, is low cost, produces small and uniform particles, can control the physicochemical properties of ZnO, has a single-step, and has good production scalability [14]. In its application as an adsorbent for heavy metal Cu2+, a test was carried out by comparing the effectiveness of absorption of heavy metals by non-functionalized ZnO particles (P-ZnO) with functionalized ZnO particles (S-ZnO) in an acidic environment. The ability to absorb heavy metals will affect the adsorption capacity and removal percentage. It is hoped that with the functionalization of ZnO particles applied to heavy metal adsorption, it will be able to reduce heavy metal waste in the waters.

2 Experimental

2.1 Chemicals and Materials

The equipment used in this study was a set of titration tools, Erlenmeyer, porcelain cup, measuring cup, Beaker glass, spatula, stirring rod, watch glass, thermometer, mortar, pestle, plastic clip, aluminum foil, magnetic stirrer, universal indicator, indicator, hot plate, rubber bulb, measuring pipette, dropping pipette, glass funnel, evaporating cup, measuring flask, filter paper (Whatman No. 42), digital balance, vial tube, centrifugation device, oven, XRD (Pan Analytical Type E'xpert Pro), SAA (Tristar II Plus 3.01), FTIR (Shimadzu), SEM (FEI Type INSPECT-S50), PSA (Horiba-SZ 100z), and AAS (Thermo Scientific iCE 3000). The materials used in this study were zinc nitrate $Zn(NO_3)_2$ (Merck), 2M NaOH solution (Merck), distilled water, acetone (Merck), methanol (Merck), copper sulfate ($CuSO_4 \cdot 5H_2O$) (99%, Merck), dimethyl sulfoxide (DMSO) (Merck), and tetraethyl orthosilicate (TEOS) (Merck).

2.2 Procedure

2.2.1 Synthesis of ZnO Particles

A total of 9.47 grams of zinc nitrate $Zn(NO_3)_2$ dissolved in 25 mL of methanol solution in a round bottom flask. Furthermore, the precursor solution is heated to a temperature of 70 ℃, heating is done to speed up the reaction. When the temperature has reached 70 ℃, the precipitation titration is carried out using 2M NaOH until the pH of the precursor solution becomes 13. When the pH of the solution has become 13, it is continued by heating which is carried out above a hot plate at 70 ℃ for 2 hours. To introduce the silanol functional group, the procedure was modified at this stage by adding 2 mL of tetraethyl orthosilicate (TEOS) to the solution and continued heating under the same conditions. After the heating is done, do the stirring using a magnetic stirrer for 4 hours. Then centrifuged at 3000 rpm for 20 minutes, then washed with acetone and distilled water, and then filtered with filter paper. After filtering, and obtaining a white solid, it is dried in an oven with a temperature of 100 ℃ for 1 hour.

2.2.2 Characterization of ZnO Particles

The synthesized P-ZnO and S-ZnO particles were then characterized using an XRD instrument. XRD testing to analyze the crystal structure by comparing the diffraction peaks synthesized with a standard diffractogram from the Crystallography Open Database so that the successful synthesis of ZnO particles is known. Then proceed with FT-IR analysis to identify compounds based on the resulting infrared spectral pattern. Each compound has a unique infrared spectrum, which can be used to identify that compound in a sample. A test was carried out using Particle Size Analyzer (PSA) to determine the particle size and homogeneity of the particles. To determine the morphology of the particles, the analysis was continued using a Scanning Electron Microscope (SEM). Furthermore, to determine the surface area of ZnO particles is used Surface Area Analyzer (SAA).

2.2.3 Adsorption of Heavy Metal Cu^{2+} by ZnO Particles

Preparation of a standard calibration curve for $CuSO_4.5H_2O$ solution was made with various concentrations of 1 ppm, 2 ppm, 3 ppm, 4 ppm, and 5 ppm, the calculations are presented in. Next, the absorbance was measured using Atomic Absorption Spectrophotometry and a relationship curve was made between the concentration and absorbance. The particle adsorption ability test was carried out by adsorbate mass variations. To determine its adsorption capacity, 10, 13, and 16 mg of $CuSO_4 \cdot 5H_2O$ solids were in Erlenmeyer. The addition of P-ZnO and S-ZnO solids was carried out in each erlenmeyer as much as 20 mg and dissolved with 40 mL of distilled water. Shaking is done using a shaker at 225 rpm for 20 hours. Then centrifuged at 9000 rpm for 15 minutes. The resulting supernatant was filtered using filter paper Whatman no. 42. The supernatant obtained was then measured by atomic absorption spectroscopy.

3 Results and Discussion

3.1. Synthesis and Characterization of ZnO Particles

The synthesis of ZnO particles was carried out using $Zn(NO_3)_2$ the Zn. While the functionalization is performed using tetraethyl orthosilicate (TEOS), the use of tetraethyl

orthosilicate (TEOS) is used as a source of silanol groups (≡Si-OH). Tetraethyl orthosilicate (TEOS) which acts as a capping agent or a particle stabilizer that will cover the surface of partially formed crystals and will only provide a small space for the growth of these crystals, so that the resulting particle size will be smaller and uniform and will prevent agglomeration from occurring [16]. The synthesis process is carried out using the coprecipitation technique, this technique has the advantage of using low temperatures in the ZnO particle synthesis process so that the time required is relatively shorter and can produce smaller and more homogeneous particle sizes [15].

The synthesized P-ZnO and S-ZnO particles were characterized using several instruments, namely X-ray crystallography (XRD), Fourier-transform infrared spectroscopy (FT-IR), Surface Area Analyzer (SAA), Particle Size Analyzers (PSA), and Scanning Electron Microscope (SEM). Measurement of the absorption ability of particles against heavy metal Cu^{2+}, using the instrument atomic absorption spectroscopy (AAS). XRD was performed to analyze the crystal structure by comparing the synthesized diffraction peaks with standard diffractogram data Crystallography Open Database (COD no. 1011258). The results of the analysis were carried out using the Match! software and Qualx software, the results of the diffraction pattern analysis from XRD are shown in Figure 1 and Table 1. The S-ZnO XRD pattern shows that the particles have similar diffraction peaks with much noisier data and a broad peak between 2θ indicating the presence of silica on the surface. Based on the results of the XRD sample of the S-ZnO particles, it can be seen that the coating which was carried out as a form of functionalization did not change the position of the peaks and did not change the crystal lattice. This means that the coating process does not cause changes to the particles and emphasizes that functionalization only occurs on the surface of the particles.

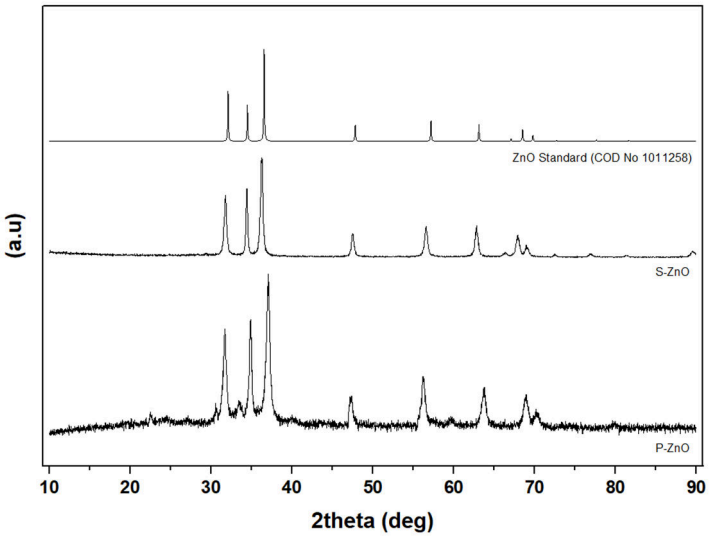
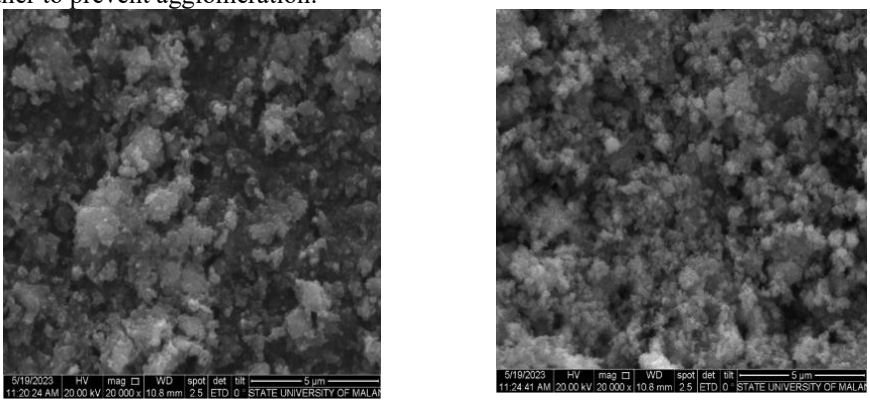


Fig. 1. Standard ZnO (COD no 1011258), P-ZnO and S-ZnO.

Table 1. Sharp peaks in diphragtogram diffractogram of synthesized ZnO particles.

Adsorbent	2θ (º)
Database (COD no. 1011258)	32,15º; 34,53º; 36,51º; 47,87º; 57,07º; 63,15º; 68,49º; and 69.73º
S-ZnO	32,18º; 34,53º; 36,48º; 47,90º; 57,11º; 63,16º; 68,51º; and 69.67º
P-ZnO	32,15º; 34,48º; 36,52º; 47,85º; 57,07º; 63,15º; 68,46º; and 69,70º

P-ZnO and S-ZnO particle shapes can be determined using a Scanning Electron Microscope (SEM). Both ZnO show similar morphological shape, round in shape, as shown in Figure 2. From the two pictures, there is a difference namely in Figure 2 (a). The particles form clumps or what is called agglomeration. When compared with Figure 2 (b), then there will be a difference in the occurrence of agglomeration in the two particles. Agglomeration can occur because no layer on the P-ZnO particles can bind the ZnO surface maximally. This causes ZnO to bond with each other so that the molecule will have a larger size (macro) [24]. Meanwhile, a different thing happens to the S-ZnO particles which have silanol groups whose job is to protect the surface of the particles, to prevent the ZnO particles from interacting with each other to prevent agglomeration.



(a) **(b)**

Fig. 2. Morphological image of synthesized (a) P-ZnO and (b) S-ZnO

Functionalization is carried out by adding tetraethyl orthosilicate (TEOS) which also plays a role capping agent able to control the size of the particle by covering the surface of the particle when an event occurs which is referred to as Ostwald ripening. Ostwald ripening is an event of the growth of large particles by combining smaller particles [17]. This event will occur when the particles are dispersed in a solution, where the dissolution of small particles in a solution will be stored again and then form a large mass or describe the formation of a large mass from a small mass. This can happen because the atomic particles are larger, and have higher stability. Therefore, atomic particles that have a smaller size will tend to gather into larger particles by lowering their energy. To lower its energy, small particles will escape and then diffuse which then attaches to larger particles. So that the large particles will get bigger, while the small particles will continue to shrink [18].

The functionalization carried out in the particle synthesis also affects the particle size. To determine the particle size, a test is carried out using an instrument Particle Size Analyzer (PSA). Based on the test results, the particle size is shown in Table 2.

Table 2. Particle size and polydispersity index synthesized ZnO particles

Particle Type	Particle Size(nm)	*Polydispersity Index* (PI)
P-ZnO	881,0	0,414
S-ZnO	803,3	0,345

Based on the table above, it shows that the functionalized particles (S-ZnO) have a smaller particle size when compared to non-functionalized particles (P-ZnO). This can happen because the P-ZnO particles and ZnO particles experience interactions with one another. This interaction occurs due to the absence of a layer protecting the particles. Unlike the case with S-ZnO particles which have a silanol layer that protects the particles from events Ostwald

ripening, thereby preventing interactions between ZnO particles and agglomeration can be avoided [19].

Further characterization was carried out using FT-IR spectroscopy. The peak at 470 cm-1 is associated with vibrations in the S-ZnO bond. When measurements were made on functionalized particles (S-ZnO) many peaks were produced. The appearance of several peaks at certain wave numbers can be attributed to the presence of bending and stretching vibrations originating from the -OH groups of Zn-OH and Si-OH (silanol groups). To determine the presence of silica in ZnO particles, it can be seen from the wave numbers at 787-802 cm-1 and 1072-1126 cm-1, as the Si-O-Si group. Besides being seen from the presence of Si-O-Si groups, it can also be seen from the presence of Si-O-H groups which are shown in the band 810-960 cm-1. The spectrum that occurs is not very visible due to overlapping due to stretching vibrations from other groups such as the Si-O-Si groups [20]. The results of the FT-IR analysis can be seen in Figure 3.

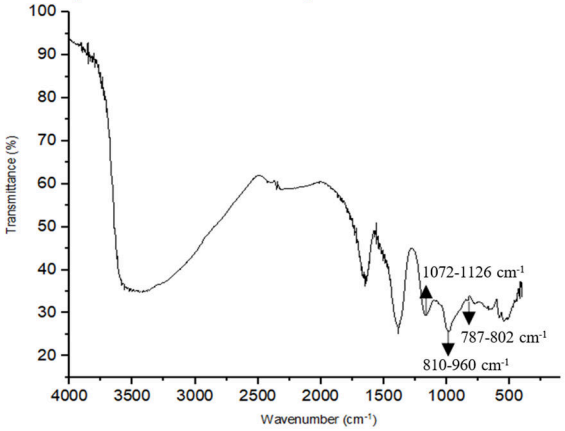


Fig. 3. FT-IR spectrum of S-ZnO synthesis results

The surface area and pore size of the particles can be measured using analysis Surface Area Analyzer (SAA), this analysis was carried out to determine the relationship of surface area and the ability of ZnO particles to adsorb heavy metal Cu2+. Results of the analysis Surface Area Analyzer (SAA) are given in Table 3.

Table 3. Data surface area analyzer (SAA) particle synthesis results

Particle type	Surface Area (m^2/g)
P-ZnO	19,5604
S-ZnO	30,8383

Based on the results of the previous analysis the analysis Particle Size Analyzer (PSA) concluded that the particle size of the S-ZnO particles has a smaller size. Changes in particle size will greatly affect the physical and chemical properties. The smaller the particle size, the larger the surface area ratio compared with similar particles, so the reactivity also increases. Based on this, there is a correlation between particle size and surface area. The synthesized particles proved that S-ZnO particles have a small size with a large surface area, while P-ZnO particles have a larger size with a small surface area. The smaller the particle size, the better the adsorption properties. This is due to an increase in the surface area of the adsorbent which has an impact on increasing the attractive force between the adsorbent and the adsorbate so that the heavy metal Cu2+ absorbed will be more and more. When used as a heavy metal adsorbent, it means that more and more heavy metals are attached to the surface of the adsorbent [29].

3.2. Adsorption of Heavy Metal Cu2+ with Particle Results of Synthesis

Adsorption is a process in which an absorption event is carried out by a certain solid to a certain substance that occurs on its surface, this can occur due to the attractive force of attraction between a molecule or atom that occurs on the surface. The adsorbents used in this study were ZnO particles that had and had not been functionalized. To determine the adsorption capacity of P-ZnO and S-ZnO particles, a variation of the mass of the adsorbate was carried out using 10, 13, and 16 mg of $CuSO_4 \cdot 5H_2O$ solids, this is done to know the amount of Cu^{2+} capable of accumulating on the surface of the adsorbent particles. The mass variation of the adsorbate was carried out by preparing a solution containing $CuSO_4 \cdot 5H_2O$ solids 10, 13, and 16 mg of O with an adsorbent mass of 20 mg of P-ZnO and S-ZnO particles which were then made in an acidic atmosphere with a pH of 4, then stirring was carried out shaker at 225 rpm for 20 hours. Then centrifuged at 9000 rpm for 15 minutes. The resulting supernatant will be filtered using filter paper. Absorption Spectrophotometry will then measure the supernatant results obtained.

Based on the research results, it is known that increasing the mass of the adsorbate causes an increase in adsorption capacity. A mass of 20 mg adsorbent has absorbed heavy metal Cu2+ maximally because the mass of the particles is also increasing. Based on the data obtained, there is an increase in the adsorption capacity which is directly proportional to the increase in the concentration of heavy metal Cu2+. This happens because with the increasing concentration of heavy metal Cu2+, more ions will be Cu2+ which can be bound to the surface of the adsorbent, so that the adsorption capacity will certainly increase [25]. Calculation results are presented in Figure 4. When compared between the two types of particles used, it can be seen that the ability of the S-ZnO particles have a better adsorption ability than the P-ZnO particles. The percentage of heavy metal reduction Cu2+ can be calculated by reducing the initial concentration of the solution with the final concentration and then percentage. This method is considered effective in determining the adsorption ability of an adsorbent. The results of the calculation of the adsorption capacity and the percentage of removal are presented in Table 4.

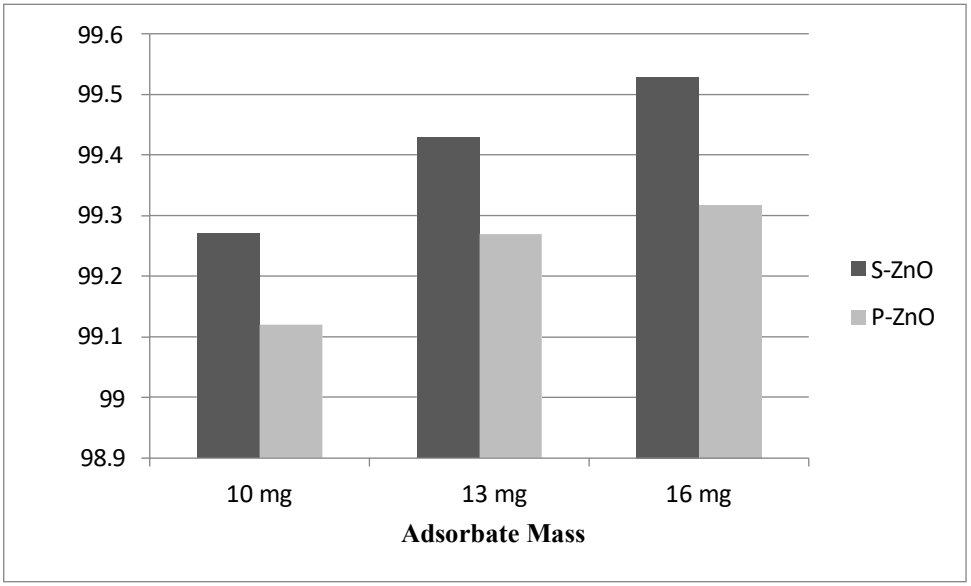


Fig. 4. Percentage of adsorption of heavy metal Cu2+ adsorbate mass variation.

Table 4. Calculation of adsorption capacity and adsorption percentage of heavy metal Cu2+.

Adsorbent type	Adsorbate Mass (mg)	Adsorption Capaciy (mg/g)	Adsorption (%)
	10 mg	125,882	99,120
P-ZnO	13 mg	163,794	99,269
	16 mg	202,111	99,317
	10 mg	126,073	99,270
S-ZnO	13 mg	164,058	99,429
	16 mg	202,541	99,528

The results of the calculations that have been carried out show that the adsorption capacity of S-ZnO has better results when compared to the adsorption capacity of P-ZnO. The results of the highest adsorption capacity of S-ZnO were at 16 mg adsorbate mass, namely 202.541 mg/g, whereas with the same adsorbate mass P-ZnO had an adsorption capacity value of 202.111 mg/g. The insignificant difference in results between the two types of adsorbents is thought to be due to the not much use of tetraethyl orthosilicate (TEOS) in functionalization. Based on previous research literature [23], the adsorption capacity value of this study was considered better under acidic conditions.

The absorption that occurs is influenced by several factors, including the type of adsorbent, the surface area of the adsorbent, the type of adsorbate, the concentration of the adsorbent and adsorbate, and temperature. Due to these factors, an absorption event that absorbs a substance with a substance that may not have the same adsorption pattern. Three types of adsorption isotherms are commonly used, namely the Langmuir, Freundlich, and Temkin adsorption equations [21].

Particles that have been synthesized and characterized are then tested for their adsorption ability with various concentrations of the heavy metal Cu2+. The results that have been obtained are then entered into the equation of a straight line so that the value of R is obtained2 served in Table 5. The Langmuir, Freundlich, and Temkin isotherm curves are given in Figure 5 and Figure 6.

Table 5. R2 value on Isothermal Models Langmuir, Freundlich, dan Temkin

		Nilai R^2	
Adsorbent	Langmuir isotherm	Freundlich Isotherm	Temkin isotherm
P-ZnO	0,9689	0,9893	0,9987
S-ZnO	0,7799	0,9446	0,9714

Based on R2 value presented, it can be concluded that the P-ZnO and S-ZnO particles have the Temkin adsorption isotherm model, which assumes that the adsorbate forms a multilayer layer on the surface of the adsorbent, where the amount of adsorbed tends to reach a saturation limit when the concentration of adsorbate in the solution increases. The Temkin adsorption model takes into account the effect of adsorbate interactions in chemical adsorption processes. Temkin's adsorption isotherm assumes that the adsorption of all molecules on the surface of the adsorbate will decrease linearly with the number of interactions between the adsorbate covering the surface. The Temkin adsorption model is more suitable for physical adsorption cases or cases where the change in adsorption energy tends to be more linear as the surface covering of the adsorbed molecules increases [22].

The adsorption mechanism can be known in another way, namely by calculating the isosteric heat of adsorption. Based on the calculation results, P-ZnO has a q value of -38.415 kJ/mol, and S-ZnO has a q value of -4.315 kJ/mol. The difference in the values of the two adsorbents indicates that there are differences in the strength of the interaction between the surface of the adsorbent and the adsorbate. The higher the value of q indicates that the adsorption that

occurs is stronger. Based on the calculation results, it can be concluded that the value of the S-ZnO adsorbent has a greater value which indicates a stronger interaction between the adsorbent and the adsorbate, so that the adsorption process tends to be more stable and takes place strongly [28].

The calculation is continued by calculating the ΔH and ΔS values to further determine the adsorption mechanism. Based on the equation that has been presented in Figure 7, we get the regression equation which shows the value of ΔS and the value of ΔH. The ΔH value indicates that the adsorption is exothermic or endothermic. The ΔH value of P-ZnO is 12.341 kJ/mol and the ΔH value of S-ZnO is 7.213 kJ/mol, with positive results indicating that the reaction is endothermic. The ΔS value obtained from P-ZnO has a value of 0.087 kJ/mol.K and S-ZnO has a value of 0.068 kJ/mol.K. Gibbs energy calculations are also carried out to find out the spontaneity of the reactions that occur. To calculate the Gibbs energy value, the equation is used:

$$\Delta G^{o} = \Delta H - T\,\Delta S \quad (1)$$

Based on the calculations that have been done, the -ZnO particles have a ΔG^{o} value of -14.033 kj/mol, while the S-ZnO particles have a ΔG^{o} value of -13.401 kJ/mol. Based on the literature, the S-ZnO and P-ZnO particles have a negative ΔG^{o} value indicating that the adsorption occurs spontaneously and is thermodynamically beneficial. Negative values indicate that the system energy will decrease during adsorption, so that molecules or particles will tend to be attracted to interact with the surface of the adsorbent [27]. Based on the results obtained, the P-ZnO and S-ZnO particles have a spontaneous adsorption mechanism obtained from the negative ΔG^{o} value.

The reactions that occur in P-ZnO and S-ZnO are endothermic as indicated by the positive ΔH value. A positive ΔH value indicates that the reaction releases energy into the surrounding environment [26]. When the value of ΔG^{o} is negative, it explains that the energy is spontaneous and will release free energy in the form of heat or other energy. The insignificant difference in ΔG^{o} between the two particles explains that the two reactions have a strong tendency to move towards the desired reaction or to be spontaneous. The more negative the ΔG^{o} value, the more likely the reaction will take occur spontaneously [27]. The value of ΔH on both particles shows that the value of the S-ZnO particle has a greater value, this shows that S-ZnO tends to release a greater amount of heat into the environment during the reaction when compared to P-ZnO. Based on the results obtained, the ΔS value of the two adsorbents is positive, indicating that the adsorption entropy indicates the effectiveness of these adsorbents for heavy metal ions. A high value of ΔS indicates a higher disorder, which causes the spontaneity of the reaction to increase, which is favorable for adsorption [25]. The following presents the value of the gibbs energy, ΔH and ΔS of the P-ZnO and S-ZnO particles at Table 6.

Table 6. Differences in the values of ΔG^{o}, ΔH and ΔS in P-Zno and S-ZnO particles

Adsorbent type	ΔG^{o} (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
P-ZnO	-14,033	12,341	0,087
S-ZnO	-13,401	7,213	0,068

4 Conclusion

Synthesis of P-ZnO and S-ZnO particles has been successfully carried out using the coprecipitation method with functionalization in the form of the addition of tetraethyl orthosilicate (TEOS) as a source of silanol groups which are used as capping agent. The test results showed that the adsorption capacity of P-ZnO was 202.11 mg/g and S-ZnO was 202.54 mg/g with an adsorbent mass of 16 mg. The adsorption isotherm model of P-ZnO and S-ZnO follows the Temkin model, with heat of adsorption on P-ZnO particles of 1.35 x 10^{-3}

kJ/mol and S-ZnO particles of 7.67 x 10^{-3} kJ/mol, as well as the interactions that occur between the adsorbent and the adsorbate follow the physical interaction mechanism. P-ZnO particles have ΔG values of 14.00 kJ/mol and ΔS of 0.09 kJ/mol.K while S-ZnO particles have ΔG values of -13.401 kJ/mol and ΔS of 0.07 kJ/mol. K which indicates the occurrence of spontaneous adsorption. The value of ΔH P-ZnO was 12.34 kJ/mol and S-ZnO was 7.21 kJ/mol indicating that the reaction was endothermic.

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