

Influence of Calcination Temperatures on Gunningite-Based Gelatin Template and Its Application as Ibuprofen Adsorption

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Abstract: Gunningite has been successfully synthesized using the soft template method with the Pluronic F127-gelatin template. Gunningite was calcined at diverse temperatures of 500, 600, and 700 °C for 12 h and characterized by XRD, SEM, and FTIR. A UV-Vis Spectrophotometer measured the adsorption capacity of Gunningite against ibuprofen. The XRD results showed that the crystal sizes of Gunningite decreased from 35.41 to 28.31 nm with the increasing calcination temperature from 500 to 700 °C. Besides, the crystallinity degrees also increased from 49.94% to 56.13% as calcination temperature increased from 500 to 700 °C. The Gunningite formed aggregates in the form of tiny particles that merge and experience agglomeration. The FTIR spectra of the Gunningite samples demonstrated the functional groups -OH, Zn-OH, Zn-O-Zn, and gunningite vibrations. The maximum adsorption capacities of Gunningite to adsorb ibuprofen were 233.161 mg g⁻¹ (500 °C), 219.543 mg g⁻¹ (600 °C), and 227.033 mg g⁻¹ (700 °C). The kinetic model of Gunningite on the ibuprofen adsorption followed the kinetic model of Ho and McKay.

Keywords: zinc sulfate (Gunningite); gelatin; temperature calcination; characterization; adsorption ibuprofen

■ INTRODUCTION

Gunningite (ZnSO₄·H₂O) is a stable, hydrated crystalline state with solid hydrogen bond interactions between ZnSO₄ and water molecules as a monohydrate [1]. It has been considered a potential material for heat storage, thermochemical storage, important zinc supplement, and storage of related drugs [2]. Gunningite is also very promising because it is an inexpensive, sustainable source, easy to synthesize, has an extraordinary ability to adsorb various molecules, especially drug molecules, and can store the drug in a delivery system [3]. However, the water molecules in the hydrates either coordinate with zinc ions or form hydrogen bonds; both have essential impacts on the structure, and the chemical and physical properties of a material, including Gunningite [1-3]. One factor affecting crystalline forms and interaction between water molecules and zinc ions of Gunningite is calcination temperature. As reported, the different crystalline forms

of Gunningite can affect the stability, homogeneity, and drug safety if it is used for drug storage [1]. Gunningite was rarely used after synthesis at variation high-temperature treatment. The effect of high-temperature treatment is needed to observe the structural change that can contribute to the adsorption performance. In this work, additional insights into the crystallinity, particle size distribution and functional group of Gunningite at calcination temperature 500–700 °C are observed, highlighting the role of calcination temperature. For this, gunningite synthesis at different calcination temperatures will be studied to gain insight into the role of calcination temperature in the gunningite structure ad adsorbent of ibuprofen.

Analgesics is one drug type, including ibuprofen, for relieving symptoms of inflammation, acute pain, and fever [4]. The low solubility and short half-life lead to low bioavailability of ibuprofen which has adverse effects such as dyspepsia and diarrhea [5]. However, by

embedding drugs in a stable particle system, the bioavailability of ibuprofen could be enhanced, and its adverse effects could also be alleviated [6-9]. The loading of ibuprofen on Gunningite has never been reported in a previous paper, especially with variations in calcination temperatures. This work will focus on the loading of ibuprofen on Gunningite via simple adsorption and the effect of calcination temperatures on adsorption capacity as the first work for further drug loading study.

■ EXPERIMENTAL SECTION

Materials

Pluronic F127, ethanol, gelatin, ibuprofen (2-[4-(2-methylpropyl)phenyl]propanoic acid), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and *n*-hexane were obtained from Sigma Aldrich and used without prior pretreatment.

Instrumentation

The characterizations of the synthesized Gunningite samples involved several instruments, including Small angle X-Ray Diffraction (SAXRD) XRD/MAX-2550 HB/PC (Rigaku Co., Tokyo, Japan), Scanning Electron Microscopy (SEM) (JEOL JMS-700), and Fourier Transform Infrared (FTIR) with spectra recorded with a Bruker Vertex 70 spectroscope. The SEM test was performed at a voltage of 15.0 kV with a magnification of 10.000×. Meanwhile, the FTIR analysis was done at a wavelength of 500–4000 cm^{-1} .

Procedure

Synthesis of zinc sulfate (Gunningite)

Synthesis of Gunningite was initiated by dripping ethanol into Pluronic F127 with a burette (1 drop per 20 s) at room temperature. It was kept from the air during dripping by making a drip hole in the crepe and covering the mouth with a mask. After the ethanol was dripped, it was added with gelatin and stirred for 60 min. This solution was then called Solution A. Next, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was added to Solution A and stirred for 24 h while covering it with a wrap so that no air entered. The mixture was divided into three parts and put in a hydrothermal reactor while the oven was set at 100 °C for 24 h and then cooled. After that, each mixture was filtered, and the solids were dried in the oven at 100 °C for 24 h. They were

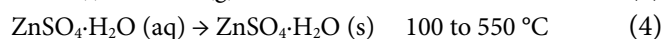
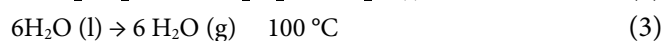
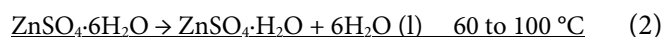
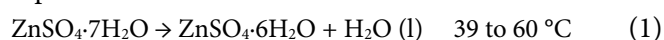
then calcined with temperatures of 500, 600, and 700 °C, respectively, for 12 h. Finally, the solids were stored in closed and clear bottles. Further, the samples were labeled as Gunningite-500 °C, Gunningite-600 °C, and Gunningite-700 °C for each varied calcination temperature.

Ibuprofen adsorption

Ibuprofen was dissolved in hexane as a solvent to obtain 100 mL ibuprofen solution with a concentration of 100 ppm. Next, 50 mL of the 100 ppm ibuprofen solution was taken and put in a beaker. Twenty milligrams of the synthesized Gunningite were added while stirred at room temperature (25 °C). Finally, 1 mL of the sample solution was taken every 5 min to be analyzed with UV-Vis spectroscopy at 272 nm.

■ RESULTS AND DISCUSSION

The chemical reactions of the Gunningite structures formation in the reaction system can be represented as follows:



During the Gunningite synthesis, it involves several functional groups as a result of the interaction between precursors and gelatin. These functional groups persist and are helpful for adsorption after the synthesis. This research used the F127 template with hydrophilic and hydrophobic parts acting as surfactants and gelatin as the co-template. Gelatin is an organic species that acts as a particle-forming [10-12]. Besides, ethanol is an organic compound with a hydroxyl group (OH). The OH group will bind to the hydrophilic part of the Pluronic F127. Meanwhile, like protein, gelatin generally contains amine groups with high affinity, which will interact strongly with ethanol and Pluronic F127. The interaction in Pluronic F127 with hydroxyl or amino acids will enhance the stability of Pluronic F127 [4,13].

Next, hydrothermal treatment at 100 °C was carried out before calcination to improve the mechanical strength of the Pluronic F127-gelatin template. The involvement of gelatin as an organic species can improve

the binding affinity between the Gunningite source and other chemical functional groups during the synthesis process. Then, Zn^{2+} from zinc sulfate heptahydrate will enter and interact with hydrophilic F127-gelatin, and sulfate will interact with the hydrophobicity of Pluronic F127. The heptahydrate of the Zn source has been decomposed by heat treatment at 100 °C before aging (Eq. (1-4)). Afterward, the sample enters the hydrothermal reactor to grow various forms of Gunningite solid structures. All elements except zinc sulfate monohydrate have been successfully decomposed by high-temperature treatment during calcination. XRD, SEM, and FTIR confirmed all the gunningite samples.

XRD analysis on Gunningite aims to identify its crystal structure and crystallinity degree. Fig. 1 displays the diffraction patterns of Gunningite with different calcination temperatures. Each sample was treated with the same calcination time of 12 h. The patterns from all synthesized samples could be used to estimate the crystal size through the Scherrer equation as Eq. (5).

$$D = \frac{k\lambda}{B\cos\theta} \quad (5)$$

Materials with larger crystal sizes have a sharp diffraction pattern, while materials with smaller ones experience peak widening [14]. This widening can be used to measure the crystallinity degree of a material with the Debye-Scherrer equation. The crystal size and the crystallinity degree of each synthesized Gunningite sample can be seen in Table 1.

Based on Table 1, although the difference is not significant, the crystal sizes of Gunningite are smaller as the calcination temperature increases. The smallest crystal size is 28.31 nm at 700 °C, compared to Gunningite crystal sizes synthesized at 500 °C and 600 °C, which are 35.41 nm and 31.30 nm, respectively. Nevertheless, the Gunningite sample at 700 °C has the highest crystallinity

degree of 56.13%. It then decreases from 53.40% to 49.94% at the calcination temperatures 600 and 500 °C. Thus, the crystallinity degree of a compound will be greater with increasing calcination temperature. Finally, based on the data, it is known that the calcination temperature affects the crystal structure formed, where the higher calcination temperature induces a better crystal structure [14-15]. It happens because calcination decomposes impurities from compounds by heating but still below the compounds' melting point. Therefore, if the temperature is higher, the chemical bonds in a compound will be more tenuous. At a specific temperature, the bonded atoms will move freely, causing chemical bonds to break. Based on this, it can be said that the higher calcination temperatures lead to a purer compound. Hence, the Gunningite sample at 700 °C has the smallest crystal size and the highest crystallinity degree. In other words, the higher calcination temperature improves crystallization.

Furthermore, the crystals of a powder compound would be perfectly formed at a calcination temperature of

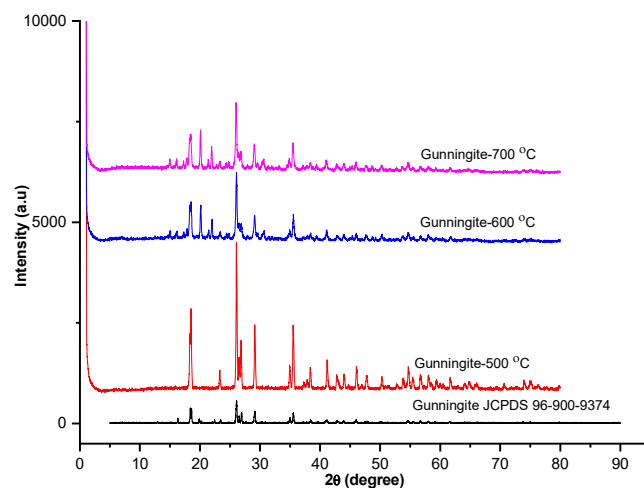


Fig 1. Gunningite diffraction patterns with the variation of calcination temperatures

Table 1. Crystallinity degree (% C) and crystal size (CS) of Gunningite

Sample	SCF	SFW	% C	CS (nm)	P (μm)
Gunningite-500 °C	4981.01	9973.43	49.94	35.41	2.40
Gunningite-600 °C	3328.76	6233.49	53.40	31.30	4.06
Gunningite-700 °C	4070.73	7251.79	56.13	28.31	4.62

SCF = Size Crystal Fraction, SFW = Size Fraction whole, % C = crystallinity, CS = Crystallite Size; all item determined by Scherrer equation; P = particle size determined by SEM

around 800 °C. However, in this condition, the bonds between the powder particles are not strong and easily separated. However, on the contrary, the calcination treatment below 750 °C indeed leads to imperfect crystal formation.

Characterization via SEM is to determine the morphology of the synthesized Gunningite. Fig. 2 presents the SEM images of the synthesized Gunningite samples, which have an irregular flower-like morphology. The observed characteristics exhibit that Gunningite aggregates in the form of small particles merging and agglomerating with a size range of 2–4 μm . This morphological irregularity is supported by the XRD results, where several peaks appear with weak intensity. It indicates that the crystallinity degree is low since the higher intensity demonstrates a more crystalline sample. The increasing calcination temperature from 500 °C to 700 °C enlarges the particle size from 2.4 to 4.6 μm . It implies that particle size becomes larger by 1 μm every 100 °C during calcination due to the crystal growth and agglomeration. Agglomeration also occurs in the Gunningite samples because of decreasing surface tension of the P127-gelatin-zinc precursors during a long time heating process. It is because of a large amount of energy on the sample surface as grain growth phenomenon to

obtain material stability.

Characterization employing FTIR aims to identify the main functional groups in the synthesized Gunningite qualitatively. FTIR spectra in Fig. 3 show that solid and broad absorptions at about 3170 cm^{-1} are stretching vibrations of the OH group of free H_2O as a monohydrate molecule in Gunningite. Another water molecule in the zinc sulfate layer is revealed in 1637 cm^{-1} as H-O-H bending vibration. The stretching vibration at 1000–1200 cm^{-1} is due to the sulfate group containing symmetric and asymmetric vibrations of S=O at 1056

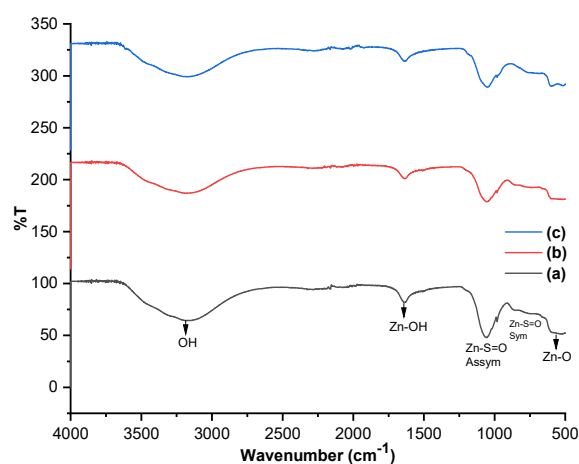


Fig 3. FTIR spectra of (a) Gunningite-500 °C, (b) Gunningite-600 °C, and (c) Gunningite-700 °C

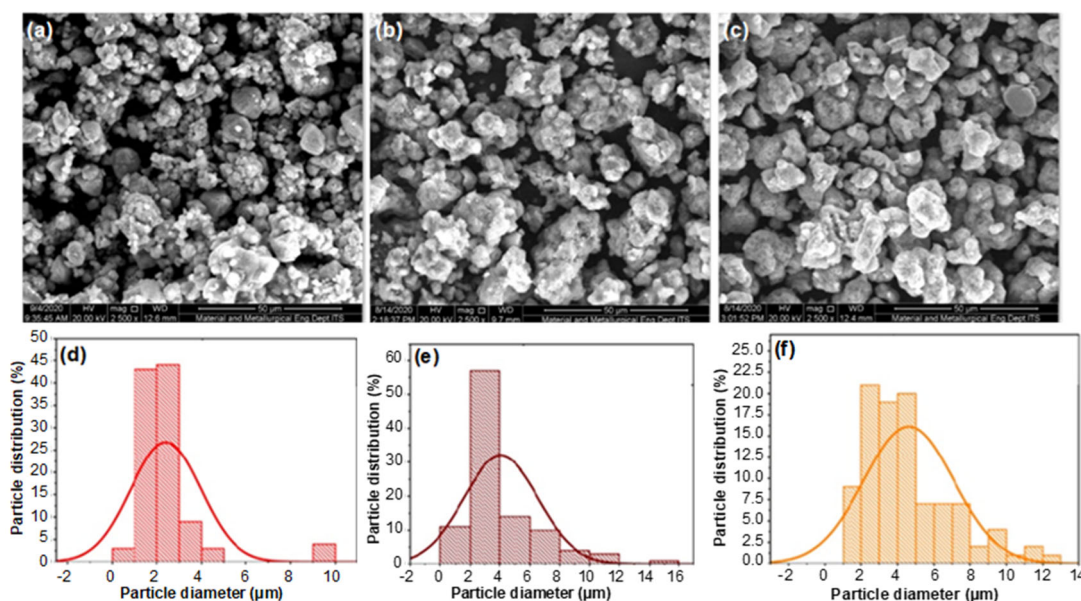


Fig 2. The SEM images (5000 \times magnification) and particle size distribution of (a, d) Gunningite-500 °C; (b, e) Gunningite-600 °C; and (c, f) Gunningite-700 °C

and 1200 cm^{-1} , respectively. Both peaks confirm the S=O bond strength in the sulfate group via electrostatic attraction with hydrogen bonds and zinc ions as S=O-H-O-Zn form. Meanwhile, the existence of Gunningite is exhibited by the peak at 521.81 cm^{-1} as Zn-O form. All these results are in line with the previous research [16].

Based on the FTIR analysis, the -OH group presents due to the attendance of water molecules adsorbed in the Gunningite surface. It makes Gunningite hydrophilic and could be a significant factor for drug adsorption. At the Gunningite-500 °C, the results exhibited that the OH group content was the highest compared to the other samples. Therefore, it proves that the higher calcination temperature could decrease the OH content in the sample and affect its mass. All samples with calcination temperature variations reveal the presence of Zn-O-Zn absorption and Gunningite vibrations. It means that the synthesis of Gunningite has been successfully conducted in this study.

Ibuprofen Adsorption

The test results of ibuprofen adsorption on Gunningite with the UV-Vis spectroscopy were made into a calibration curve for the relationship between concentration and absorbance. The adsorption equation during the absorption process was calculated based on the adsorption capacity equation as Eq. (6).

$$q_t = \left(\frac{C_o - C_t}{W} \right) \times V \quad (6)$$

C_o is the initial concentration of adsorbate (mg/L), C_t is the concentration of adsorbate (mg/L) at time t (min), W is the mass of adsorbent (g), V is the volume of adsorbate (L), q_t is the adsorption capacity at time t (min) (adsorption capacity at equilibrium was obtained experimentally and graphically). The relationship between concentration at equilibrium (C_e), adsorption capacity (q_t), and equilibrium time (t_e) are shown in Table 2.

Table 2 and Fig. 4 reveal the relation between calcination temperature and maximum adsorption capacity of Gunningite with ibuprofen adsorption (q_t max). It can be identified that the concentrations at the equilibrium point at 500, 600, and 700 °C are 6.175, 12.157, and 9.085 mg L^{-1} , respectively. Meanwhile, the adsorption capacities are

Table 2. The relationship between maximum adsorption capacity and equilibrium time

Sample	C_e	q_t max (mg g^{-1})	t_e (min)
Gunningite-500 °C	6.175	233.161	55
Gunningite-600 °C	12.157	219.543	10
Gunningite-700 °C	9.085	227.033	55

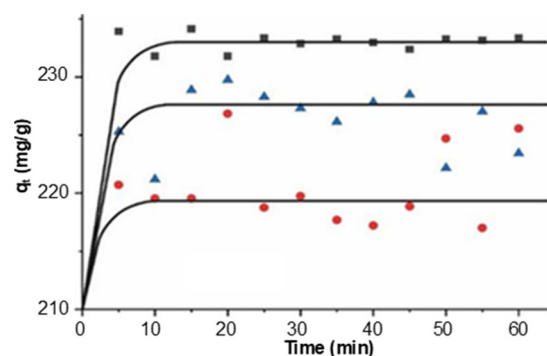


Fig 4. Adsorption performance of Gunningite-500 °C (black box), Gunningite-600 °C (red circle), and Gunningite-700 °C (blue triangle)

233.161, 219.543, and 227.033 mg g^{-1} for 500, 600, and 700 °C, respectively. Several factors influence the adsorption kinetics model during adsorption. Based on the order, there are two kinds of adsorption kinetics models: the first-order adsorption kinetics model by Lagergren and the pseudo-second-order adsorption kinetics model by Ho and McKay.

Further, the equation formula for the adsorption kinetics model was used to achieve the objectives of this study, namely to determine the first-order adsorption kinetics model according to Lagergren and the pseudo-second-order adsorption kinetics model according to Ho and McKay on the ibuprofen absorption by Gunningite. The determination of the adsorption kinetics model is a further analysis of measurements using a UV-Vis spectrophotometer. Fig. 5 demonstrates the first-order kinetic model by Lagergren. While the pseudo-second-order adsorption kinetics model by Ho and McKay is presented in Fig. 6.

Based on Fig. 5, the linear equation of a) Gunningite-500 °C is $y = -0.0097x + 0.1257$ with $R^2 = 0.2189$; b) Gunningite-600 °C is $y = -0.0002x + 0.0553$ with R^2 of 0.0008; c) Gunningite 700 °C is $y = -0.0014x + 0.1818$ with R^2 of 0.005. The equations have unsuitable linearity

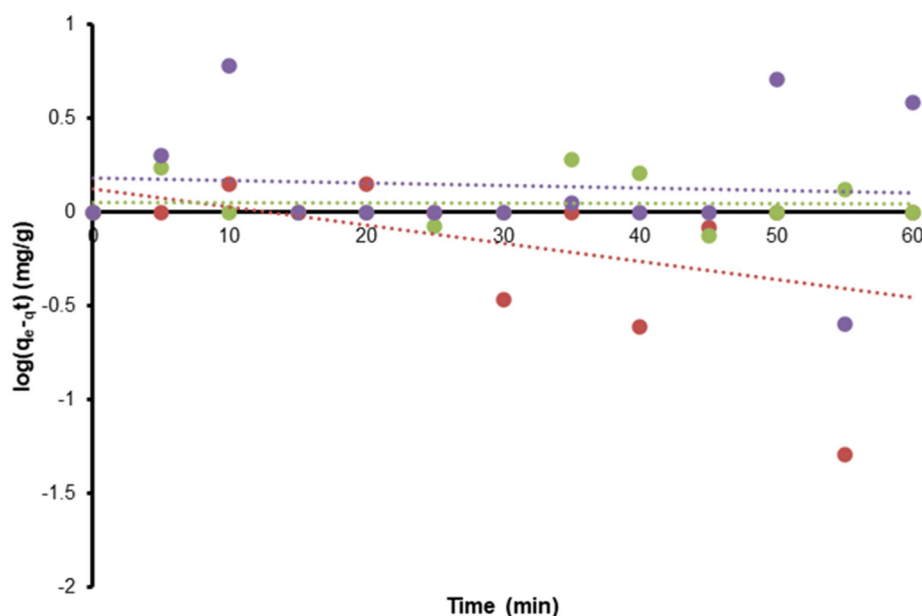


Fig 5. Graph of the relation between t and $\log (q_e - q_t)$ according to Lagergren's pseudo-first-order kinetics model of Gunningite calcined at 500 °C (red), 600 °C (purple), and 700 °C (green)

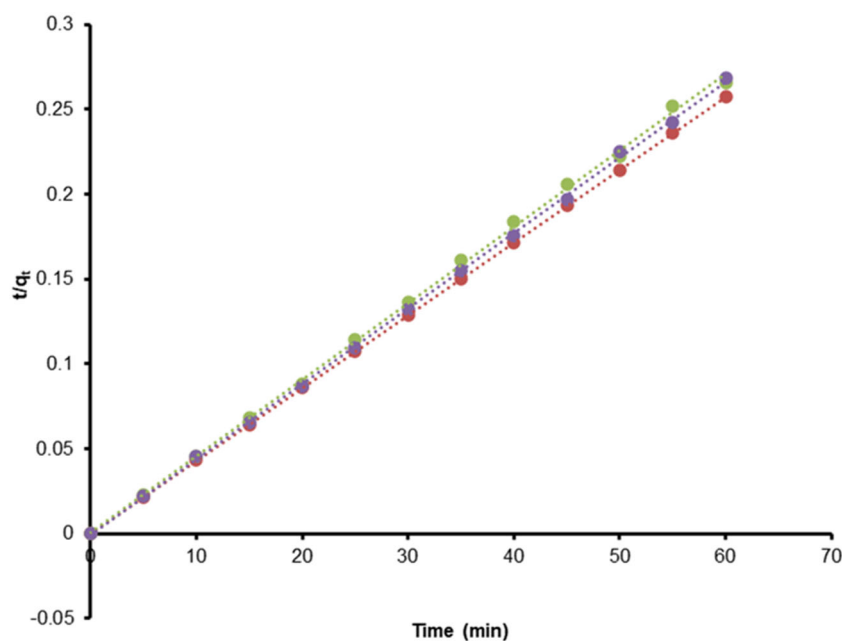


Fig 6. Graph of the relation between t and Q_t according to Ho and McKay's pseudo-second-order kinetic model of Gunningite calcined at 500 °C (red), 600 °C (purple), and 700 °C (green)

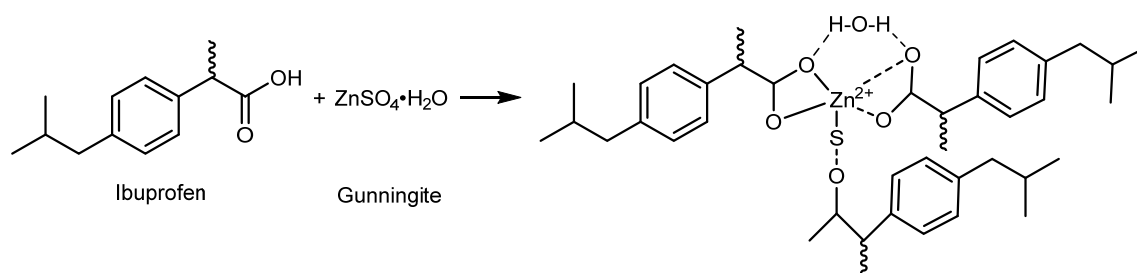
because the R^2 values are far from 1.

As seen in Table 3 and Fig. 6, the linearity levels of the Gunningite-500 °C, Gunningite-600 °C, and Gunningite-700 °C using Ho and McKay's adsorption kinetic models are 0.999, 0.998, and 0.9996, respectively. While with Lagergren's adsorption kinetics model, the

linearity levels are 0.2189, 0.0008, and 0.005 for the Gunningite-500 °C, Gunningite-600 °C, and Gunningite-700 °C, respectively. Furthermore, the adsorption capacity values based on Ho and McKay's adsorption kinetics model are closer to the adsorption capacity of the research results, namely 233.21, 219.61, and 227.286 mg g^{-1} . From

Table 3. Linear equation data of Lagergren's pseudo-first-order kinetic model and Ho and McKay's pseudo-second-order

Samples	Kinetics model	Y	R ²	q _e
Gunningite-500 °C	Lagergren	-0.0097x + 0.1257	0.2189	1.33
	Ho and McKay	0.0043x 8E-05233.21	0.999	233.8
Gunningite-600 °C	Lagergren	-0.0002x + 0.0553	0.0008	0.33
	Ho and McKay	0.0045x 0.0008+	0.998	219.61
Gunningite-700 °C	Lagergren	+ 0.1818-0.0014x	0.005	1.52
	Ho and McKay	0.0044x -0.0008	0.9996	227.286

**Fig 7.** Ibuprofen – Gunningite interaction

these data, it can be concluded that the adsorption patterns of ibuprofen in all samples are appropriate and follow the adsorption kinetics of the Ho and McKay models in pseudo-second-order. Several studies also support that the pseudo-second-order is most suitable for the adsorption of ibuprofen [4,17-18].

The highest or maximum adsorption performance is at Gunningite-500 °C because it contains a rich OH group on the Gunningite surface, which increases the interaction between the Zn²⁺ metal ions and the -OH group on ibuprofen. The chemical binding of several ions to the surface involves ion exchange between the adsorbent surface and the adsorbate (Fig. 7). Not only the rich of OH in the Gunningite surface but also the low degree of crystallinity at calcination 500 °C may have a positive effect on increasing ibuprofen adsorption due to the high degree of the amorphous phase.

Gunningite compounds act as an adsorbent for ibuprofen adsorption, which is synthesized with a hydrophilic colloid system to interact with water molecules easily. Numerous hydroxyl groups are present on the surface of Gunningite-500 °C, and zinc ions have a strong affinity for the hydroxyl group in ibuprofen [19-20]. The process of ion exchange comprises the hydroxyl group and Zn²⁺ metal ions. In a chemical reaction, the

interaction of the hydroxyl group with metal ions allows for the development a coordination complex. The hydroxyl group's O atoms have a pair of unpaired electrons that zinc metal ions can occupy.

■ CONCLUSION

Zinc sulfate (Gunningite) has been successfully synthesized via the soft template method with calcination temperatures variation of 500, 600, and 700 °C. From the XRD results, the crystal sizes of Gunningite-500 °C, Gunningite-600 °C, and Gunningite-700 °C were 35.41, 31.30, and 28.31 nm, respectively, while the crystallinity degrees were 49.94, 53.40, and 56.13%, respectively. Based on the SEM results, the surface morphology of Gunningite samples aggregated in the form of small particles fused with a heterogeneous surface. Furthermore, the results of the FTIR demonstrated several functional groups of -OH, Zn-OH, Zn-O-Zn, and Gunningite vibrations. For the ibuprofen adsorption test results, the maximum adsorption capacities of Gunningite-500 °C, Gunningite-600 °C, and Gunningite-700 °C against ibuprofen compounds were 233.161, 219.543, and 227.033 mg g⁻¹, respectively. Finally, the kinetic model of Gunningite on the ibuprofen adsorption followed the kinetic model of Ho and McKay.

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■ AUTHOR CONTRIBUTIONS

Conceptualization, M.U. and M.A.P.A.; methodology, M.U.; validation, M.U. and M.A.P.A.; formal analysis, M.U.; investigation, M.U.; data curation, M.A.P.A. and M.U.; writing-original draft preparation, M.A.P.A. and M.U.; writing-review and editing, M.U.; visualization, M.U.; supervision M.U.; and funding acquisition, M.U. All authors have read and agreed to the published version of the manuscript (Maria Ulfa as M.U. and Muhammad Ari Purnama Ali as M.A.P.A.).

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