Effect of CaO/SiO₂ compositions on the structure formation of mesoporous calcium silicate (CaSiO₃) composite particles as adsorbent for organic dye removal

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Abstract. The primary objective of this paper was to synthesize a calcium silicate (CaSiO₃) and investigate the effect of CaO/SiO₂ compositions on the structure formation of synthetic material. CaSiO₃ was prepared through the solid-state method using CaO from chicken eggshells and commercial SiO₂ powder as starting material. To investigate the effect of CaO/SiO₂ on the structure of CaSiO₃, the different molar ratios of CaO/SiO₂ (i.e., 1:1, 1:7, 2:7, and 3:7) were used. BET results show the resulting product has a high specific surface area of 13.18 ±30.53 m²g⁻¹ and a pore size of 15.16 ±18.4 nm obtained as mesoporous material. The obtained CaSiO₃ particles, then to be applied for the degradation of dye pollutants in water. The adsorption capacity was evaluated by methylene blue (MB) and brilliant green (BG) degradation. The parameters of CaO/SiO₂ mass ratio and contact time on the degradation efficiency of BG and MB were investigated, respectively. The results showed that the best model for BG adsorption onto CaSiO₃ was a pseudo-first-order model, whereas the best model for MB adsorption was a pseudo-second-order model.

1. Introduction

Wollastonite is a group of compounds obtained from calcium carbonate (CaCO₃) and silica (SiO₂) reactions. The other name of wollastonite is calcium silicate (CaSiO₃). Based on the mass calculation, CaSiO₃ has a theoretical composition of 48 wt% of CaO and 52 wt% of SiO₂, respectively [1,2]. CaSiO₃ has many uses because it has several unique properties: low conductivity, small mass loss, and high hardness [3]. This property is very important in various fields, such as in the production of high-temperature ceramics, metal coatings, and the automobile industry [4,5]. In the construction sector, calcium silicate is used as a cement additive [6]. In addition, calcium silicate is also used in the medical field, namely for artificial bone materials [7]. Nanostructured CaSiO₃ has been synthesized through several techniques through gas phase processes, such as microwave dielectric, spray pyrolysis, spray drying, etc., which can produce fine and
controlled particles [8,9]. However, the main problem with this technique is that energy recovery is limited and results in high maintenance and operating costs. So that researchers use other strategies for fabricating CaSiO₃, which can be synthesized by various methods such as sol-gel method, [10,11] hydrothermal method [12], and solid-state reaction method [13]. In synthesizing calcium silicate, the most widely used method is the solid-state reaction method. This is because this method has several advantages, that it is easier and simpler. In addition, it is non-toxic, environmentally friendly, free of synthetic waste, and inexpensive to manufacture. The solid-state reaction method can also produce calcium silicate with high purity and good crystallinity [14].

The research on calcium silicate was conducted by Sang et al. The results show that temperature of 900°C, β-CaSiO₃ phase is formed when the temperature reaches 1100°C it changes to α-CaSiO₃ phase [15]. In addition, Shukur et al. researched by synthesizing calcium oxide (CaO) from limestone with a small addition of boron trioxide (B₂O₃) and calcium silicate (CaSiO₃) from silica sand (99.56 wt%). Based on his research, at a temperature of 1050 °C showed the β-CaSiO₃ phase, then when the temperature reached 1150 °C, it changed to the α-CaSiO₃ phase [16]. Similar research has also been conducted by Phuttawong et al. (2015) by synthesizing calcium oxide (CaO) from snail shells and SiO₂ from rice husk ash using a solid-state reaction method with a milling time of 5-8 hours. The results of the research by Phuttawong et al. (2015) showed that the calcium silicate (CaSiO₃) phase was formed when milling was carried out for 7 hours at a calcination temperature of 1000 °C for 2 hours [17]. Hu et al. used CaCO₃ and SiO₂ as raw materials with a sintering temperature varied from 900 to 1200 °C producing α-CaSiO₃, [18]. Sintering at the temperature of 1320 °C transforms the α-CaSiO₃ phase to the β-CaSiO₃ phase. Liu et al. reported that sintering at a temperature of >1100°C would produce α-CaSiO₃ while at a temperature between 800-1100°C has produced β-CaSiO₃ [19]. During sintering, precursor particles could diffuse each other that affect the surface area and morphology. The surface area of CaSiO₃ is an essential parameter for advanced applications. Another research has also been reported by Rashid et al. in which employed two steps heating that is at high temperature of 1400°C and 1200°C to obtain β-CaSiO₃ while one-step heat treatment at 1200°C only generates α-CaSiO₃, [20].

Based on the above, this study aims to synthesize and characterize CaSiO₃ made from chicken egg shells and SiO2 commercial powder at a calcination temperature of 1100 °C using a solid-state reaction method. Material characterization was carried out using X-Ray Diffraction (XRD) Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), Fourier Transform Infra-Red (FTIR), and N₂ adsorption-desorption BET. The effect of temperature and ratio of CaO to SiO₂ to the crystal structure, morphology, and surface area of CaSiO₃ synthesized from eggshell as CaO source still need to be further investigated. There is still a lack of study about the effect of waste-derived precursor ratio on the obtained particles. In the present study, we attempted to produce calcium silicate (CaSiO₃) material using eggshells as CaO source and SiO₂ powder as they are easily obtained and cheap sources as starting materials. In the present study, the ability of CaSiO₃ as an adsorbent material for dye pollutants removal was also reported. Brilliant green (BG) and Methylene blue (MB) was used as adsorbates for adsorption. The effects of CaO/SiO₂ compositions, contact time, and initial dye concentration on the reaction rate constants were discussed. Degradation processes were modeled, and experimental data were fitted to a pseudo-first-order model with sufficient accuracy.

2. Materials and Method

2.1. Materials and Synthesis
Chicken eggshells as the CaCO₃ source were collected from domestic waste around North Balikpapan, East Borneo and commercial silica (SiO₂) powder (Merck, 99%) were used as precursors. CaCO₃ was prepared by the following process: eggshells are obtained from quail breeder farms and rinsed several times with water and hydrochloric acid (HCl, Merck, 37%) to remove the contaminant. Then the quail eggshell is dried
for one day. Calcium oxide (CaO) was prepared by the conventional grinding-crushing and calcination process. Ethanol (analytical grade, 96%) was used as a solvent and the mixing process was carried out at 600 rpm. The slurry was dried in a convection oven at 120°C for 1 hour after the mixing operation was done. After drying, the next step is a one-hour crush. Currently, raw eggshell is available for examination. In addition, the raw eggshell powder was calcined for 1 hour in a crucible. Crushing the as-synthesized material for 1 hour is the final step in the synthesis process. When all of the stages of the synthesis process have been accomplished, analytical grade ethanol (96%), hydrochloric acid (37%), and distilled water were employed as solvents. This study used CaO/SiO₂ with various molar ratios (i.e., 1:1, 1:7, 2:7, and 3:7) sintering at 1100 °C. The mixed powders were heated at a heating rate of 10°C min⁻¹ for 3 h. Afterward, the powders were cooled down to room temperature and ground for 30 min to obtain a fine powder.

2.2. Characterization of CaSiO₃
To observe morphology and microstructure of the resulting CaSiO₃ particle, scanning electron microscopy (SEM, FEI type Inspect 21, accelerating voltage of 100 kV) and Fourier Transform Infrared (Perkin Elmer Spectrum version 10.5.1, ranging from 400 to 4000 cm⁻¹) were used for characterization. BET N₂ adsorption/desorption isotherms (Quantachrome, NOVA 4200E, 77 K) was used to measure surface area, pore size, and pore volume distribution. While to obtain the phase structure of the particle, X-Ray Diffraction (PAN-analytical type X’Pert Pro diffractometer with Cu-Kα) was used. Each sample was scanned between 10 and 80°(2θ) with 40 kV and 40 mA operating conditions.

2.3. Dye Adsorption Experiments
At room temperature, dye doses ranging from 10 mg/L were used in the adsorption tests (10 ppm). Each experiment included the addition of 50 mg of CaSiO₃ dried powder to 100 mL of dye solution. A constant speed of 700 rpm was used to agitate the mixture. Every 10 minutes, the remaining dye concentration in the solution was measured until equilibrium was achieved and the maximum adsorption capacity was determined. The solid phase was centrifuged at 3000 rpm for 5 minutes to remove any contaminants that could impair the subsequent measurement.

3. Result and Discussion
The surface morphology and microstructure of CaSiO₃ particles at different compositions of CaO/SiO₂ are depicted in figure 1. The microstructures of samples are rough and porous, but the surface appears fractured. It is possible that the fracture and rough which is probably caused by particle deformation, or agglomeration and sintered of precursor during the solid-state reaction [21]. The EDX spectra confirm the elemental composition of CaO/SiO₂ (2:7) in the CaSiO₃ sample, which validates the possibility of forming wollastonite. Magnesium as impurities possibly from chicken eggshells. Other EDX report of wollastonite also shows magnesium and aluminum impurities. The quantitative calculation of atom composition obtained from EDX spectra indicate that alongside CaSiO₃, there is SiO₂ excess.
The XRD and FTIR tests were used to investigate the structure of the chemical further. The final product appears in the crystalline phase in all XRD patterns after calcination at 1100 °C, as illustrated in figure 2. The raw materials and product stages have overlapping peaks in the maximum peaks. Several side reactions could occur during sintering, such as the creation of quartz and calcium oxide from SiO₂ and CaO, respectively. To complete the wollastonite reaction, the synthesis temperature of 1100 °C was comparatively low. Other mineral phases such as larnite (Ca₂SiO₄), olivine (Ca₂SiO₄), and portlandite (Ca(OH)₂) were produced at low temperatures, as reported according to Wang et al. [22]. Another cause of peak widening is the fineness of the product particles and the presence of unreacted SiO₂ that might behave as an amorphous phase [23]. The addition of CaCO₃ does not affect the crystallization behavior of wollastonite; due to overlapping, the calcite phase is no longer visible [17]. It is also found that pseudo-wollastonite (α-CaSiO₃) has a rather high peak intensity at 2θ of 37.56°, which begins to expand and requires higher temperatures to change entirely.

**Figure 1.** SEM observation result of CaSiO₃ particles at different CaO/SiO₂ compositions. (a) CaO/SiO₂ = 1:1; (b) CaO/SiO₂=1:7; (c) CaO/SiO₂=2:7; (d) CaO/SiO₂=3:7, respectively. The samples were calcined at T=1100 °C and (e) EDX result of CaO/SiO₂=2:7.

| Element | Wt (%) | At (%) |
|---------|--------|--------|
| OK      | 40.42  | 60.89  |
| MgK     | 09.26  | 08.35  |
| SiK     | 27.11  | 18.05  |
| CaK     | 23.21  | 12.70  |
Figure 2. XRD pattern of CaSiO$_3$ prepared at different CaO/SiO$_2$ molar ratios: (a) 1:1; (b) 1:7; (c) 2:7 and, (d) 3:7. The samples were sintered at T=1100 °C, respectively.

Figure 3. FT-IR of calcium silicate (CaSiO$_3$) prepared under different CaO/SiO$_2$ molar ratios. The temperature of calcination was done at 1100 °C, respectively.

A large asymmetric peak can be seen in the FTIR spectra at 1786 to 1869 cm$^{-1}$ shown in figure 3. The stretch modes of Si bound hydroxyl groups, Si-OH, and the symmetric stretch modes of interstitial H$_2$O molecules contribute vibrational contributions to this region in SiO$_2$-based glasses. O-H stretching absorption bands were found at (3682 cm$^{-1}$). The asymmetric stretching vibration of Si-O-Si bonds is similarly attributed to the peak at 1010 cm$^{-1}$, while the symmetric stretching mode is attributed to the peak at 931 cm$^{-1}$. The peaks at 682 and 644 cm$^{-1}$ are caused by the strong vibrations of Si-O bonds in silicate tetrahedra. While carbonates (CO$_3$) exist naturally in the environment. Between 1400 and 1500 cm$^{-1}$, the carbonates (CO$_3$) have the strongest IR characteristic, which has a broad asymmetric profile [24]. Carbonate
is thus linked to the feature at 1458 cm$^{-1}$. In both amorphous calcium carbonate and the metastable carbonate phase vaterite, the least ordered of the three crystalline anhydrous carbonate polymorphs, a split band in the range of 1458 and 1490 cm$^{-1}$ is frequently observed [25]. This feature is caused by the carbonate ion's asymmetric stretch, with the splitting indicating a loss of symmetry in the carbonate, and should be accompanied by a typical carbonate feature at 1089 cm$^{-1}$.

Figure 4 shows N$_2$ adsorption-desorption isotherms of CaSiO$_3$. The specific surface area (m$^2$g$^{-1}$), pore volume (cm$^3$g$^{-1}$), and pore diameter (nm) of samples are listed in Table 1. The adsorption isotherms of samples can be classified as Type II that commonly found in physical adsorption and correspond to multilayer formation. The shapes of hysteresis loops were of the type H4, which was associated with particles with irregular shapes and a broad range of size distribution. The BET method was used to calculate the surface area of the samples, which affect such properties of materials as their dissolution rate and adsorption capacity [26]. It was calculated that the particles have a relatively large surface area of 13.18–30.53 m$^2$g$^{-1}$. While the value of the cumulative pore volume of the prepared particles ranges from 0.047–0.062 cm$^3$g$^{-1}$. Differential distributions of the pore sizes showed that the calcined samples are a mesoporous material because the pores with the 10–50 nm diameter are dominant, as shown in Table 1.

| Sample    | BET surface area (m$^2$g$^{-1}$) | Total pore volume (cm$^3$g$^{-1}$) | Average pore size (nm) |
|-----------|---------------------------------|-----------------------------------|------------------------|
| CaSiO$_3$ (1:1) | 23.66                          | 0.051                             | 15.98                   |
| CaSiO$_3$ (1:7) | 30.53                          | 0.062                             | 15.16                   |
| CaSiO$_3$ (2:7) | 21.19                          | 0.055                             | 17.13                   |
| CaSiO$_3$ (3:7) | 13.18                          | 0.047                             | 18.14                   |

$^a$ obtained by the BET method.

$^b$ obtained from BJH pore size distribution curve.
The effect of CaO/SiO₂ compositions and contact time between dye and CaSiO₃ adsorbent on the degradation of dye pollutant. Initial dye concentration of 10 ppm for adsorption. Dosage of CaSiO₃ powder of 50 mg was used for dye removal.

The effect of CaO/SiO₂ compositions corresponding to CaSiO₃ was investigated by adjusting the initial concentration of dye substances (i.e., BG and MB) at 10 mg per 100 ml of 10 mg/L MB and BG dye solution, respectively, as shown in figure 5. It can be seen from the figure that when the compositions of CaO/SiO₂ were increased from (1:1) to (3:7), the dye adsorption was found to be increasing, which could be caused by an increased number of active sites on the catalyst surface. A pseudo-first and second-order kinetic equation are given as follows [27]:

\[
\frac{t}{C_t} = \left(\frac{1}{k_1C_e} + \frac{t}{C_e}\right)
\]

\[
\ln(C_e - C_t) = \ln C_e - k_1 t
\]

where \(C_t\) is the amount of dye removed at time \(t\) (mg/g), \(C_e\) is the adsorption capacity at equilibrium (mg/g), \(k_1\) is the pseudo-first-order rate constant (min⁻¹), and \(t\) is the contact time (min). The fitting of experimental data to the pseudo-first and second-order plots for the adsorption of BG and MB on the different compositions of CaO/SiO₂ are shown in figure 6 and the corresponding parameters in table 2.
Figure 6. Linear dependence of $\frac{C_t}{C_0}$ on $t$ based on the Pseudo-first-order kinetics of dye adsorption onto CaSiO$_3$ at different CaO/SiO$_2$ compositions: (a) MB=10 ppm, and (b) BG=10 ppm. While linear dependence of $t/Q$ on $t$ based on the pseudo-second-order kinetics of dye adsorption onto CaSiO$_3$ at different CaO/SiO$_2$ compositions: (c) MB=10 ppm, and (d) BG=10 ppm.

Table 2. The parameters of pseudo-first and second-order kinetic model for the adsorption of MB and BG onto CaSiO$_3$ at different CaO/SiO$_2$ compositions

| Initial Dye     | CaO/SiO$_2$ compositions | % Maximum Dye removal | $k_{1obs}$ x 10$^2$ (min$^{-1}$) | $R^2$  | $k_{2obs}$ x 10$^1$ (min$^{-1}$) | $R^2$  |
|-----------------|--------------------------|-----------------------|----------------------------------|-------|---------------------------------|-------|
| Brilliant Green (BG, $C_o=10$ ppm) | CaO/SiO$_2$ (1:1) | 85,48 | 4,99 | 0,876 | 10,63 | 0,838 |
|                 | CaO/SiO$_2$ (1:7) | 88,73 | 5,61 | 0,921 | 18,11 | 0,748 |
|                 | CaO/SiO$_2$ (2:7) | 91,23 | 7,37 | 0,932 | 41,39 | 0,752 |
|                 | CaO/SiO$_2$ (3:7) | 95,28 | 7,39 | 0,929 | 50,27 | 0,606 |
| Methylene blue (MB, $C_o=10$ ppm) | CaO/SiO$_2$ (1:1) | 57,27 | 1,38 | 0,759 | 2,33  | 0,845 |
|                 | CaO/SiO$_2$ (1:7) | 64,29 | 1,74 | 0,827 | 2,82  | 0,839 |
|                 | CaO/SiO$_2$ (2:7) | 69,86 | 2,23 | 0,838 | 3,41  | 0,821 |
|                 | CaO/SiO$_2$ (3:7) | 73,36 | 2,44 | 0,851 | 4,11  | 0,851 |
The rate-limiting stage in this model is surface adsorption, which involves chemisorption, in which a solution is removed due to physicochemical interactions between the two phases. The linear determination coefficient was used to express the model's goodness of fit ($R^2$). Both kinetic models have a good enough correlation with $R^2$ more than 0.9, according to the size of the correlation coefficient ($R^2$). The value of the pseudo-first-order model for BG adsorption, on the other hand, is larger than the value of the pseudo-second-order model. As a result, the pseudo-first-order model fits the experimental data better than the pseudo-second-order model for the BG adsorption model.

Meanwhile, the correlation coefficient ($R^2$) for MB adsorption calculated using the pseudo-second-order model is higher than that calculated using the pseudo-first-order model. It's worth noting that the pseudo-second-order model fits the experimental data better than the pseudo-first-order model for the MB adsorption model. Adsorption occurs in stages, with solute molecules (dye) transported from an aqueous solution to the surface of solid particles (CaSiO3), then dye molecules diffusing onto the CaSiO3. The tests we conducted allowed us to investigate whether intraparticle diffusion is the process that regulates adsorption. The effect of CaO/SiO2 will be further studied by plotting the amount of dye adsorbed versus the square root of time, and this is the intraparticle diffusion model. The kinetics results obtained can be used to know if the intraparticle diffusion is the limiting step in the adsorption of the dye inside the CaSiO3 [28].

4. Conclusion

Calcium silicate (CaSiO3) was successfully prepared using chicken eggshell and commercial SiO2 powder as starting material via solid-state reaction at 1100°C. The functional group was characterized using FTIR, which results at 1100°C, formed functional groups O-Si-O, Si-O-Si, and Ca-O-C. It should be noted that the heating temperature at 1100°C could affect the quantity of calcium silicate formed. The BET and SEM results showed that the CaSiO3 particle is in an open framework structure with a mesoporous structure that can be functionalized. This study demonstrated that calcium silicate (CaSiO3) could be an effective and eco-friendly adsorbent material for removing organic dye pollutants from colored wastewater. The adsorption mechanism and thermodynamic study that can provide deeper information about the interaction between the adsorbent surface and the adsorbate will be evaluated for further research.

5. References

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