# Hydrothermal preparation of diatomaceous earth combined with calcium silicate hydrate gels

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## ARTICLE INFO

## ABSTRACT

A novel composite for the removal of color in waste water was prepared by subjecting slurries consisting diatomaceous earth and slaked lime to a hydrothermal reaction at 180 °C. Subsequently, calcium silicate hydrate gels covered the surface of diatomaceous earth due to the reaction between the amorphous silica of diatomaceous earth and slaked lime. The formation of calcium silicate hydrate gels led to an increase in the specific surface area. The composites showed higher methylene blue adsorption capacity compared with diatomaceous earth. The improved adsorption capacity of the composites depended on the amount of the calcium silicate hydrate gels and their silicate anion chain-lengths.

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## 1. Introduction

The removal of color produced by minute amounts of organic dye in water has increased in importance in industrial waste pollution abatement due to their potentially harmful effects and aesthetical considerations. Generally, the color is removed by biological oxidation and chemical precipitation [1,2]. Recently, many studies have been conducted on the preparation of sorption materials as an alternative method for lowering the concentration of dissolved dyes in the effluents and hence removing their color. In particular, much attention has been paid to the use of low-cost inorganic materials such as fly ash [3], rice husk [4], tea waste [5] and pineapple leaf [6] as starting materials.

Diatomaceous earth (DE) is a naturally occurring clay from geological deposits composed predominantly of the fossilized skeletons of unicellular algae-like plants [7]. These plants are an extremely abundant and inexpensive source of silica. DE has numerous applications as filters and pesticide carriers due to its specific properties such as having a high specific surface area [8]. DE has also been applied to the removal of dye in the effluent. It has been reported that chemical treatment of DE using a strong acid and base improves its removal properties [9,10].

Amorphous calcium silicate hydrate gels (C-S-H gels) are hydrothermally synthesized in a CaO–SiO$_2$–H$_2$O system with Ca/Si ratios of 0.5–3.0 below 200 °C [11,12]. C-S-H gels consist of monomer silicate anions with silanol groups. Silanol groups have been proposed to be the main functional group responsible for most of dye adsorption, especially of methylene blue [13]. We have considered that composites consisting of chemically treated DE and C-S-H gels could be used as environmentally friendly materials with excellent dye adsorption properties. Its siliceous composition allows DE to be used as a Si precursor for synthesizing C-S-H gel in a CaO–SiO$_2$–H$_2$O system. The dissolution of slaked lime—the starting material for synthesizing C-S-H gel—allows us to control alkalinity during the hydrothermal reaction and thereby improve the dye-removal properties of DE. Our strategy for synthesizing the composite to use in the purification of colored waste water was to modify the surface of DE with alkali treatment and simultaneously precipitate C-S-H gel by the hydrothermal reaction. In the present study, slurries consisting of DE and slaked lime were hydrothermally reacted to synthesize a novel composite with superior dye-adsorption abilities.

## 2. Experimental

DE calcined at 1200 °C (Fig. 1; average particle size: 50 μm, specific surface area: 3 m$^2$/g, Showa Chemical Industry Co., Ltd., Japan) and slaked lime (average particle size: 10 μm, specific surface area: 10 m$^2$/g) were used as starting materials. Lime was prepared by calcination of calcium carbonate (Wako Pure Chemical Industries Ltd.) at 1000 °C for 3 h. Slaked lime was obtained by adding distilled water to the prepared lime. The materials were mixed, and the mix-

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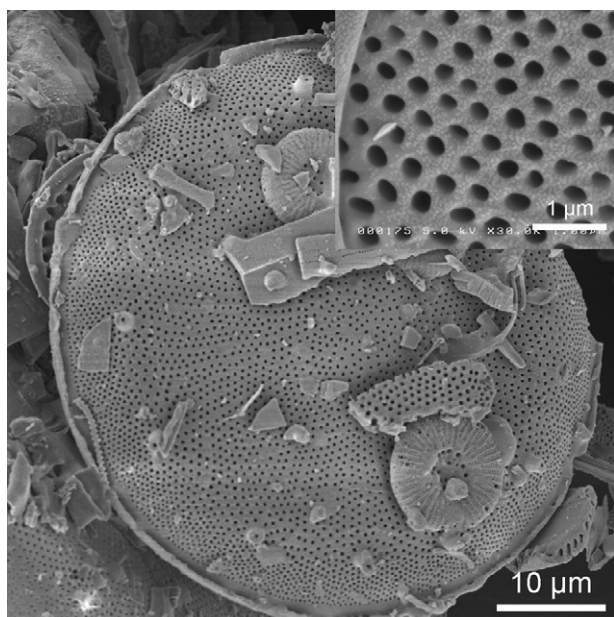
Fig. 1. SEM micrographs of diatomaceous earth.



Fig. 2. XRD patterns of the samples and diatomaceous earth. (▼) Cristobalite, (▲) albite, (■) quartz, and (○) calcium silicate hydrate gel.

ture was then added to distilled water to prepare slurries. The three mass ratios of DE/slaked lime were 90:10, 80:20, and 70:30. The slurry was hydrothermally reacted at 180 °C for 3 h. The hydrothermal reaction was carried out with a water/solid ratio of 10. The hydrothermally reacted deposits prepared with slurries containing 10, 20, and 30 mass% slaked lime were denoted as samples A, B, and C, respectively. The samples were air dried at 80 °C for 24 h and subsequently stored in desiccators for further studies.

The crystalline phases in the samples were identified by X-ray diffraction (XRD) analysis. The structure of the samples was examined by Fourier transform infrared spectroscopy (FT-IR) using the KBr method. The morphology of the samples was observed by scanning electron microscopy (SEM). The density of samples was determined by a pycnometer method. The specific surface area of the samples was measured by conducting a nitrogen gas sorption analysis at −196 °C. All samples were preheated at 80 °C in vacuum to remove the physisorbed water. In the present work, methylene blue (MB) was selected as a model compound to evaluate the capacity of the adsorbent to remove dye from its aqueous solution. The adsorbent concentration was 1 g/L. The samples were left standing to reach equilibrium for 6 h at room temperature. They were then centrifuged, and the supernatant solution was analyzed using UV/vis spectrometry by monitoring the absorbance changes at a wavelength of 663 nm.

## 3. Results and discussion

Fig. 2 shows XRD patterns of the samples and DE. The DE consisted of cristobalite, quartz, and albite in their crystalline phases and amorphous silica. In the XRD patterns of the samples, new peaks corresponding to the C-S-H gel appeared after the reaction. The halo peak originating from the amorphous silica of DE decreased as the amount of slaked lime increased. The C-S-H gel content in the samples was determined by the quantitative XRD technique. Silicon was used as an internal standard. $I_{\text{C-S-H}}$ and $I_{\text{silicon}}$ denote the integrals of the peaks at 29° due to C-S-H gel and 28° due to silicon, respectively. $I_{\text{C-S-H}}/I_{\text{silicon}}$ of samples A, B, and C was determined to be 0.34, 1.28, and 1.64, respectively. The C-S-H gel ration in sample C had much higher than that in samples A and B in the experimental condition. These findings suggest that the dis-
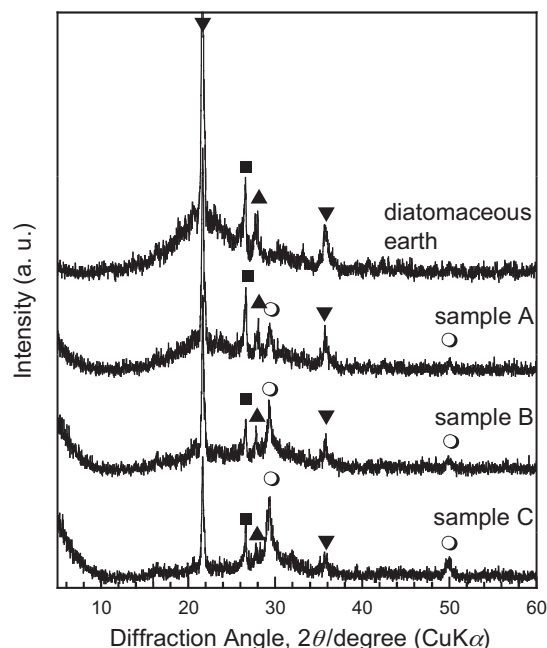
solution of slaked lime during the hydrothermal reaction increases alkalinity in the condition, resulting in accelerated reactivity of the amorphous phase of DE. That is, the amount of C-S-H gel formed depends on the amount of slaked lime in the slurry.

Fig. 3 shows SEM micrographs of the samples. The surface of DE was covered with newly deposited C-S-H gels after the reaction. Petal-like C-S-H gels can be seen in SEM micrograph of the sample A. The SEM micrograph of sample B showed lath-like C-S-H gels. The C-S-H gels of sample C showed rectangular morphologies which were larger in size than those of samples A and B. The specific surface areas of samples A, B, and C were measured to be 62, 121, and 181 m²/g, respectively, using nitrogen gas sorption analysis. The amount of C-S-H gel was associated with an increase in the specific surface area of the samples. The density of samples A, B, C, and DE was determined to be 0.89, 1.40, 1.63, and 0.16 g/cm³ by pycnometer method. On the other hand, the density of C-S-H gel (C/S = 1.7) was reported to be 2.86 g/cm³ [14]. Considering the prediction based on the theory of composite material, DE is supposed to remain as a substrate in the samples even after the reaction.

The FT-IR spectrum of DE showed four adsorption bands at around 470, 800, 1090, and 1200 cm⁻¹ (Fig. 4), which were due to Si–O–Si bending vibrations, O–Si–O groups (polymerization), Si–O–Si in-plane vibrations, and Si–O bonds in $Q^3$ sites of DE, respectively [10,13,15,16]. In the sample spectra, four adsorption bands appeared at around 530, 970, 1115, and 1630 cm⁻¹ due to various bonds in C-S-H gels. The bands at 800 and 1200 cm⁻¹ due to the degree of SiO₄ tetrahedron polymerization in DE decreased with an increase in the amount of slaked lime in the slurry. This implies that a large amount of silanol groups was formed at the surface of DE by polymerization degrading under alkaline conditions due to the dissolution of slaked lime. The adsorption band at 970 cm⁻¹ due to Si–O in $Q^2$ sites of C-S-H gel [17] increased with the amount of slaked lime in the slurry. C-S-H gels contain $Q^1$ and $Q^2$ sites because of monomer silicate anions [18]. A large number of $Q^2$ sites lead to the formation of monomer silicate anions with a long chain. It is proposed that the larger amount of silicon species from the dissolution of amorphous silica in DE promotes polymerization during the formation of C-S-H gels, resulting in the construction of long-chain silicate anion structures.
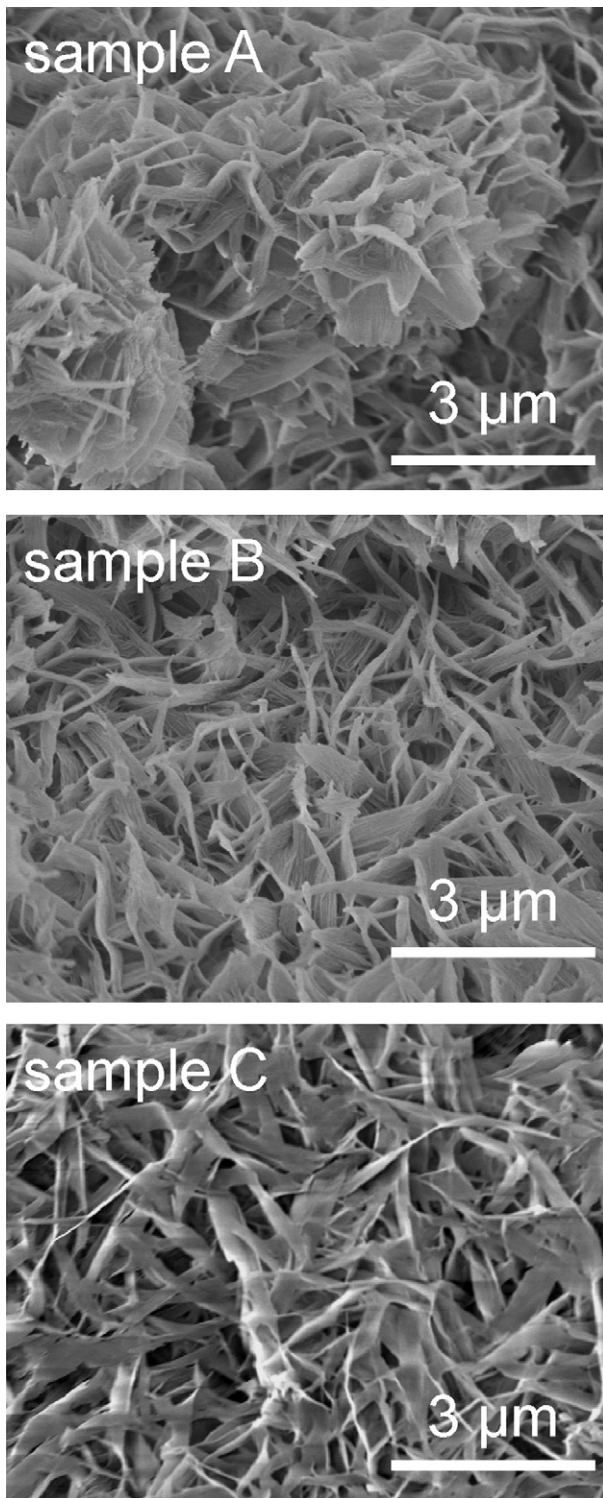
Fig. 3. SEM micrographs of the samples.

To evaluate the properties of removing dye in effluent, MB adsorption data for samples in the range of 10–40 mg/L were plotted according to the linear form of the Langmuir equation, as shown in Fig. 5. Thus

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \times \frac{1}{C_e}$$

where $q_e$ is the amount of MB adsorbed on the sample at equilibrium (mg/g), $C_e$ is the concentration of MB in solution at equilibrium
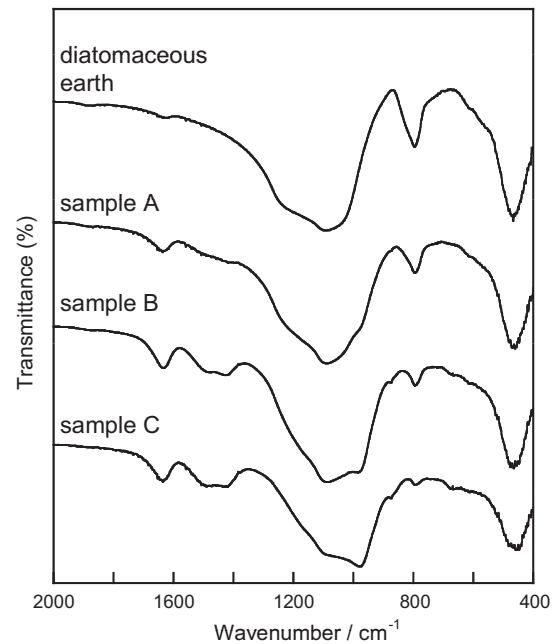


Fig. 4. FT-IR spectra of the samples and diatomaceous earth.

(mg/l), and $q_0$ and $K_L$ are the Langmuir constants representing the maximum adsorption capacity for the sample (mg/g) and the energy constant related to the heat of adsorption $(mg/L)^{-1}$, respectively. In our preliminary experiments, the equilibrium data shown by the Langmuir equation was better fitting than that shown by the Freundlich equation. This model described the adsorption of MB on the samples with $R^2 > 0.95$. This expects that the monolayer adsorption of MB on the samples. The Langmuir constants $q_0$ and $K_L$ for each sample are shown in Table 1. The value of $K_L$ increased with the amount of slaked lime in the slurry. This suggests that the amount of C-S-H gel and the surface of alkali-treated DE depend on the value of $K_L$. On the other hand, sample B exhibited the highest MB adsorption capacity among the samples. The MB adsorption capacity on DE and alkali-treated DE was reported to be 2.2 and
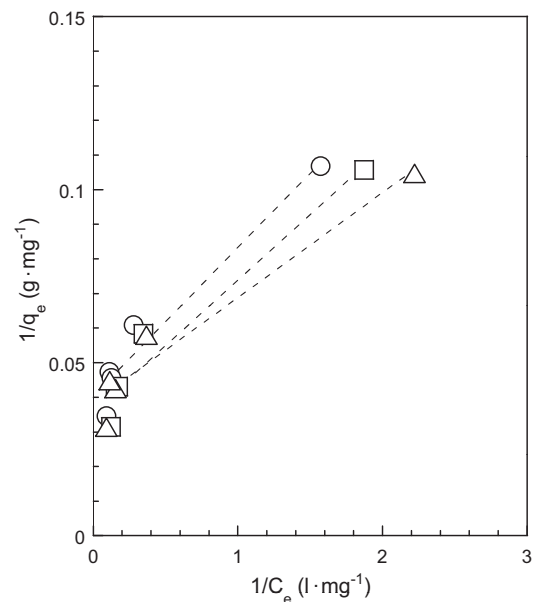


Fig. 5. Langmuir plot for methylene blue adsorption on the samples A (○), B (□), and C (△).

**Table 1**
Langmuir constants for the adsorption of methylene blue on three samples.

|  | $q_0$ (mg/g) | $K_L$ (mg/L)$^{-1}$ |
|---|---|---|
| Sample A | 24.8 | 0.937 |
| Sample B | 27.8 | 0.951 |
| Sample C | 26.1 | 1.263 |

18.5, respectively [10]. C-S-H gel combined with alkali-treated DE enhances the adsorption capacity.

In monolayer adsorption, an increase in the specific surface area of the samples improves their maximum adsorption capacity. The attraction of MB to the surface of the samples (i.e., MB adsorption capacity) was calculated by dividing the value of $q_0$ by the specific surface area, to clarify an interaction between the material and MB. The MB adsorption capacities of samples A, B, and C were determined to be 0.40, 0.23, and 0.14 mg/m$^2$, respectively. Sample C had the largest amount of C-S-H gel and silanol groups at the surface of DE, but exhibited the lowest MB adsorption capacity. Sample A showed about twice the MB adsorption capacity of samples B and C. This suggests that the amount of C-S-H gel has a slight influence on the MB adsorption capacity. C-S-H gels in sample A contained fewer Q$^2$ sites than in samples B and C, as shown in the FT-IR spectra of Fig. 4. In sample A, C-S-H gels showed a short-chain silicate anion structure, resulting in the large number of Q$^1$ sites (silanol groups). When sample A was evaluated for its properties of dye removal, MB in the solution easily came into contact with the surface of alkali-treated DE due to the smaller number of C-S-H gels. As a result, sample A showed the highest MB adsorption capacity.

## 4. Conclusion

A novel composite, consisting of alkali-treated diatomaceous earth and calcium silicate hydrate gels for removing the color in effluent, was hydrothermally reacted using diatomaceous earth and slaked lime. After the reaction, the surface of diatomaceous earth was coated with the calcium silicate hydrate gel. The amount of slaked lime in the slurries depended on the specific surface area, as well as the amount of calcium silicate hydrate gels in the composite and their monomer silicate anion structures. Compared to alkali-treated diatomaceous earth, the composite had a higher capacity for methylene blue adsorption. Enhancement of MB adsorption capacity was shown to play an important role in controlling the amount of calcium silicate hydrate gels and their silicate anion chain-length.

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