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Effect of Processing Conditions on the Absorption Behavior of 3D Boron Nitride Foams in Various Aqueous Mixtures

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Abstract In this work, we successfully fabricated boron nitride foams by assembling boron nitride into a 3D porous structure using freeze drying. Boron nitride was modified by Hummers method and NaOH, which results in the functionalization with OH groups. Such chemical functionalization enabled the attachment of the surfactant molecules, leading to a 3D foam structure. We found that the type of the surfactant molecules and method of freezing (in liquid nitrogen or in a deep freezer) have significant impact on the structure of the foams and consequently their absorbent properties. Fast freezing technique (with liquid nitrogen) created more stable and porous structures compared to the slow freezing technique (in a deep freezer). The best foam structures were obtained for the samples coded as h-BN-B-H-SA and h-BN-N-DA. The highest absorption capacity was found as 2014.3% for h-BN-B-H-SA. Absorption capacity results show that foams can absorb approximately 2–20 times their own weight. The method we use here is easy to apply, environmentally friendly, and can be readily scaled up for industrial use.

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Keywords Boron nitride foam · Surfactant · 3D materials · Absorbent · Wastewater treatment

1 Introduction

Millions of tons of wastewater containing both inorganic and organic pollutants are produced every day. This causes important social, environmental, and economic problems. At the same time, wastewater produced in high amounts is discharged to rivers and oceans, causing environmental pollution and disrupting the ecological balance (Lei et al., 2013). High surface area materials have been effectively used to remove oils, organic solvents, and dyes from water. In this sense, there is a demand to develop materials with high sorption capacity. To meet this demand, boron nitride foam composites with high surface area and high absorption capacity can be effectively used for several dyes, oils, and organic solvents (Wang et al., 2017). Recently, boron nitride (BN) has drawn tremendous attention for various applications due to their encouraging properties such as high mechanical strength, thermal conductivity, and chemical stability (Maleki et al., 2016; Owuor et al., 2017). Besides, the high polarity of B-N bonds and the high surface area of the boron nitride make it attractive for the absorption of several waste components from aqueous solutions (Portehault et al., 2010). Many studies have focused on the graphene-based absorbents to remove organic dyes, oil contamination, and heavy metal ions from wastewater (Lu et al., 2013; Shen et al., 2015; Wan et al., 2016; Zhang et al., 2015; Zhao et al., 2015). Zhang et al. developed two types of graphene spongy structures with the combinative use of freeze-drying and surfactants. Three-dimensional graphene foams with abundant pores were obtained by using detergent lather as the template. The foam structures were controlled by changing the freezing and surfactant type as well as mixing speed. On the other hand, by directly freeze-drying the graphene oxide/surfactant suspension, the porous frame with unidirectionally aligned pores was prepared. The surfactant created a high specific surface area that provides a better distribution of the graphene oxide layers. It provides wide range of possible applications such as excellent absorption capacity and good compression performance (Zhang et al., 2014). Lately, 3D BN materials are also commonly studied for the removal of various waste products. Lei et al. reported that porous BNNSs having high surface area could absorb water-repellent oils and organic solvents up to 33 times of their own weight. BNNSs could be regenerated by burning the adsorbed waste substances thanks to strong oxidation resistance of boron nitride (Lei et al., 2013). BN-based porous monoliths were produced by a simple self-foaming solidification and high-temperature pyrolysis method. Monoliths showed effective purification capability of oil/water mixtures with excellent volume-based adsorption capacity up to 71–98% for many oil contaminants (Xue et al., 2016). Moreover, 3D carbon boron nitride structures have been demonstrated as an efficient adsorbent material for dyes, oils, and heavy metal ions. In the work of Liu et al. a novel porous cheese-like structure made of carbon boron nitride was prepared. The maximum removal capacities were found as 408 mg/g for methyl blue and (MB) and 307 mg/g for congo red (CR). Furthermore, it has been reported that 3D C-BN can efficiently remove oils and heavy metal ions from wastewater (Liu et al., 2018). These studies clearly suggest that 3D boron nitride nanostructures with high surface area can be useful as for waste water treatment applications. Different freezing methods have been used to freeze nanoparticles suspensions (Abdelwahed et al., 2006; Patapoff & Overcashier, 2002; Roy et al., 1997; Searles et al., 2001). Fast freezing with liquid nitrogen, slow freezing in a deep freezer, or different freezing techniques provide different cooling effects. The most ideal cooling effect is achieved by freezing with small volumes of liquid nitrogen, while the worst cooling effect is achieved by the pre-cooled shelf method. Fast freezing results in small ice crystals and a larger specific surface area (Abdelwahed et al., 2006). More effective super cooling can cause the formation of smaller ice crystals, preventing the mechanical stress on the nanoparticles and consequently the aggregation of these particles (Heurtault et al., 2003).

Here we fabricated 3D boron nitride foams by freeze drying of boron nitride suspensions containing different surfactant agents. The effect of surfactant type and the method of freezing on the structural properties of the foams were investigated by various characterization methods such as Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET)/Barrett-Joyner-Halenda (BJH) analysis, and thermogravimetry (TGA) analysis. On the other hand, commercial detergent was used as a template for the production of boron nitride foam structures for the first time. The usability of the produced foams as absorbents was investigated in the water–oil and water-organic solvent mixtures for wastewater treatment purpose. The method we use here is easy to apply, environmentally friendly, and allows producing several porous absorbents on an industrial scale, while the surfactants can be removed from the structure after washing or burning at high temperatures.

2 Materials and Method

2.1 Materials

Micron-sized hexagonal boron nitride powder (2.27 g/cm^3, > 98.0% purity, Bortek Boron Technologies and Mechatronics Ind. Co.) was used to produce the boron nitride foams. In the functionalization of boron nitride powder, sodium hydroxide (NaOH, 2.13 g/cm^3, ≥ 97.0% purity, Merck), potassium permanganate ($KMnO_4$, 2.70 g/cm^3, 99.0–100.5% purity, Merck), sulfuric acid (H_2SO_4, 1.840 g/cm^3, 95–97% purity, Riedel–de Haen), phosphoric acid (H_3PO_4, 1.71 g/cm^3, 85.0% purity, Merck), hydrogen peroxide (H_2O_2, 1.110 g/cm^3, 30% (w/w) in H_2O, Sigma-Aldrich), hydrochloric acid (HCI, 1.18 g/cm^3, 37% purity, VWR Chemicals), and ethanol (C_2H_6O, 0.79 g/cm^3, ≥ 99.9% purity,

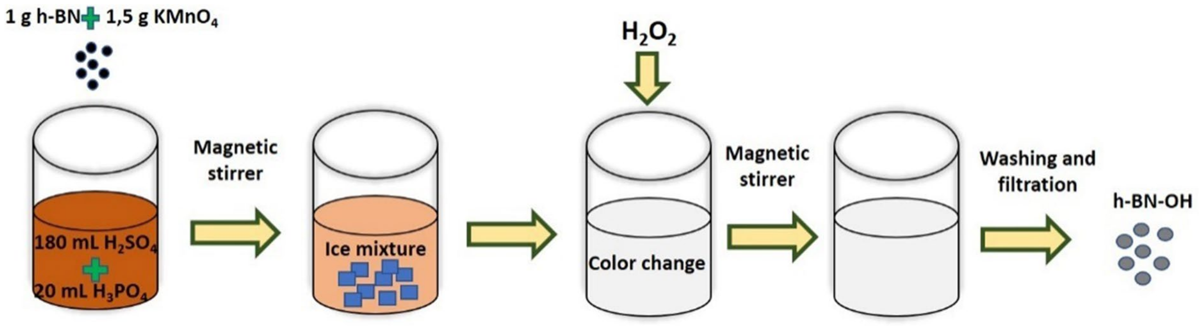


Fig. 1 Functionalization of h-BN by Hummer's method

Merck) were used. Powder laundry detergent (brand name: Alo), sodium dodecyl sulfate (SDS, 1.01 g/cm^3, 98.5% purity, Sigma-Aldrich), and deoxycholic acid (DA, > 98.5% purity, Sigma-Aldrich) were employed as surfactant. Olive oil–water mixture, cyclohexane-water mixture, 2-propanol-water mixture, and toluene-water mixture were used to determine the absorption capacity of the foams.

2.2 Method

2.2.1 *Functionalization of h-BN Using the Hummer's Method*

Functionalization of hexagonal boron nitride with OH groups facilitates the attachment of surfactant molecules to form a 3D structure (Wang et al., 2016). For this purpose, we used Hummers method whose schematic diagram is given in Figure 1.

In this method, 1 g h-BN and 1.5 g $KMnO_4$ powder were slowly added into 180 mL H_2SO_4 and 20 mL H_3PO_4 solution, which was then stirred for 8 h at 50℃ with a temperature-controlled magnetic stirrer. The resultant mixture was transferred into an ice bath to which, H_2O_2 was added drop wise until a color change was achieved. The final solution was kept stirring for 1 h and then washed with distilled water, HCl, and ethanol, respectively, followed by filtering and drying at 50℃ in an oven for 24 h.

2.3 Functionalization of h-BN Using NaOH

In addition to Hummers method, hexagonal boron nitride powder was functionalized with NaOH. The schematic diagram of this procedure is given in Figure 2. 0.2 g of h-BN powder and 1 g NaOH were transferred to a beaker and 40 mL of distilled water was added. This mixture was stirred using a magnetic stirrer for 24 h. To remove the water, the mixture was kept at 80℃ in the oven. The powder mixture remaining at the bottom of the beaker was washed 3 times with distilled water to remove residual sodium hydroxide, then filtered, and finally dried in an oven at 80℃ for 12 h.

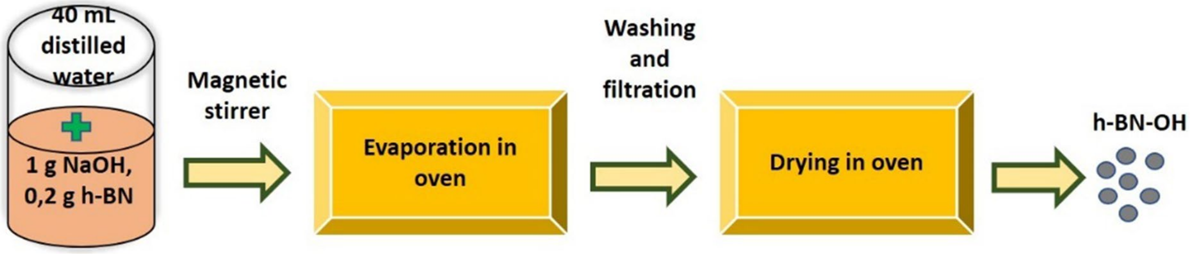


Fig. 2 Functionalization of h-BN by NaOH method

2.4 Fabrication of 3D Boron Nitride Foams

We used a previously reported detergent method (Zhang et al., 2014) to produce the 3D boron nitride foams whose fabrication procedure is illustrated in Figure 3. Experimental conditions for the foam production and the corresponding sample codes are presented in Table 1.

First, 2 g of powder laundry detergent was mixed with 100 mL of distilled water for 30 min using magnetic stirrer, which resulted in lather formation. The lather and liquid part of the mixture was transferred to separate beakers. Two milliliters of the OH functionalized boron nitride suspension was added to each beaker so that the concentration of the boron nitride was 10 mg/mL. The lather part was then stirred on a magnetic stirrer whereas the liquid part was sonicated in an ultrasonic bath for 30 min. Finally, the resulting solutions were frozen either in a deep freeze or by liquid nitrogen and subsequently freeze dried for 24 h to remove the water. For comparison, 3D boron nitride foams were prepared using sodium dodecyl sulfate (SDS) and deoxycholic acid (DA) as surfactants instead of detergent using the following procedure: 1 g SDS and 1 g DA were dispersed in 50 mL of distilled water and sonicated for 2 h, then 2 mL of OH functionalized boron nitride suspension (modified by

Fig. 3 Fabrication of 3D boron nitride foam

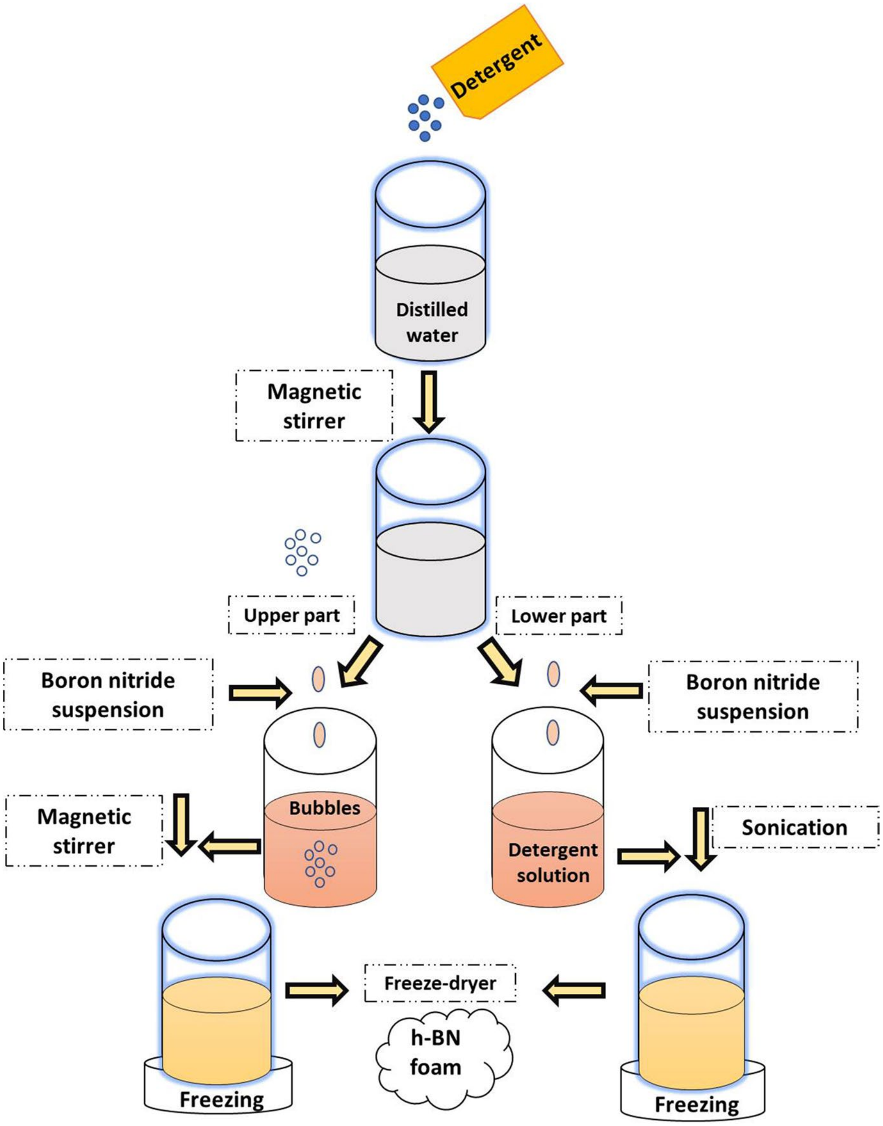


Table 1 Experimental conditions for the fabrication of boron nitride foams

Sample codes	Surfactant	Functionalization method	Freezing method
h-BN-B-H-SA	Laundry detergent (lather part)	Hummer's	Liquid nitrogen
h-BN-S–H-SA	Laundry detergent (liquid part)	Hummer's	Liquid nitrogen
h-BN-B-N-SA	Laundry detergent (lather part)	NaOH	Liquid nitrogen
h-BN-S–N-SA	Laundry detergent (liquid part)	NaOH	Liquid nitrogen
h-BN-B-H-DD	Laundry detergent (lather part)	Hummer's	Deep freeze
h-BN-S–H-DD	Laundry detergent (liquid part)	Hummer's	Deep freeze
h-BN-B-N-DD	Laundry detergent (lather part)	NaOH	Deep freeze
h-BN-S–N-DD	Laundry detergent (liquid part)	NaOH	Deep freeze
h-BN-H-SDS	SDS	Hummer's	Liquid nitrogen
h-BN-N-SDS	SDS	NaOH	Liquid nitrogen
h-BN-H-DA	DA	Hummer's	Liquid nitrogen
h-BN-N-DA	DA	NaOH	Liquid nitrogen

NaOH and Hummer's methods) was added. Stirring was applied on a magnetic stirrer for 30 min to form a homogeneous solution. The final solutions were frozen by liquid nitrogen and dried in a freeze drier for 24 h.

2.5 Determination of Absorption Capacity

Olive oil–water mixture, cyclohexane-water mixture, 2-propanol-water mixture, and toluene-water mixture were used to determine the absorption capacity of the foams. In order to determine the absorption capacity of the foams, the foams were immersed in the prepared aqueous mixtures of oil and organic solvents for full saturation. After absorption was completed, the foams were removed from the mixture and waited until no droplets remained on them. The weight of the foam before and after the absorption was recorded and the absorption capacity was given in % according to the following calculation:

$$\mathrm{absorptioncapacity}\% = (W_b - W_f)/W_b \times 100 \quad (1)$$

W_b is the weight of the foam before the absorption, and W_f is the weight of the foam after the absorption.

2.6 Physical and Chemical Characterization

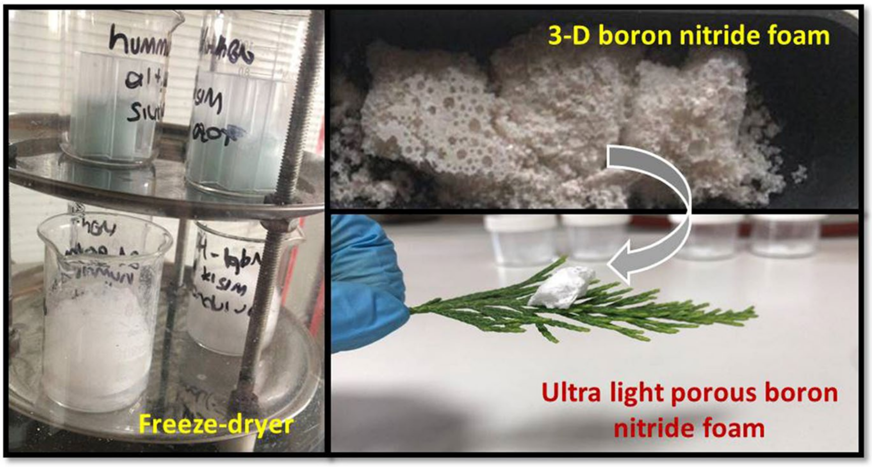
FTIR measurements were carried out on Agilent Cary 630 FTIR. SEM images were obtained using Zeiss Supra 40VP. The foam surface was covered with gold/palladium mixture before the SEM analysis. BET-BJH analysis was performed with Micromeritics 3flex instrument. Prior to the analysis, the samples were degassed at 200 °C for 12 h. The thermal stability of the foam was determined using the TGA (Exstar SII TGA/DTA 7200 TG/DTG). The samples were heated to 1000 °C in nitrogen environment with a heating rate of 10 °C/min.

3 Results and Discussion

Optical images of the 3D boron nitride foams are given in Figure 4. The foams are highly porous and ultra-light. Macroscopic pores with a diameter of a few hundred microns can be seen with the naked eye.

FTIR spectra of the unmodified and modified boron nitride (by either Hummers method or NaOH) are compared in Fig. 5. The stresses observed at 800 and 1382.08 cm^{-1} are characteristic to hexagonal boron nitride. The stress at 1382.08 cm^{-1} is resulted from B-N stress in sp^2 mode whereas the stress at 800 cm^{-1} is due to out-of-plane vibration mode of the B-N-B atoms (Smith, 2017). An additional peak appears at 3435 cm^{-1} for the modified boron nitride, which indicates the presence of hydroxyl groups (B-OH). This result evidences that hydroxyl groups are successfully attached on the surface or edges of the h-BN by the Hummer's method and NaOH modification (Sudeep et al., 2015). The basic principle of the functionalization method with NaOH is the separation of the h-BN layers from each other by the reaction between the h-BN and the OH ions. With mechanical stirring, Na and OH ions slowly settle between the BN layers. The reason for this scaly separation taking place in the alkaline environment is that Na

Fig. 4 Images of ultra-light boron nitride foam



and OH ions are driven by their high chemical potentials and enter the upper intermediate layer space. In addition, the self-bending ability of BN nanosheets helps the binding of the cation and anion groups. Anions are adsorbed on a positively curved surface, while cations are adsorbed on a negative curved surface (Li et al., 2013).

IR spectra show that surface modification has been successfully performed and h-BN underwent oxidation and -OH groups bound to its structure (Huang et al., 2009). The reason for the shift in 1382 cm^{-1} in the modified samples is that the BN particles attached with hydroxyl groups are broken down during the modification (Ryu et al., 2019). The IR spectra of the foams obtained under different conditions are given in Fig. 6.

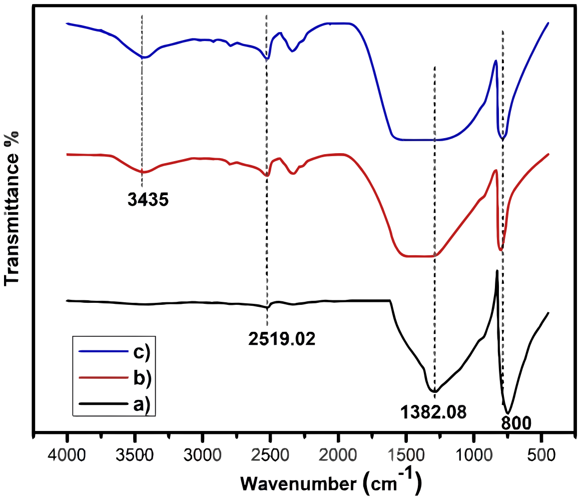


Fig. 5 IR spectra of h-BN **a**) unmodified, **b**) modified with Hummer's method, **c**) modified with NaOH method

The stress observed at 3434.25 cm^{-1} represents hydroxyl groups (B-OH) (Sudeep et al., 2015). Similar stresses were recorded for almost all foams. The IR spectra of the samples exhibit a notable difference depending on the freezing and functionalization methods. The stresses in the samples prepared by freezing with liquid nitrogen are sharper than that are obtained by freezing in the deep freezer. The junction points of boron nitride and surfactants in foams produced with NaOH modification are weaker than foams produced with Hummer's modification; therefore, the tension bands appear at a lower intensity. In addition, slow freezing in the deep freeze caused less interaction with boron nitride due to the rapid degradation of the laundry detergent lather (Saye & Sethian, 2013), leading to weaker band intensities in the FTIR spectra (Zhang et al., 2014). The morphology of the 3D foams was evaluated by SEM analysis, which indicated that surface functionalization and freezing methods control the pore structure of the foams. The SEM images in Figure 7a–d show the morphology of the foams obtained after freezing in the deep freezer. The SEM images of the foam samples produced with deep freeze method show randomly distributed micron-sized pores on the walls of the foam structure. At low magnification (Fig. 7d), the SEM image shows fluffy boron nitride wall layers and irregular pores resulted from the detergent lather.

However, at high magnification (Fig. 7a), there appear some small polygon-like pores that retain the shape of the bubbles. The foams produced with deep freezing method have smooth walls because lather bubbles have enough

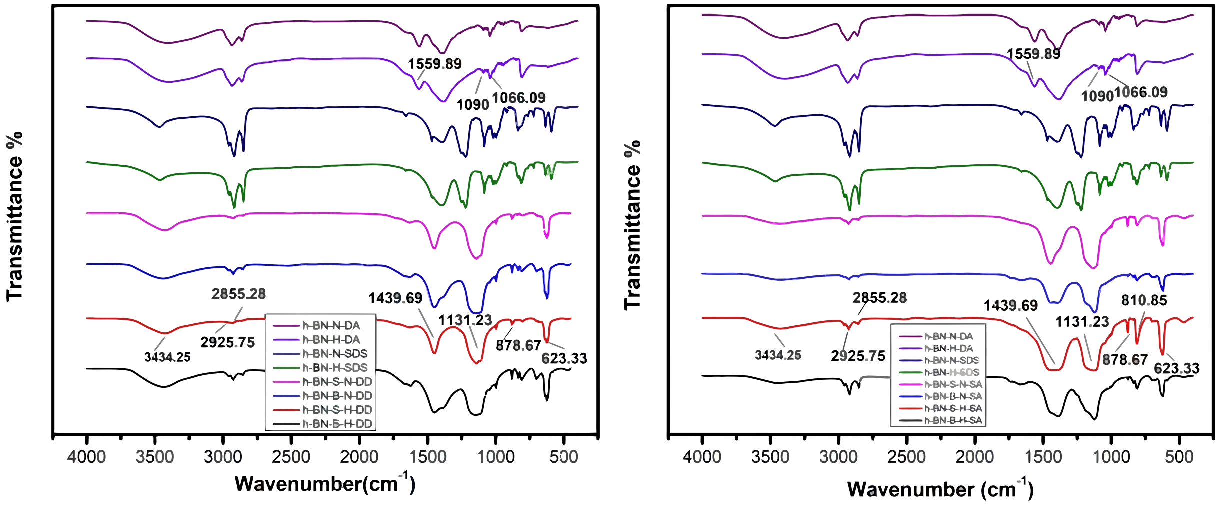


Fig. 6 IR spectra of foams obtained under different conditions

time to tear and drain out (Estevez et al., 2011). Figure 7 to 7 show the structure of the foams produced by freezing with liquid nitrogen. One of the important factors affecting the porous foam structures is the freezing rate that triggers the formation of ice paths (Yao et al., 2009). It was observed that micropores appeared more regularly in the foams produced with h-BN modified by Hummer's method (Fig. 7, 7). Rapid freezing with liquid nitrogen caused ice crystallization on the walls for a long time and the h-BN layers adhered to the ice crystals

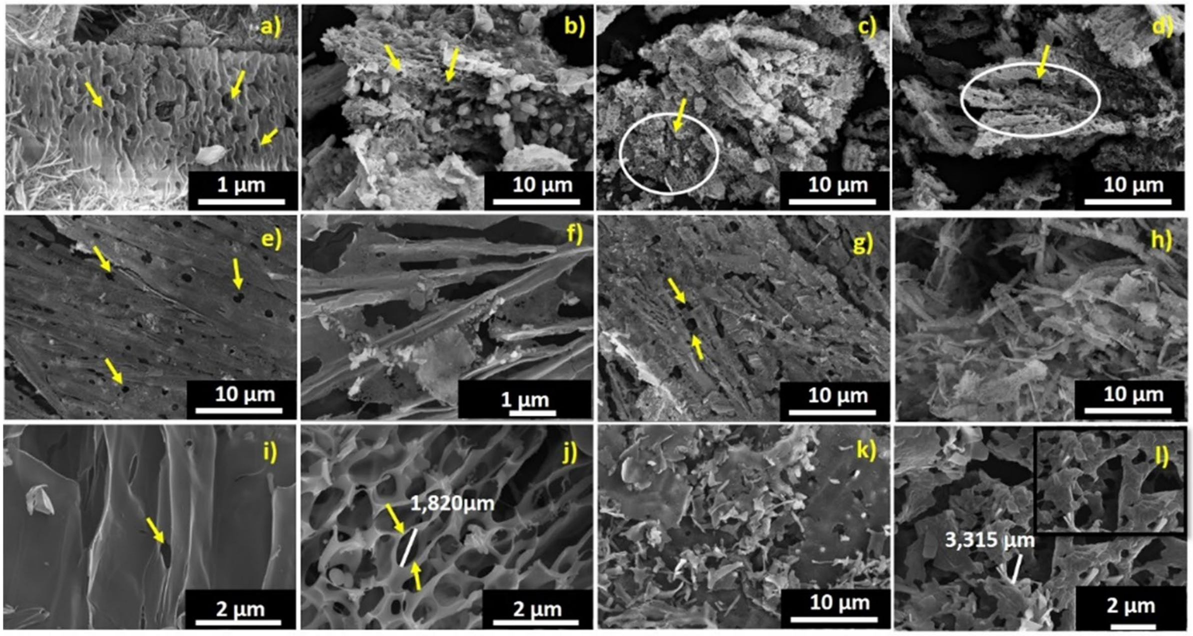


Fig. 7 SEM images of the 3D foams prepared under different conditions **a**) h-BN-B-H-DD, **b**) h-BN-B-N-DD, **c**) h-BN-S-H-DD, **d**) h-BN-S-N-DD, **e**) h-BN-B-H-SA, **f**) h-BN-B-N-SA, **g**) h-BN-S-H-SA, **h**) h-BN-S-N-SA, **i**) h-BN-H-DA, **j**) h-BN-N-DA, **k**) h-BN-H-SDS, **l**) h-BN-N-SDS

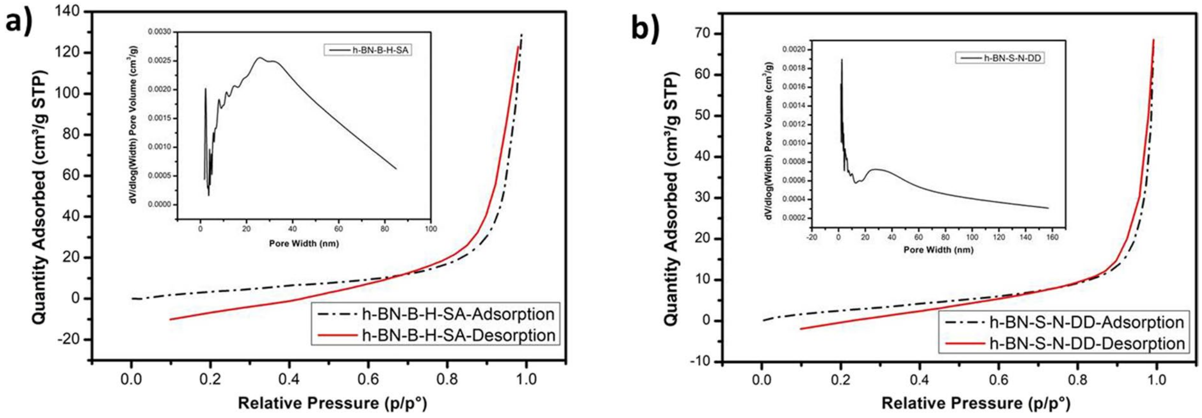


Fig. 8 N2 adsorption-desorption isotherms and pore size distribution curve of **a**) h-BN-B-H-SA, **b**) h-BN-S-N-DD

and were oriented in the direction of the ice paths (Wang et al., 2014). Figure 7 to 7 show the morphology of the foams prepared using different surfactants. While there is almost no pore formation in foams produced by Hummers method using DA surfactant (Figure 7), the pores in the foams produced with NaOH are quite distinct (Figure 7). BET-BJH analysis was conducted to determine the surface area of the foams. While the N$_2$ isotherm of the porous BN nanosheets can be defined as type II^1 adsorption/desorption isotherms of the produced boron nitride foams show the characteristic H3 hysteresis, indicating a character of open-shaped capillaries between the parallel layers (Figure 8–8) (Wang et al., 2012). Furthermore, the relative pressure between 0.4 and 1.0 represents the mesopores with a diameter below 20 nm (Lei et al., 2013). The surface area of the h-BN-B-H-SA sample was obtained as 31.29 m^2/g according to the Brunauer–Emmett–Teller (BET) model. For a comparison, this value is larger than the surface area of BN nanoparticles (27 m^2/g) (Perdigon-Melon et al., 2002). In addition, we found that deep freezing led to lower surface area. For example, the surface area of the foam prepared by slow freezing (h-BN-S–N-DD) was found to be 12.42 m^2/g. The pore size distribution curve of h-BN-B-H-SA consists of one sharp peak at 25 nm. Overall, the pore size analyses of each sample are compatible with the morphological analysis as the micron-sized pores are formed.

Figure 9 displays the TG curve of the sample coded with h-BN-B-H-SA. The mass loss below 100℃ is caused by the desorption of water molecules adsorbed on the sample surface, which continues towards higher temperatures. At 600℃, 25% of the sample decays, while the decay is 40% at 1000℃, which indicates that the foam can maintain its structure at even high temperatures.

Absorption capacity of the 3D boron nitride foams determined in different aqueous mixtures is presented in Figure 10. The absorption properties of porous BN-nanolayers for oils and some organic solvents are associated with the adsorption of molecules on hydrophobic BN nanosheet surfaces, capillary action to fill the spaces in in the nanosheet, and the penetration of molecules between the BN layers (Fei et al., 2008; Perdigon-Melon et al., 2002; Wang et al., 2012). From Figure 10, the absorption capacity of h-BN-B-H-SA and h-BN-N-SDS samples is especially high in relatively more dense mixtures such as olive oil–water, toluene-water, and cyclohexane-water. The high absorption capacity of boron nitride foams may be due to capillary effects in the samples. The porous structure of

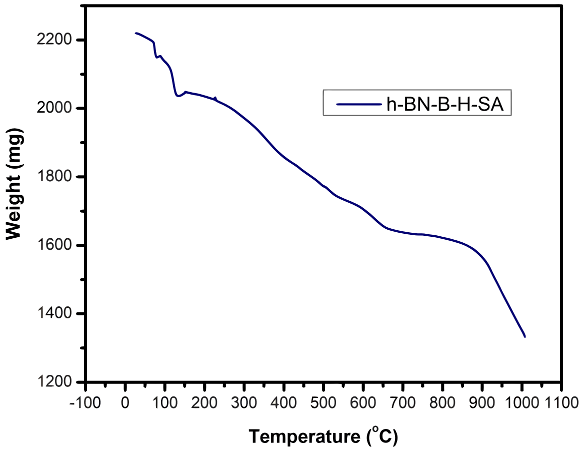


Fig. 9 TG curve of h-BN-B-H-SA sample

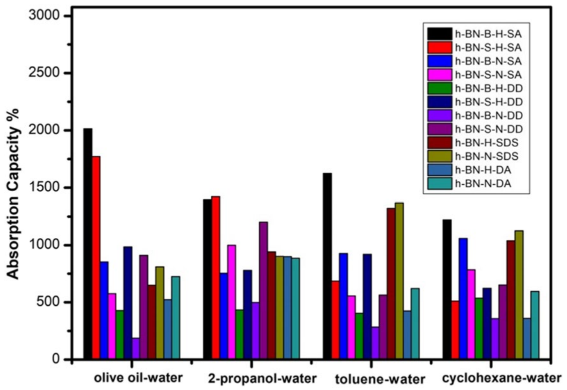


Fig. 10 Absorption capacities of foams produced in different conditions in different mixtures

the foams provides high surface area and sufficient space to absorb large amounts of oil (Maleki et al., 2016). In the 2-propanol-water mixture, h-BN-B-H-SA and h-BN-S–H-SA perform better than other foams. Freezing with liquid nitrogen gives rise to larger number of pores in the foams leading to higher absorption capacity compared to deep freezing, which is consistent with the SEM observations. This is because the slow freezing is not effective to create enough pores in the foam structure as the lather bubbles degrade during the slow freezing process (Estevez et al., 2011). The graph shows that the lowest absorption capacity is between 200 and 1200% for the samples coded with h-BN-B-H-DD and h-BN-B-N-DD. In their study, Zhang et al. also showed that fast freezing gives better absorption performance than slow freezing for graphene foams (Zhang et al., 2014). The absorption capacities were also consistent with BET analysis. The surface area and consequently the absorption capacity of the foam obtained by slow freezing were found to be lower for slow freezing.

4 Conclusion

In summary, porous boron nitride foam was successfully synthesized by a simple method using detergent and surfactant as a template. The effect of different conditions on boron nitride foam production was investigated. It was determined that the fast freezing technique (with liquid nitrogen) creates more stable and porous structures in foam formation compared to the slow freezing technique (with deep freezer). Especially, the foams modified by Hummers method, frozen with liquid nitrogen, and produced with detergent formed more pores and therefore their absorption capacities are higher. In addition, it has been concluded that the sample coded h-BN-B-H-SA is thermally degraded by 40% up to 1000 ℃. The highest absorption capacity is defined in h-BN-B-H-SA coded sample as 2014.3%. The surface area of the foam coded as h-BN-B-H-SA is determined to be 31.29 m^2/g. Absorption capacity results show that foams can absorb approximately 2–20 times their own weight. Therefore, boron nitride foams could be well-considered as an efficient and economical absorption material to be used in wastewater treatment.

Author Contribution D. Kuru conceived of the presented idea. D. Kuru and G. Sezer conceived and planned the experiments and carried out the experiments. A. Akpinar Borazan supervised the project and verified the analytical methods. All authors discussed the results and contributed to the preparation of the final manuscript.

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Data Availability Data will be made available on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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