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Chemical Activation of Boron Nitride Fibers for Improved Cationic Dye Removal Performance†

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Abstract: Adsorption represents an efficient and economical approach for water purification and substantial research are being performed to developing effective sorbent materials. Porous boron nitride (BN) composed of light elements is considered as a promising candidate for pollution treatment due to its unique polarity of B-N bonds, high specific surface area, numerous structural defects, chemical stability, and oxidation resistance. However, adsorption performance based on porous BN is hindered by either few activated sites or low degree of crystallinity. In this work, we have developed a simple chemical method to activate pre-obtained well-crystallized porous BN fibers in acid solution. The successful chemical activation has been identified by FTIR spectra and zeta potential measurement. Benefiting from these advantageous features, the activated BN fibers with high stability exhibited enhanced cationic dye removal performance compared to the un-activated ones. The effects of pH value, contact time, temperature and adsorbent amount on the methylene blue (MB) adsorption properties were analyzed. The adsorption equilibrium data were interpreted in terms of the Langmuir and Freundlich models and the results showed that Langmuir isotherms best represent the adsorption system. The maximum adsorbed amount for MB was high up to 392.2 mg/g at pH 8.0 and 30 °C. The adsorption rate was sharply enhanced after chemical activation. The excellent reusability of the activated BN was also confirmed. It is shown that the chemical activation plays a key role in enhanced dye adsorption performance. Therefore, our developed chemical activation method for porous BN fibers opens the door toward to the practical activated BN for drinking water purification.

1. Introduction

Environmental pollution problem has attracted great attention because many industries such as dye manufacturing and printing have produced highly coloured effluents, and disposal of these wastes into water has resulted in larger volume of dye wastewaters [1]. The coloured effluents not only lead to organic load and toxicity to the environment, but also impede light penetration to affect aquatic ecosystems [2]. The adsorption has been found to be superior as compared to other traditional treatment methods for wastewater treatment due to its low-cost, easy availability, simplicity of design, high efficiency, ease of operation and ability to treat hazardous dyes and metal ions [3, 4]. Various adsorbents have been applied for the hazardous dyes removal from aqueous solution, including activated carbon [5], fly ash and red mud [6], mesoporous aluminophosphate [7], free-standing carbonaceous nanofiber membranes [8], magnetic powder MnO-Fe_2O_3 composite [9], and porous CeO_2 [10]. However, the high-quality adsorbents with high removal capacity and reusability are still required. Compared with the traditional carbon material, BN can be considered as promising adsorbent due to their highly stability in harsh conditions, which enables more treatment technique for recycled usage[11, 12].

Very recently, several kinds of porous BN nanostructured materials have been successfully fabricated, and their applications in water purification and treatment have been extensively investigated due to their high specific surface area, numerous density defects and large void volume[13-15]. Specially, activated BN has also been developed by our group to improve their adsorption performance, in which more crystal defects and hydroxyl or organic surface groups have been introduced via the presence of P123 (poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)) as a activating reagent [16]. Note that the obtained activated BN is not only short of stability in very harsh conditions due to their poor degree of crystallinity, but also

contains many impurities because of the introduction of P123. Hence these shortcomings such as instability and lack of numerous adsorption sites need to overcome to further improve their performance in wastewater treatment. Herein, we report a kind of novel porous BN fibers with high crystallinity and abundant activated sites via a two-step synthesis route, which exhibited greatly improved cationic dye removal performance. Firstly, BN fibers with high degree of crystallinity were prepared by using boric acid and melamine as the starting reactants in NH_3 flow at a high temperature. Secondly, a new chemical activation pretreatment was utilized to activate as-received BN fibers to obtain numerous surface functional groups and defects, so as to increase their adsorption capacity. The resultant adsorbents were subsequently tested in the removal of cationic dyes in different experimental conditions to confirm the validation of chemical activation to enhance adsorption capacity (up to 392.2 mg/L) and uptake rate. Langmuir and Freundlich isotherms models have been used to further analyze the adsorption data. Furthermore, the removal efficiency of ~ 94 % was still retained even after fifteen adsorption-regeneration cycles. A thorough knowledge of activated BN enables the preparation of adsorbents with appropriate characteristic for drinking water purification.

2. Experimental

2.1. Material Synthesis

Analytical grade H_3BO_3 and $C_3N_6H_6$ were used directly without further purification as starting materials to synthesize porous BN fibers. Methylene blue, as a model cationic dye contained the aromatic rings, was used to study the hazardous dye removal nature of activated BN. Table S1 and Figure S1 (Supporting Information) exhibit the property and structure of cationic dye MB. A mixture of H_3BO_3 and $C_3N_6H_6$ at a molar ratio of 1:2 was dissolved in 300

ml of the distilled water. The reaction mixtures were heated and kept at a boiling state to completely evaporate of the distilled water. The white precipitate ($C_3N_6H_6 \cdot 2H_3BO_3$, M·2B) was obtained. Subsequently, the precursors were treated through a multi-stage heat process to produce BN fibers in an alumina tube using a resistance-heating horizontal furnace. Firstly, the precursors were calcined at 546°C for 2 h (ramp rate 5°C/min). Secondly, they were heated at 1560 °C for 4 h at a heating rate of 10 °C/min. All reaction was carried out in a flow of NH_3 (200 ml/min).

The activation process was carried out by adding 3g of above obtained BN fibers into 50% (w/w) of the activating reagent (1 M H_2SO_4 aqueous solution and 8 M HNO_3 aqueous solution mixed together with their weight ratio of 1:1). After sonication for 30 min at room temperature, the obtained slurry was mechanically stirred in an 80 °C water bath for 2 h. After activation, the sample was washed with deionized water for several times until the pH of the rinse became neutral (pH 6.8-7.2), following by drying at 105 °C for 24 h. The sample prepared was labeled as activated BN.

2.2. Characterization techniques

The structure of the samples was examined using X-ray powder diffraction (XRD, BRUKER D8 FOCUS) analysis. Fourier transformer infrared (FTIR) spectra were recorded on a Nicolet 7100 spectrophotometer between 400 and 4000 cm^{-1}. Transmission electron microscopy (TEM) experiments were performed on a Tecnai F20 electron microscope (Philips, Netherlands) with an acceleration voltage of 200 kV. The nitrogen physisorption isotherms were measured at -196 °C on an AutoSorb iQ-C TCD analyzer. Prior to the measurement, the samples were activated in vacuum at 300 °C for 3 h. The Brunauer-Emmett-Teller (BET) specific surface area was

calculated from the nitrogen adsorption data in the relative pressure ranging from 0.01 to 0.3. The pH values of the solutions were measured by pH meter (PHS-25, Hangzhou). A double beam UV/vis spectrophotometer (HITACHI, U-3900H) was used to determine the concentration of dye samples. The thermostability of the products was tested by simultaneous thermal analysis (SDT-Q600). Conventional elemental analyzers (Leco, TC500 and CS230, USA) were applied to analyze the detailed N, O, and C contents of the two adsorbents, respectively. X-ray photoelectron spectroscopy (XPS) measurement was performed in an ultrahigh vacuum with a VG ESCALAB 210 electron spectrometer equipped with a multichannel detector.

2.3. Adsorption experiment

For all adsorption experiments in this work, the studies were carried out in glass flask with a magnetic stirrer. Stock solution (100 mg/L) of MB dye was prepared via adding MB dyes (100 mg) into 1 L of distilled water, which acts as the source for dissolution. The mixtures were continuously stirred by a magnetic stirrer at 150 rpm, and then centrifuged and filtered. For the adsorption rate tests, 250 ml of MB solution at the initial concentration of 25 mg/L and 60 mg adsorbents were used. The solution pH was adjusted to 8. The two adsorbents were taken at different time intervals. In order to obtain the maximum removal of MB over the two adsorbents, optimized conditions, such as contact time, adsorbent dosage and contact temperature, and pH value, were investigated. In the experiments of equilibrium adsorption isotherm, the solution equilibrium pH was maintained at 8, and 250 ml MB solution was mixed with the dosages of adsorbents ranging from 10 to 100 mg. The temperature effect of adsorption of MB on the activated BN and the BN fibers was measured in the range of 10-50 °C. The pH values of dye solutions were adjusted from 2 to 12 by adding amount of 0.1 M HCl or NaOH solutions, respectively. The solution concentrations (the supernatants) were determined by UV/vis

spectrophotometer at the corresponding λ_{max} = 663 nm. The dye removal percentage of MB over the two adsorbents was calculated by the Equation 1

$$\eta\ (\%) = (C_0 - C_e) \cdot 100 / C_0 \quad (1)$$

Where C_0 and C_e (mg/L) are the initial solution concentration and equilibrium concentration, η is the dye removal percentage of MB, respectively.

2.4. Regeneration

The regeneration of activated BN was carried out by thermal degradation method. After the filtration, the collected adsorbent containing MB was dried at 100 °C, then placed into a muffle furnace and heated at 400 °C for 1 h. the obtained adsorbent was chemically re-activated with the mixed solution of dense sulfuric acid and nitric acid for use in the further test.

3. Results and discussion

3.1. Characterization of activated boron nitride

XRD patterns of the as-growth adsorbents, the activated BN and the BN fibers, are displayed in Figure 1a, respectively. Both of them display similar sharp diffraction peaks at 2θ= ~ 26.7 ° and ~ 43.8°, corresponding to the (002) and (100) plane spacing of hexagonal BN [17, 18]. When comparing with our previously reported activated BN by P123 [16], as illustrated by the XRD pattern in Figure S2 (Supporting Information), currently obtained BN fibers exhibits higher degree of crystallinity. The higher crystallinity of as-obtained activated BN endows its better stability during adsorption process as sorbent, which has been further identified by the thermogravimetry measurement as shown in Figure S3 in Supporting Information. Figure 1b shows FTIR spectra of the activated BN and the BN fibers, respectively. Two main peaks at ~

1400 and ~ 800 cm^{-1} are verified to the B-N stretching vibrations and B-N-B bending vibrations [19-22], which can be both detected in the two samples. Moreover, intensity increased vibration band of ~3420 cm^{-1} ($B-NH_2$) and a new emerging peak located at ~3250 cm^{-1} (B-OH) can be observed in the activated BN [14, 20]. We deduce it should be ascribed to the chemical activation process, which facilitates functionalization of hydroxyl and organic groups ($B-NH_2$/B-OH) on the BN fibers. Besides, additional surface bonds were also measured on the surface of activated BN, i.e. B-N-O and B-N-O [20]. In addition, XPS spectra and elemental analysis further suggest that the possible functional groups were introduced onto the surface of the as-prepared BN fibers via chemical activation, as shown in Figure S4 and Table S3 (Supporting Information). The external morphology and microstructures of the activated BN and the BN fibers were investigated by TEM, as displayed in Figure 1(c,d). As compared in the rectangle regions in Figure 1c and 1d, BN fibers exhibit smooth edges in the TEM image, whereas the edges of activated BN are rather rough, suggesting numerous surface defects were introduced after chemical activation. Taking into account of the unchanged crystal structures of two kinds of porous BN fibers as shown in Figure 1a, the chemical activation reaction should mainly take place on surface rather than inside.

The possible activated reaction schemes of the BN fibers by the treatment of the mixed acid solution are provided in Figure 2. Because the melamine was selected as one of the stating reactants, the decomposition of melamine resulted in the present of carbonaceous composition in the as-prepared BN fibers [23]. It is known that carbonaceous composition could be removed from the lattice and/or surface of BN via the reaction with dense nitric acid at 80 °C (reaction equation (1) of Figure 2). This reaction is help to improve the number of defects, the specific surface area, and the pore volume, as illustrated in Figure 1d and 2. The addition of sulfuric acid can

accelerate the rate of the reaction 1 by capturing water. A high-concentration acidic solution creates sufficient oxidized radicals on the BN fibers surface, as displayed in reaction equation (2) of Figure 2 [24]. The reaction equation (3) of Figure 2 shows that a low-concentration solution results in the formation of functional groups on the BN fibers surface [25]. Therefore, chemical activation to the BN fibers via the mixed solution of sulfuric acid and nitric acid is favorable to introducing functional groups and defects onto the surface, which can enhance the adsorption ability of the activated BN.

Figure 3 illustrates nitrogen adsorption/desorption isotherms (-196 °C) and the corresponding pore size distributions of the two adsorbents, respectively. The measured isotherms (Figure 3a) can be classified as type I isotherm according to the IUPAC nomenclature, and exhibit a H4 type broad hysteresis loop. Since type I isotherm and Type H4 loops also indicate that the pores contain microporosity and narrow slit-shaped mesopores, we use a Non-Local Density Functional Theory (NLDFT) method to determine the pore widths and size distribution for the activated BN and the BN fibers, respectively [23, 26]. Both samples exhibit a broad pore size distribution (PSD), as shown in Figure 3b, which are given a bimodal distribution with the main characteristic pore sizes of ~1.3 and ~3.9 nm. Comparing with both curves, we clearly observe that the surface area of the activated BN slightly increased from 1045 to 1104 m^2/g when activated by activating reagent. Accordingly, the pore volumes also increased from 0.57 to 0.63 cm^3/g. Therefore, the activation process influences its specific surface area and pore volume simultaneously without destruction of their integrity.

To further identify the validity of activation, their surface charge conditions were monitored by zeta potential. Figure 4 show that the activated BN had an overall negative surface charge at above pH 2, whereas the BN fibers exhibited almost an overall neutral charge even at pH 8. In

addition, the zeta-potential of activated BN rise as pH value increase due to protonation of the hydroxyl and amino groups on the surface. Therefore, one can say that the chemical activation leads to more negative charge surface, which come from the induced functional groups and defects. Accordingly, more negative charge results in enhancement of the electrostatic attraction between the activated BN and the pollution dye molecules.

3.2. Adsorption studies

Considering its porous structure with high specific surface area also with more negative charges, the as-obtained chemical activated BN fibers should have an excellent adsorption activity when used as a sorbent in wastewater treatment. To demonstration the potential applicability of the present activated BN fibers in these applications, we investigated its adsorption activity for the removal of MB in aqueous solutions relative to that of the untreated one. MB adsorption capacity was observed to be excellently up to 392.2 mg/g. Furthermore, the extremely rapid adsorption was observed that the residual dye was just 1.5 wt % within 5 min and 0.2 wt % within 30 min, respectively, when 20 mg of activated BN was applied in a 250 ml of the dye solution (25 mg/L) at 30 °C and pH value of 8. The effect of removal of MB depends on the experimental parameters, such as the characteristic of the adsorbents, contact time, pH value, adsorption temperature, etc. Therefore, these experimental parameters are optimized with the aim of achieving maximum adsorption.

Figure 5a exhibits the rates of MB adsorption on the activated BN and the BN fibers obtained by batch contact time studies with an initial MB concentration of 25 mg/L and the adsorbents of 60 mg at pH of 8, respectively. It is worthy to note that, for the activated BN, the removal was very fast during the first 5 min, and then the equilibrium was reached within 30 min. In addition,

the adsorption capacities onto the two adsorbents were in the order of the activated BN > the BN fibers. The fast adsorption reveals a high complexation rate between the activated BN and the dye molecules, which is correlated to its surface defects and hydroxyl and organic groups on the surface. More hydroxyl and organic groups and surface defects are favorable for the diffusion of dye molecules onto much more activated sites within a shorter time [27].

The MB adsorption as a function of the activated BN dosage (10-100 mg) at pH of 8 is depicted in Figure 5b. The adsorption percentage of MB rise with the increase of activated BN dosage since the increase of adsorbent dosage enlarged the surface area and activated sites for adsorption. The adsorption of MB on the BN fibers is also displayed in Figure 5b as a comparison. It clearly indicates that the removal percentage on the BN fibers was much lower than that of MB on the activated BN under same experimental conditions. The chemical activation process leads to improving number of hydroxyl and amino groups and surface defects, which work as mainly effective sites for adsorption leading higher adsorption capacity.

The effect of temperature on adsorption of MB is analyzed at temperatures ranging from 10-50 °C, which is shown in Figure 5c. The removal percentage of MB using activated BN increased with increasing temperature from 10 to 30°C, suggesting that the adsorption process is endothermic. The temperature has two major effects on the adsorption process. On one hand, increasing the temperature contributes to the decrease of the solution viscosity, and in turn, results in the increase of diffusion rate for the adsorbate molecules across the external boundary layer and the internal pores of the activated BN. On the other hand, changing the temperature also elevates the equilibrium capacity between the absorbent and adsorbate in the solution. However, with the further increase of the temperature up to 50°C, the adsorption percentage of MB quickly decreased. This is mainly because increasing the temperature weakens the

interactions between the activated BN and MB, and hinders the MB adsorption. The temperature effect on the adsorption of un-activated BN fibers also exhibits the similar phenomenon as shown.

We also detected the effect of pH value of the MB solution on the adsorption amount of the two sorbents. Figure 5d indicates that the removal ability of MB has been enhanced with the increase of pH value and reaches the maximum point at pH value of 8, which is consistent with the zeta-potential results (Figure 4). In the process of adsorption, the heterocharge between the adsorbate and adsorbent is favorable for adsorbing reaction. More protons are available on the surface of the adsorbents when pH < 7, which lead to decreasing negative charges of adsorbent surface [28]. Additionally, the protonate amino groups of MB create repulsive force with the electron deficient boron active sites of the activated BN, so the adsorption capacity increases with rise of pH value [7]. A weakly alkaline environment is in favor of the adsorption of MB since the surface of activated BN may occupy more negatively charged OH^- ions. However, the adsorption amount decreases gradually when pH > 8, owing to the excessive negatively charged OH^- ions in the solution blocking the beneficial effects of that of the surface [9, 27].

To verify the great advantages of negatively-charged activated BN adsorbing cationic dye molecules by electrostatic interaction, we compare the adsorption performance based on neutral (neutral red) and anionic (methyl orange) dyes. Figure 6 (a,b) shows that the adsorption rate and capacity of methylene blue onto the activated BN is much higher than that of neutral red and methyl orange, respectively. Additionally, after deactivation by ammonia treatment at 900 °C, the adsorption rate and capacity of methylene blue of the resultant BN (deactivated BN) is much lower than that of the activated BN, as illustrated in Figure 6c and 6d. We notice that the deactivated BN still exhibits a high surface area of 1100 m^2/g and a large pore volume of 0.62

cm^3/g. This deactivation reaction only resulted in less negative charge surface (the zeta-potential of the deactivated BN was almost zero even at pH 7). Therefore, the strong electrostatic interaction between methylene blue and activated BN is believed to be the key point causing the high adsorption rate and capacity.

The adsorption isotherm is one of the most useful methods to understand the mechanisms of the adsorption process, to detect how the adsorbent interacts with the adsorbate and to evaluate the application of the process. Figure 7 shows the adsorption isotherms of MB onto the surface of two sorbents at pH 8 and 30 °C. In the entire concentration range from 0.38 to 20 mg/L, the adsorption capacities of MB on the two adsorbents are in the order of activated BN > BN fibers. This order is the same as that of the influences of contact time, adsorbent dosage, contact temperature, and pH value mentioned above. The maximum adsorption capacities are 392.2 mg/g for activated BN and 243.2 mg/g for BN fibers, respectively. The different adsorption capacities for activated and un-treated ones might be the overall effects of electrostatic interactions, which have significant difference in surface charges. It worth noting that the maximum value of adsorption capacity for the present activated BN (392.2 mg/g) is remarkably larger than those of most common commercial and state-of-the-art sorbents [7, 11, 14, 15, 29-31]. Specially, the adsorption capacity and rate of the activated BN for methylene blue are about 2 and 10 times higher than that of the commercial activated carbon, respectively [8]. The improved adsorption ability of the activated BN mainly ascribes to the chemical activation via the mixed solution, which is favorable to introducing functional groups and defects onto the surface. The result suggests the excellent adsorption capacity in our newly prepared activated BN material.

Since the surface of the BN fibers is negatively charged, the chosen cationic dye MB can be adsorbed by the electrostatic interactions. The observed high adsorption capacity of activated BN

mainly originates from the following several aspects. For BN, the polar B-N bond is suitable for the MB chemisorption, because the BN fibers exhibit the "lop-sided" densities characteristic of a considerable degree of ionic B-N bonding, and the polyelectron nitride can transfer more electron density to cationic dye [32]. After activation, the activated BN has an overall negative surface charge at above pH 2, which can easily adsorb positively charged dye. The porous BN has high specific surface area of 1104 m^2/g and large pore volume (0.63 cm^3/g) also facilitates the adsorption [33, 34]. Most importantly, much more activated sites in the activated BN can lead to a great enhancement of the MB adsorption due to the high density structural defects and numerous hydroxyl and amino groups, which could offer strong binding sites and enhancing the dissociation of MB on BN fibers.

The Langmuir adsorption isotherm has been widely used to investigate the adsorption process of pollutants from the liquid solutions[33]. It assumes that the adsorption of pollutants takes place in the specific homogeneous sites within the adsorbents, and many successful monolayer adsorptions have been found. The Langmuir isotherm is represented in the form as (Equation 2)

$$Q_e = Q_m K C_e/(1+KC_e). \quad (2)$$

Where Q_e is the adsorbed amount of dyes on the equilibrium concentration (mg/g), C_e is the equilibrium concentration in solution (mg/L), Q_m is the maximum adsorption capacity corresponding to complete monolayer covering on the adsorbents (mg/g), and K is the equilibrium constant related to the free energy of adsorption.

The Freundlich isotherm is an empirical equation, which has usually been employed to represent the heterogeneous systems[9]. The Freundlich equation is written as (Eq. 3)

$$Q_e = KC_e^{1/n}. \quad (3)$$

Where, *K* and *n* are the Freundlich adsorption constants, which indicate that the extent of the adsorption and the degree of nonlinearity between adsorption and solution concentration, respectively.

Figure 7 reveals that the Langmuir model had well fit with the experimental data for the two adsorbents in the order of activated BN > BN fibers with the correlation coefficients (R^2) of 0.998 and 0.993, respectively (Table S2, Supporting Information). While for the Freundlich model, the correlation coefficients (R^2) of activated BN and the BN fibers were 0.916 and 0.92, respectively. This result also reveals that all sites were equal (equal energies and enthalpies). Moreover, we note that the curve for activated BN had a very high slope in the initial portion and then level off, revealing that the activated BN possesses incredible adsorption density even at low equilibrium hazardous dye concentrations and high affinity for MB molecules. Hence, this is suitable for lowering hazardous dye concentration by adsorption in wastewater.

3.3. Regeneration of activated boron nitride

As known, the feasibility of applying the adsorbent systems in large-scale operations is determined by the cost of their disposal or regeneration. The high-temperature calcination method has been paid extensive attention because it is a feasible disposal and energy-saving process. Due to its high thermal stability, a simple regeneration experiment (calcining at 400 °C for 1 h in air) was carried out for the removal of adsorbed MB and the regeneration of activated BN. Batches of regeneration experiment for 10 activated BN samples were carried out to evaluate their cycle property for MB removal. The removal efficiency of about 94 % was still retained even after 15 runs, as presented in Figure 8, which is higher than that of the activated BN reported in our previous work[16]. And then the removal efficiency has no obvious change

with further increasing of cycles. It should be noticed that the decrease of adsorption efficiency after several cycles dose not ascribe to the deactivation, due to the low temperature regeneration process. In addition, the activated BN still exhibits excellent removal capacity of methylene blue even when pH < 3 or pH > 11 due to its novel properties, which enables its actual applications in harsh conditions.

4. Conclusions

In summary, the activated BN with high adsorption capacity and degree of crystallinity were synthesized by a two-step synthesis route. Chemical activation of the BN fibers via using the mixed solution of sulfuric acid and nitric acid as activating reagent assisted by ultrasonication increases their hydroxyl and organic groups and surface defects. The activated BN exhibited excellent adsorption capacity as high as 392.2 mg/L and adsorption rate (effectively eliminating ~98.5 wt % within 5 min) at 30 °C and pH value of 8 for the cationic dyes. Compared with the BN fibers, the removal of MB on the activated BN was greatly improved. Moreover, only 6% efficiency lost after fifteen cycles. Therefore, we believe that the activated BN is a very promising candidate for hazardous dyes removal from aqueous solution, and open a door for increasing dyes adsorption weight density in the BN system, by more considerations on chemical activation.

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Figures and Captions:

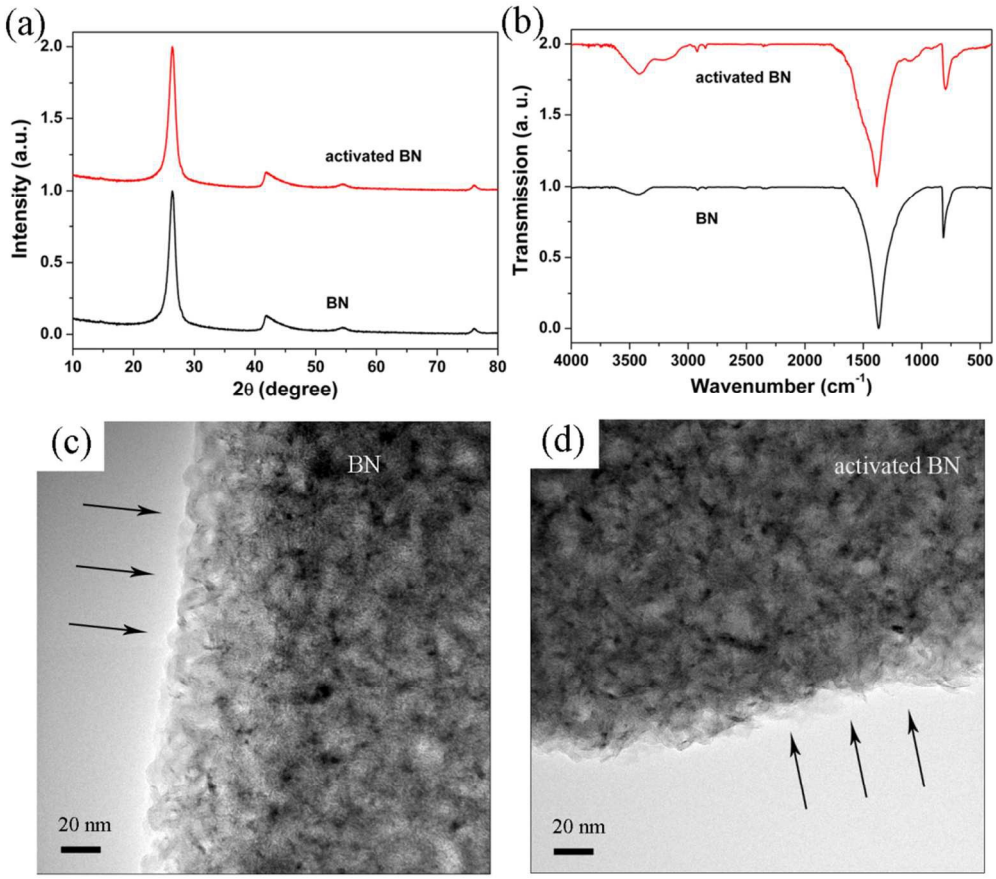

Figure 1. (a) XRD patterns and (b) FTIR spectra of the activated BN and the BN fibers, TEM images of (c) the BN fiber and (d) the activated BN.

$$C + 2\,HNO_3 \longrightarrow CO_2 + 4\,NO_2 + 2\,H_2O \qquad (1)$$

$$3\,N\text{-}B + 2HNO_3 \longrightarrow 2\,N\text{-}B\text{-}NO_3 + B\text{-}N\text{-}H_2 \qquad (2)$$

$$N\text{-}B\text{-}NO_3 + H_2O \longrightarrow N\text{-}B\text{-}OH + HNO_3 \qquad (3)$$

Figure 2. Chemically activated reactions of the BN fibers in the mixed acid solution.

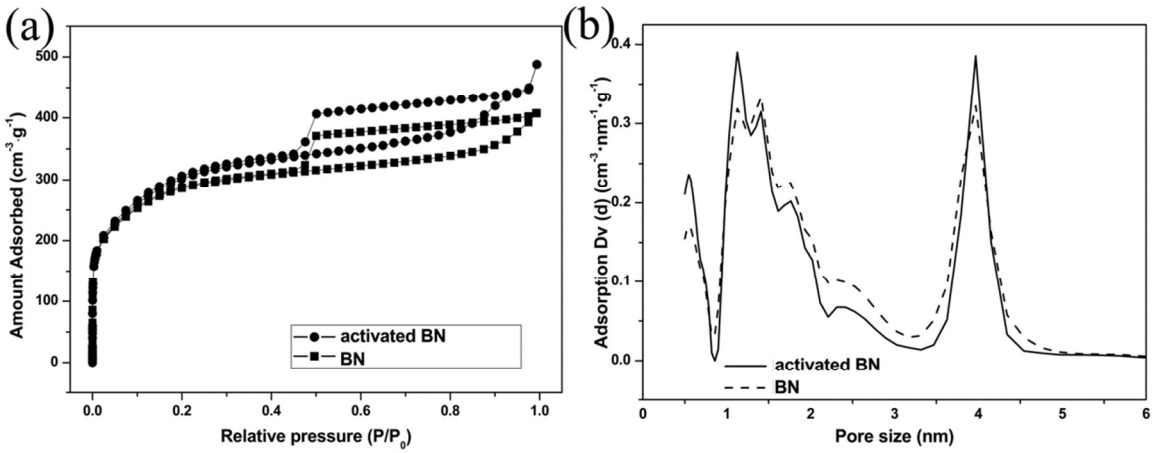

Figure 3. Characterization of pore structure of the two adsorbents. a) Nitrogen adsorption/desorption isotherms, b) the corresponding pore size distributions obtained by NLDFT method.

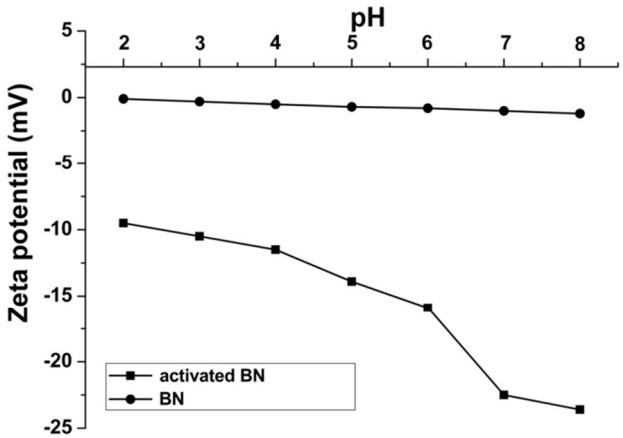

Figure 4. Zeta potential vs. pH values of the activated BN and the BN fibers.

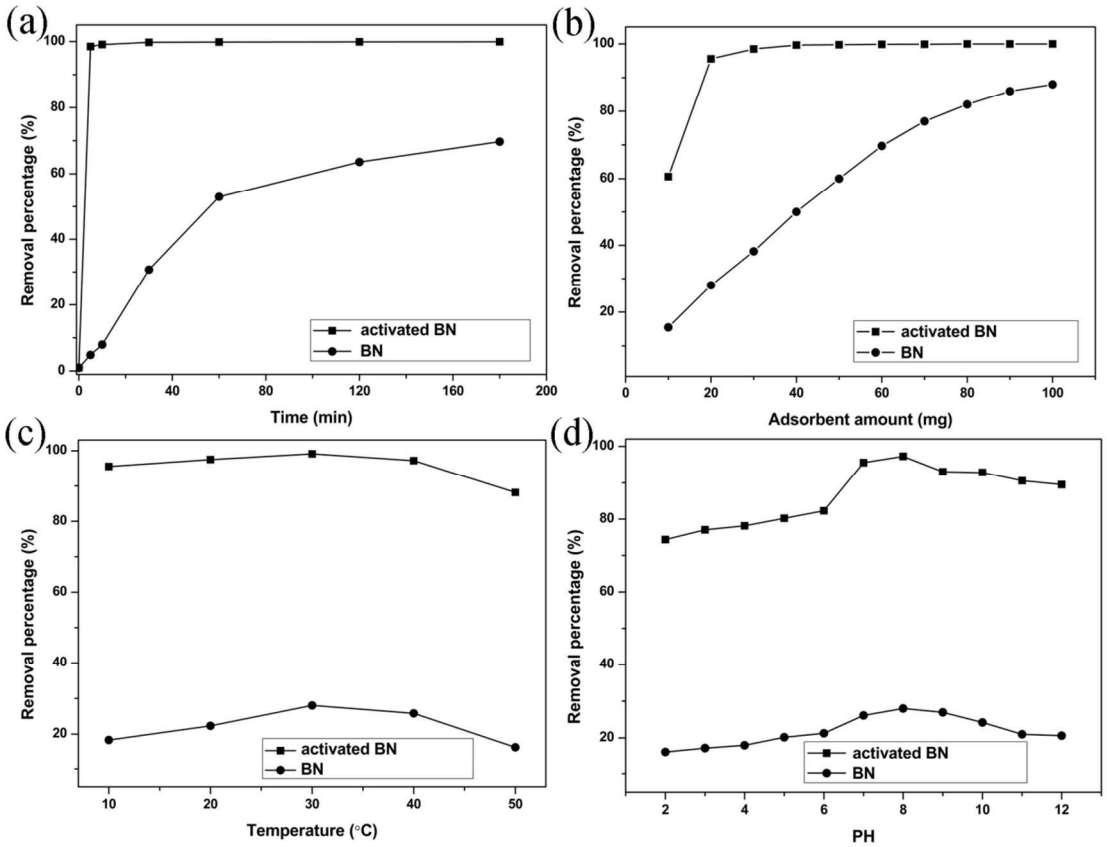

Figure 5. (a) Adsorption rate of MB on the two adsorbents (pH value: 8, adsorbent dosage: 60 mg, adsorption temperature: 30 °C, dye concentration: 25 mg/L). (b) Effect of adsorbent dosage for adsorption of MB (pH value: 8, contact time: 180 min, adsorption temperature: 30 °C, dye concentration: 25 mg/L). (c) Effect of temperature for adsorption of MB (pH value: 8, contact time: 180 min, adsorbent dosage: 20 mg, dye concentration: 25 mg/L). (d) Effect of pH value for adsorption of MB (Contact time: 180 min, MB concentration: 25 mg/L, temperature: 30 °C, adsorbent dosage: 20 mg).

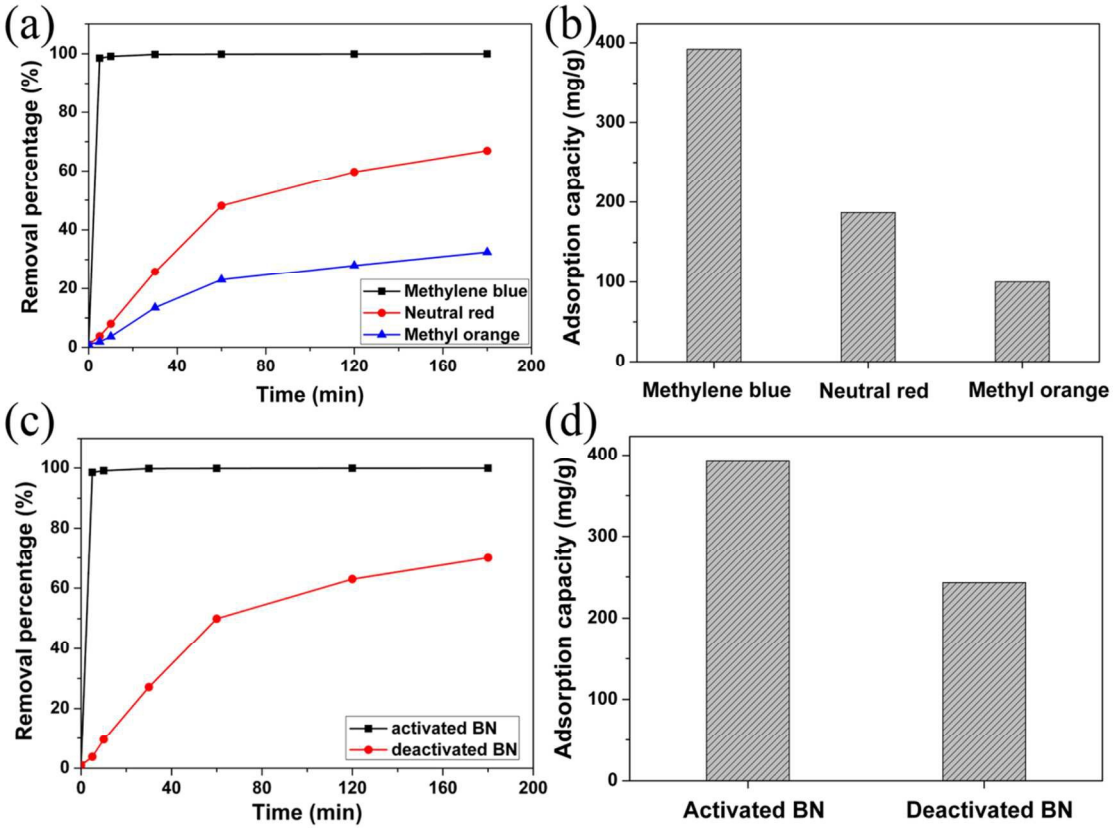

Figure 6. (a) Comparison of adsorption rates of methylene blue, neutral red, and methyl orange on the chemically activated BN (pH value: 8, adsorbent dosage: 60 mg, adsorption temperature: 30 °C, dye concentration: 25 mg/L, solution volume: 250 mL), respectively. (b) The corresponding comparison of adsorption capacities for the different styles of dye. (c) Comparison of adsorption rates of methylene blue on the activated BN and deactivated BN, respectively. (d) The corresponding comparison of adsorption capacity.

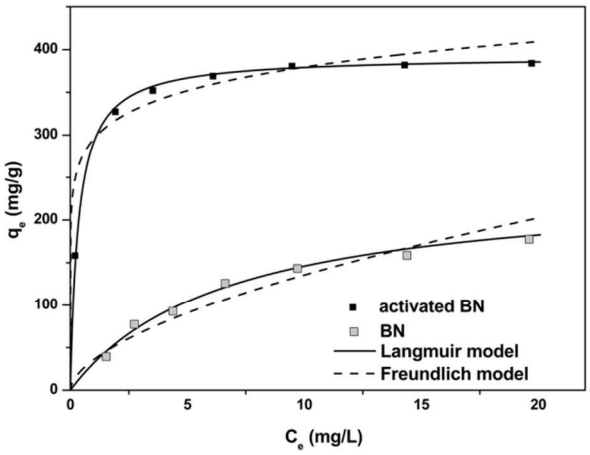

Figure 7. Adsorption isotherms of MB on the two adsorbents. Contact time: 180 min, pH: 8, temperature: 30 °C, dye concentration: 25 mg/L.

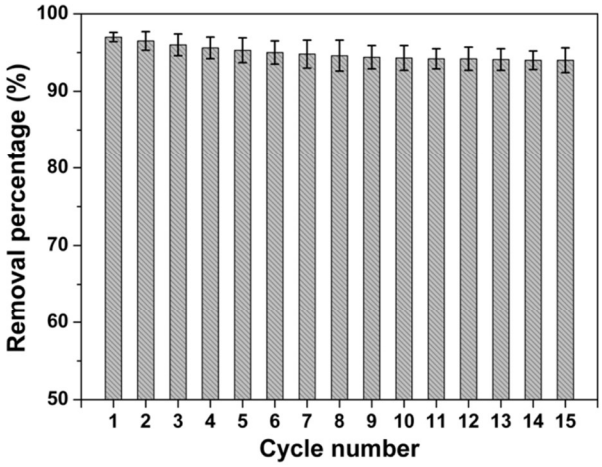

Figure 8. Reusability of the activated BN regenerated by calcinations.