Fe₃O₄-Functionalized Boron Nitride Nanosheets as Novel Adsorbents for Removal of Arsenic(III) from Contaminated Water

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1. INTRODUCTION

The contamination of natural water by arsenic (As) has become a global problem. According to estimates, 70.4 million people in India and 140 million people around the globe are exposed to drink As-contaminated groundwater. Exposure to As-contaminated water in the long term may result in cancer, neurological diseases, and muscular weakness, to name a few. Due to its superparamagnetic nature at room temperature, the nanocomposite can be easily isolated from the solution under an external magnetic field. For As(III) ions, the maximum adsorption capacity of the nanocomposite is obtained as 30.3 mg g⁻¹, which is approximately 4 times more than that of the bare BNNSs (8.5 mg g⁻¹). The results from density functional theory calculations are also in close agreement with experimental findings and show that As(OH)₃ binds more (∼4 times) efficiently to the BNNS-Fe₃O₄ nanocomposite than the bare BNNSs, implying a 4 times higher adsorption capacity of the nanocomposite. Especially, it is found that the synthesized nanocomposite could lessen the concentration of As(III) ions from 134 to 2.67 ppb in a solution at 25 °C. On increasing the temperature to 35 °C, the level of As(III) ions could be reduced from 556 to 10.29 ppb, which is close to the limit prescribed by the World Health Organization. The adsorbent was easily separable and showed regeneration properties. These outcomes depict the prospect of using BNNS-Fe₃O₄ nanocomposites as commercial adsorbents for the removal of As(III) ions from contaminated water.
one of the seminal papers, Chandra et al. removed As(III) by the incorporation of magnetite on the surface of reduced graphene oxide. The adsorption capacity was found to be 13.1 mg g⁻¹. Further, Andjelkovic et al. reduced 150 ppb of As(III) of real water sample to 10 ppb (i.e., 93.3% removal) with the three-dimensional (3D) graphene–iron oxide nanoparticle aerogel composite and an adsorption capacity of 13.42 mg g⁻¹. Carbon nanotubes (CNTs) have also been coated with iron oxide for As(III) remediation. The iron oxide–multiwalled carbon nanotube (Fe–MWCNT) hybrid synthesized by Ntim and Mitra, with an adsorption capacity of 1723 μg g⁻¹, worked effectively to bring down the arsenic level to the drinking water level. Using the magnetic iron oxide/CNT combination, Ma et al. demonstrated the adsorption capacity of As(III) as 8.13 mg g⁻¹. Iron and aluminum oxide-coated 3D-organized mesoporous silica has also been reported in the literature for the removal of As(III) from synthetic contaminated water. However, the adsorption capacity was found to be low (0.21 mg g⁻¹).

An adsorbent to be used for water remediation should have a high adsorption capacity in addition to a good physical and chemical stability, large surface area, nontoxicity, high recyclability, and ease of separation. In light of these requirements, we have synthesized and characterized boron nitride nanosheets (BNNSs) of large specific surface area. The unique bipolar nature and planar bonding make BNNSs chemically stable. BNNSs have been functionalized with Fe₃O₄ nanoparticles, and the adsorption performance studies of As(III) of both unmodified and Fe₃O₄ functionalized BNNSs have been carried out. In addition to enhancing the adsorption capacity, the Fe₃O₄-functionalized nanocomposite adsorbent easily separates from water under a magnetic field. Further, the experimentally calculated adsorption capacities are in agreement with the density functional theory (DFT) simulations. The results demonstrate the potential of these nanocomposites for arsenic removal from water.

2. MATERIALS AND METHODS

2.1. Computational Details: DFT Calculations. The initial structure of the boron nitride sheet was prepared using visual molecular dynamics (VMD), whereas other structures such as Fe₃O₄ and As(OH)₃ were built and optimized using Avogadro. Theoretical calculations were performed using first-principles DFT, as implemented in the Quantum ESPRESSO code. Generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional of ultrasoft pseudopotentials type was used in this case. Ultrasoft pseudopotentials were generated using the Rappe–Rabe–Kaxiras–Joannopoulos (RRKJ3) method. The Kohn–Sham wave functions were expanded in a plane-wave basis set with kinetic energy cutoffs of 650 and 600 Ry for charge density. Brillouin zone (BZ) integration with a Monkhorst–Pack k-point grid of 5 × 5 × 5 was used for geometry optimization, and 10 × 10 × 1 for self-consistent calculations. The cell parameters and atomic positions were relaxed until the forces on each ion and atom became smaller than 0.03 eV A⁻¹. To avoid interaction within periodic images, 20 Å of vacuum was used between periodically repeated layers. As is well known that the van der Waals (vdW) interaction is important for adsorption energy calculation, we applied Grimme’s dispersion correction to DFT calculations (DFTD3) for the PBE functional. In the current work, the binding energy (BE) calculations of As(OH)₃ on both the adsorbents have been computed and compared. The BEs were calculated using the following relations

\[
BE = E(\text{BNNS} - \text{Fe}_3\text{O}_4 + \text{As(OH)}_3) - [E(\text{BNNS} - \text{Fe}_3\text{O}_4) + E(\text{As(OH)}_3)]
\]

(BNNSs)

\[
BE = E(\text{BNNSs} + \text{As(OH)}_3) - [E(\text{BNNSs}) + E(\text{As(OH)}_3)].
\]

2.2. Experiments. 2.2.1. Materials. The chemicals used in this study were the same as the ones reported in our earlier work and are mentioned in the Supporting Information. In addition, hydrochloric acid (∼37%) and methanol were received from Thermo Fisher Scientific, India. Sodium arsenite (≥98.5% purity) that was used a source of As(III) and the standard As ion solution were purchased from Loba Chemie, India.

2.2.2. Synthesis of BNNSs. BNNSs were synthesized by easily available and low-cost precursors boric acid and urea. The molar ratio used was 1:30. Accurately weighted (using ME 204, Mettler Toledo electronic weighing machine) boric acid and urea were mixed physically with a mortar and pestle. Further, methanol and deionized (DI) water were added into the mixture and subsequently dried inside an oven at 45 °C. Afterward, the dried mixture was placed in a quartz boat and kept in a tubular furnace. The mixture was heated up to 900 °C and maintained at this temperature in a N₂ gas environment for 2 h. Once the chemical reaction was complete, the temperature of the furnace was decreased gradually to room temperature. At the end, white BNNSs were received.

2.2.3. Synthesis of BNNS-Fe₃O₄ Nanocomposites. To functionalize BNNSs with Fe₃O₄ nanoparticles, a known amount of BNNSs was added in 100 mL of DI water. Thereafter, the solution was subjected to ultrasonication (Oscar, India) for 1 h. To synthesize Fe₃O₄ nanoparticles, FeCl₃·6H₂O and FeCl₂·4H₂O in a molar ratio of 2:1 were added to the stirring solution. During the start of the reaction, the pH of the solution was adjusted to 8.0 by a dropwise addition of 3 mL of NH₄OH through a syringe. The solution was magnetically stirred further for 3.5 h. The whole reaction was performed under a N₂ gas environment. At the end of the reaction, the synthesized product was washed with ultrapure deionized (DI) water and dried at 65 °C to get Fe₃O₄-coated BNNSs.

2.2.4. Characterization and Measurements. Imaging techniques such as field emission scanning electron microscopy (FESEM, Carl Zeiss) and high-resolution transmission electron microscopy (HREM, FEI Titan G2 60-300 microscope) were used to characterize the morphologies, elemental distribution, and nature (amorphous/crystalline) of synthesized materials. A N₂ gas adsorption–desorption isotherm at −196 °C (Quantachrome Autosorb iQ) was used to calculate the specific surface area (SBET), pore size distribution, and pore volume. To examine the structure of BNNSs and BNNS-Fe₃O₄, X-ray diffraction (XRD, Panalytical X’Pert Powder) was used. The plots of the synthesized products were noted by Cu Kα radiation (λ = 1.506 Å) from 10 to 70°. The surface functional groups were analyzed by Fourier transform infrared (FTIR) spectroscopy (PerkinElmer Spectrum Two spectrometer). The saturation magnetization (Mₛ) of the nano-
composite was determined by a vibrating sample magnetometer (VSM, EV7 ADE-DMS) at room temperature. The concentrations of As(III) in the aqueous solution were measured by inductively coupled plasma mass spectrometry (Agilent 7900, ICP-MS) with the help of a standard calibration curve prepared by the standard solution of As. The synthesized adsorbent was mounted on conductive carbon tape and examined by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe-ULVAC-PHI Inc.). Raman spectroscopy was carried out using a 532 nm laser (Airix micro-Raman spectrometer) to characterize the adsorbed sample.

2.2.5. Arsenic(III) Adsorption Experiments. All of the adsorption experiments were performed at room temperature (25 °C). The batch experiments were performed to determine the effect of various adsorption parameters (initial pH, contact time, dosage, and isotherm) on the As(III) adsorption capacity of both the adsorbents. In the batch experiments, 0.4 g per liter of adsorbents were added into As(III) (25 mL, 25 mg L⁻¹). Subsequently, the solutions were subjected to ultrasonication for 5 min to disperse the adsorbents into the As(III) solution. The initial pH, kinetics, and dosage studies were performed by fixing the concentration of As(III) solution at 25 mg L⁻¹. The effect of pH on the adsorption capacity was studied by varying the pH in the range of 2–12. HCl (0.1 M) and NaOH (0.1 M) solutions were used to maintain the initial pH. All of the adsorption experiments were conducted at 200 rpm and 25 °C inside a thermally controlled orbital shaker purchased from Mahendra Scientific, India. After taking out the equilibrated samples, a 0.22 μm syringe filter (Milllex) was used to separate the adsorbents. It was followed by the determination of As(III) concentration in the aqueous solution using ICP-MS.

The following equation was used to calculate the equilibrium uptake \( q_e \) (mg g⁻¹)

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

(1)

where \( C_0 \) (mg L⁻¹) is the initial As(III) ion concentration, \( C_e \) (mg L⁻¹) is the equilibrium As(III) ion concentration, \( V \) (L) is the volume of solution, and \( m \) (g) is the mass of the adsorbent. In this work, all of the experiments were performed in triplicate and their mean values have been presented.

2.2.5.1. Kinetic Studies. The kinetic studies were performed by adding a known amount of adsorbent into 100 mL of the As(III) solution (25 mg L⁻¹) at the optimum pH value obtained through the pH study. Thereafter, the experimental data were analyzed with pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. These models are used to determine the kinetic parameters of BNNSs and BNNS-Fe₃O₄. The linear forms of PFO and PSO models are expressed using eqs 2 and 3, respectively, as

\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]

(2)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]

(3)

where \( q_t \) is the amount of adsorbed solute at time \( t \), \( k_1 \) (min⁻¹) is the pseudo-first-order rate constant, and \( k_2 \) (g mg⁻¹ min⁻¹) is the pseudo-second-order kinetic rate constant.

2.2.5.2. Adsorption Isotherm Study. This study was carried out to investigate the effect of the initial concentration of As(III) on the adsorption capacity. The dose was kept constant at 0.4 g L⁻¹, and the pH was maintained at the value obtained through the optimization study. Thereafter, samples were transferred to a thermo-controlled orbital shaker. It was kept at 25 °C and 200 rpm. Moreover, two isotherm models, viz., Langmuir and Freundlich, were applied to analyze the adsorption data. The Langmuir isotherm is represented by the following equation

\[
q_e = \frac{q_m C_e K_L}{1 + C_e K_L}
\]

(4)

In eq 4, \( K_L \) (mL mg⁻¹) and \( q_m \) (mg g⁻¹) denote the Langmuir adsorption equilibrium constant and the maximum adsorption capacity of the adsorbent, respectively. Similarly, the following equation is used to represent the Freundlich isotherm

\[
q_e = K_F C_e^{1/n}
\]

(5)

In eq 5, \( K_F \) is a constant that measures the adsorption capacity, while \( n \) is another constant that measures the adsorption intensity.³⁵

3. RESULTS AND DISCUSSION

3.1. DFT Calculations on As(III) Adsorption. To assess the binding ability of As with Fe₃O₄, the first-principles DFT approach was used to compute the interaction strength between As(OH)₃ with both the adsorbents. The theoretically optimized (relaxed) structures of BNNSs and As(OH)₃, are displayed in Figure 1a,b, respectively. Similarly, the side and top views of the BNNS-Fe₃O₄ nanocomposite are displayed in Figure 1c,d, respectively, from which one can see the formation of the BNNS-Fe₃O₄ nanocomposite through B—O and N—Fe bonds. The computed average distance between the BNNSs and the Fe₃O₄ surface was found to be ~2.45 Å. Further, the geometric relaxation of As(OH)₃ with BNNSs and BNNS-Fe₃O₄ structures were performed using a similar approach stated above, and the BEs were evaluated later using the same method described in Section 2.1. The computationally relaxed structures of BNNS-As(OH)₃ and BNNS-Fe₃O₄-As(OH)₃ systems are shown in Figure 2a,b, which were computed using the DFT approach. The calculated values of BEs for both As(OH)₃ with BNNSs and BNNS-Fe₃O₄-As(OH)₃ systems are ~27.160 and ~113.272, in units of kJ mol⁻¹, respectively. These results demonstrate that As(OH)₃ shows ~4.15 times more binding energy strength with BNNS-Fe₃O₄ than the unmodified BNNSs. This indicates a higher adsorption capacity for BNNS-Fe₃O₄ between the two adsorbents.

3.2. Characterization of the Adsorbents. The morphology, crystallinity, and elemental distribution of the synthesized adsorbents were characterized by FESEM and HRTEM. The layered structure of the sheets can be easily seen by FESEM (see Figures S1a). In the HRTEM image in Figure 3, the fringes of BNNSs are clearly seen in Figure 3a-i. Moreover, the BNNS-Fe₃O₄ nanocomposite depicts the cubic structure of the Fe₃O₄ nanoparticles (see Figure 3b-i) deposited on the layers of BNNSs. The selected area electron diffraction (SAED) pattern of BNNSs shows the diffuse rings, implying its amorphous nature. Each ring corresponds to the (002), (100), and (101) planes as we move in the outward direction from the center of the ring, as shown in Figure 3c. On the other hand, the SAED pattern of the BNNS-Fe₃O₄ nanocomposite shows rings with spots as shown in Figure 3d. This indicates the crystalline nature of the nanocomposite. The high-angle annular dark field (HAADF) image and elemental
BNNS-Fe₃O₄ nanocomposite may be attributed to the N₂ adsorption on its surface. A decrease in the specific surface area (SBET) and pore size distribution (PSD). The SBET values for BNNSs and BNNS-Fe₃O₄ were obtained as 1801.9 and 63.07 m² g⁻¹, respectively. The reduction in the total pore volume and the corresponding specific surface area of the BNNS-Fe₃O₄ nanocomposite may be attributed to the filling of pores of BNNSs during the growth of magnetic (Fe₃O₄) nanoparticles on its surface. A decrease in the specific surface area with magnetite loading was also observed in the case of graphene oxide.³⁸

The XRD patterns of BNNSs and BNNSs-Fe₃O₄ are shown in Figure 4. BNNSs show their characteristic diffraction peaks at 25.4 and 41.2° that correspond to (002) and (101) planes. Due to the broadening of diffraction peaks, two close peaks (100) and (101) were merged at 41.2°. The peak broadening of BNNSs indicates the amorphous behavior of BNNSs. The XRD pattern of BNNS-Fe₃O₄ shows various crystalline peaks at 2θ = 30.37, 35.65, 43.53, 53.85, 57.37, and 63.07°.³⁶⁻³⁸ These peaks correspond to the (220), (311), (400), (422), (511), and (440) planes. The positions of all of the peaks and the corresponding planes matched with JCPDS card no. 19-0629. Further, all of the planes perfectly match and are well supported by the corresponding SAED patterns.

To characterize further, FTIR spectroscopy was used to record the vibrating signature of the functional groups that existed on the synthesized materials through transmission/adsorption spectra in the range of 4000–400 cm⁻¹. Figure 5 shows the FTIR spectra of BNNSs and BNNS-Fe₃O₄ with black and red colors, respectively. The spectra of BNNSs show two characteristics peaks at 780 and 1380 cm⁻¹. The peak at 780 cm⁻¹ corresponds to the out-of-plane vibration of B–N–B, while the peak at 1380 cm⁻¹ represents the in-plane vibration of B–N–B. The peak at ~1644 cm⁻¹ corresponds to the bending vibration of H–O–H from the water molecule. The low-intensity peaks at 2852 and 2925 cm⁻¹ represent the –BNH₂ group formation at the edges.³⁹ Finally, a broad peak is observed at 3415 cm⁻¹ that can be ascribed to the B–OH group.⁴⁰ In the case of BNNS-Fe₃O₄, the FTIR spectrum clearly shows the symmetric vibration of Fe–O at 583 cm⁻¹. The out-of-plane vibration of B–N–B bonds and its intensity are related to the stacking order of BNNSs. The in-plane vibration of BNNSs at 1380 cm⁻¹ indicates no change in the structure of BNNSs after the formation of BNNS-Fe₃O₄ nanocomposite. Moreover, the peak at 923 cm⁻¹ is due to the stretching vibration signals of Fe–O–Fe.

To determine the percentage composition of BNNS-Fe₃O₄, an XPS study was carried out. As can be seen in Figure 6, the percentages of boron, carbon, nitrogen, oxygen, and iron were found to be 12.2, 17.1, 6.4, 53.9, and 10.3, respectively. The percentages of boron, carbon, nitrogen, oxygen, and iron were found to be 12.2, 17.1, 6.4, 53.9, and 10.3, respectively. The reduction in the total pore volume and the corresponding specific surface area of the BNNS-Fe₃O₄ nanocomposite may be attributed to the filling of pores of BNNSs during the growth of magnetic (Fe₃O₄) nanoparticles on its surface. The percentage composition of BNNS-Fe₃O₄ nanoparticles as well as boron and nitrogen on BNNS-Fe₃O₄ nanocomposite, respectively. The nitrogen (N₂) adsorption–desorption isotherms (see Figure S2) of both the adsorbents were used to calculate the specific surface area (SBET) and pore size distribution (PSD). The SBET values for BNNSs and BNNS-Fe₃O₄ were obtained as 1801.9 and 179.5 m² g⁻¹, respectively. The reduction in the total pore volume and the corresponding specific surface area of the BNNS-Fe₃O₄ nanocomposite may be attributed to the filling of pores of BNNSs during the growth of magnetic (Fe₃O₄) nanoparticles on its surface. A decrease in the specific surface area with magnetite loading was also observed in the case of graphene oxide.³⁸ The XRD patterns of BNNSs and BNNSs-Fe₃O₄ are shown in Figure 4. BNNSs show their characteristic diffraction peaks at 25.4 and 41.2° that correspond to (002) and (101) planes. Due to the broadening of diffraction peaks, two close peaks (100) and (101) were merged at 41.2°. The peak broadening of BNNSs indicates the amorphous behavior of BNNSs. The XRD pattern of BNNS-Fe₃O₄ shows various crystalline peaks at 2θ = 30.37, 35.65, 43.53, 53.85, 57.37, and 63.07°.³⁶⁻³⁸ These peaks correspond to the (220), (311), (400), (422), (511), and (440) planes. The positions of all of the peaks and the corresponding planes matched with JCPDS card no. 19-0629. Further, all of the planes perfectly match and are well supported by the corresponding SAED patterns.

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3.3. Effects of Adsorption Parameters. 3.3.1. Effect of pH. The surface charge of the adsorbent plays a decisive role in the adsorption process, which is directly affected by the pH of the solution among others. To investigate the surface charge, ζ-potential measurements were performed to determine the point of zero charge (PZC). Additionally, the pH drift method was also used to find the same. In the case of BNNS-Fe₃O₄, the Ms was determined to be 47.39 emu g⁻¹ and is shown in Figure 7. The inset image shows the separated adsorbent from the aqueous solution. Therefore, one can easily separate the adsorbent (BNNS-Fe₃O₄) from the aqueous solution with the help of a magnet.

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to 8 since there is no electrostatic attraction between the neutral H$_3$AsO$_3$ and the positive surface of the adsorbents (see Figure 8b). Therefore, the increase of the adsorption capacity in the slightly alkaline solution can be attributed to the surface complexation reaction between the adsorbent surface and H$_3$AsO$_3$. With a further increase in pH, As(III) becomes negatively charged due to the formation of H$_2$AsO$_3$$^-$$^-$$^-$$^-$$^-$ and HAsO$_3$$^-$$^-$$^-$$^-$$^-$ species. Therefore, the adsorption capacity decreases rapidly due to the electrostatic repulsion between the arsenic species and negatively charged adsorbent. Another reason behind the decline in the adsorption capacity of both the adsorbents with an increase in the pH value beyond 8 may be the competition between H$_2$AsO$_3$$^-$$^-$$^-$$^-$$^-$(the form in which As(III) exists) and the high OH$^-$$^-$$^-$$^-$$^-$ concentration present in the aqueous solution for active sites of the adsorbents.

3.3.3. Adsorption Kinetics. To carry out the contact time study, the adsorbent dose was taken as 0.4 g l$^{-1}$. The adsorption capacities of both the adsorbents increase with time, as shown in Figure 10. The adsorption capacity of BNNS-Fe$_3$O$_4$ increases rapidly up to 120 min. Thereafter, the adsorption increases gradually and achieves equilibrium at 480 min. The adsorption plot becomes a plateau after 240 min. The kinetic behavior shown by both the adsorbents is quite different. This is mainly due to the high affinity of the BNNS-Fe$_3$O$_4$ nanocomposite for As(III) due to the presence of Fe$_3$O$_4$. The adsorption rate is initially high. It saturates later due to the
saturation of available active sites on the adsorbent. The kinetic data were analyzed by PFO and PSO models, and the corresponding parameters of the adsorbents are listed in Table 1. The kinetics rate constants $k_1$ and $k_2$ were determined from eqs 2 and 3, respectively. The PSO kinetic model showed a higher correlation ($R^2 = 0.99$) than the PFO ($R^2 = 0.97$) kinetic model. Consequently, it can be assumed that both the adsorbents followed this model.

3.3.4. Adsorption Isotherms. To determine the effect of the initial concentration of As(III) on the adsorption capacity, an adsorption isotherm study was performed (see Figure 11). Langmuir and Freundlich models were used to analyze the experimental data. The Langmuir isotherm model assumes the monolayer adsorption behavior of the adsorbent. On the
other hand, the Freundlich model represents the multilayer adsorption behavior of the adsorbent. The experimental value of the As(III) adsorption capacity shown by BNNSs and the nanocomposite were obtained as 8.50 and 26.70 mg g\(^{-1}\), respectively. The high correlation \((R^2 = 0.98)\) in the case of BNNSs implies that the adsorption of As(III) is dominated by the Freundlich isotherm model. Conversely, the Langmuir isotherm model governs As(III) adsorption in the case of BNNS-Fe\(_3\)O\(_4\) as indicated by its correlation coefficient \((R^2 = 0.96)\). All of the calculated adsorption parameters are listed in Table 2. The maximum adsorption capacity of BNNS-Fe\(_3\)O\(_4\) calculated through the Langmuir isotherm model was found to be 30.30 mg g\(^{-1}\). This nearly 4 times enhancement is in line with the theoretical simulations performed by DFT calculations.

3.3.5. Possible Mechanism of As(III) Adsorption. The good performance of BNNS-Fe\(_3\)O\(_4\) is attributed to the As(III) adsorption on the iron oxide surface through the inner-sphere ligand-exchange mechanism. This is followed by monodentate and outer-sphere complex formation that are expressed by eqs 6 and 7. Figure 12 shows the presence of As(III) in the elemental distribution mapping of BNNSs and BNNS-Fe\(_3\)O\(_4\) nanocomposite after adsorption. This reveals the bonding of As(III) with the nanocomposite. Further, the FTIR spectrum shows a peak at 773.20 cm\(^{-1}\), which is indicative of the stretching vibration
of the As–O bond (see Figure 13). This also confirms the adsorption of As(III) through the inner-sphere ligand-exchange mechanism. Therefore, both the analyses support the mechanism of inner-sphere complex formation that is in agreement with the literature.

\[
\begin{align*}
\text{Fe}_3\text{O}_4 - \text{OH} + \text{H}_2\text{AsO}_3^- & \rightarrow \text{Fe}_3\text{O}_4 - \text{O} - \text{As} - (\text{OH})_2 + \text{H}_2\text{O} \\
\text{Fe}_3\text{O}_4 - \text{OH} + \text{H}_2\text{AsO}_3^- & \rightarrow \text{Fe}_3\text{O}_4 - \text{O} - \text{H} - \text{O} - \text{As} - (\text{OH})_2 + \text{H}^+ 
\end{align*}
\]

To investigate further, the pristine and arsenic adsorbed samples were analyzed by Raman spectroscopy. The Raman spectrum (see Figure 14) clearly shows the presence of a peak at 380 cm\(^{-1}\). This peak corresponds to the presence of As–(OH) symmetric stretching bonds.\(^{53}\) Moreover, the survey and narrow spectra of As 3d in Figure 15 confirms the presence of As(III) in the adsorbed sample. The broad peak of As 3d depicts the presence of As(III) and As(V) at 43.20 and 44.6 eV, respectively.\(^{52,54}\) The presence of As(V) in the adsorbed sample is attributed to the oxidation of As(III) during the adsorption of As(III) on the BNNS-Fe\(_3\)O\(_4\) nanocomposite.\(^{52}\)

### 3.4. Adsorption Thermodynamics

In this study, the effect of temperature too has been investigated since it also plays a significant role in adsorption. Accordingly, the adsorption experiments were carried out at three different temperatures (25, 35, and 45 °C). Further, the thermodynamic parameters such as change in Gibbs free energy change (\(\Delta G^0\)), enthalpy change (\(\Delta H^0\)), and entropy change (\(\Delta S^0\)) were evaluated by the following equations\(^{55-57}\)

\[
\begin{align*}
K_c &= q_e / C_e \\
\Delta G^0 &= -RT \ln K_c \\
\Delta G^0 &= \Delta H^0 - T \Delta S^0 
\end{align*}
\]

where \(K_c\) is the equilibrium constant, \(q_e\) is the amount of solute adsorbed on the adsorbent, \(C_e\) is the remaining concentration of the adsorbate at equilibrium in the solution, \(T\) is the temperature in Kelvin, and \(R\) is the universal gas constant. The slope and intercept of the \(\Delta G^0\) vs \(T\) plot in Figure 16 were used to calculate \(\Delta H^0\) and \(\Delta S^0\), respectively. The calculated values of \(\Delta G^0, \Delta H^0,\) and \(\Delta S^0\) are listed in Table 3. One can see that \(\Delta G^0\) decreases from \(-15.35\) to \(-16.92\) (kJ mol\(^{-1}\)) with an increase in temperature for BNNS-Fe\(_3\)O\(_4\). This indicates that the adsorption is more favorable at a high temperature for BNNS-Fe\(_3\)O\(_4\). On the other hand, \(\Delta G^0\) increases from \(-12.47\) to \(-9.05\) (kJ mol\(^{-1}\)) for BNNSs, which means that the adsorption of As(III) on BNNSs is unfavorable at higher temperatures. Positive (+7.999 kJ mol\(^{-1}\)) and negative (−13.099 kJ mol\(^{-1}\)) values of \(\Delta H^0\) for BNNSs and BNNS-Fe\(_3\)O\(_4\) and BNNSs indicate the endothermic and exothermic behavior of the reaction, respectively. Therefore, both the analyses support the mechanism of inner-sphere complex formation that is in agreement with the literature.

### 3.5. Regeneration Study

From the pH study, it was found that the adsorption capacity decreases continuously when the pH increases from 8.0 to higher values. Therefore, to regenerate the As(III)-adsorbed adsorbent (BNNS-Fe\(_3\)O\(_4\)), it was further added in 1.0 M NaOH solution for 24 h. For the regeneration analysis, three samples, named as pristine, after adsorption, and after regeneration, were examined by FTIR.
spectroscopy. The corresponding spectra (see Figure 17a) of the sample after adsorption showed a peak at 835 cm$^{-1}$, which corresponds to the As–O stretching vibration. The same peak was missing in the pristine and after regeneration in samples. Therefore, this result confirms the successful regeneration of BNNS-Fe$_3$O$_4$. The regenerated samples were further examined for the adsorption capacity. Figure 17b shows the adsorption capacity of the adsorbent after adsorption–desorption–regeneration cycle. It was found that the adsorbent retained the same adsorption capacity for five cycles.

3.6. Application of BNNS-Fe$_3$O$_4$ Nanocomposite for Higher Concentrations of As(III) ions. Finally, with the aim of testing the efficacy of the synthesized adsorption in real samples, we have considered the Ballia district in the state of Uttar Pradesh of India where severe health problems as a result of high concentration of As ions (as high as 218 ppb As(III)) in potable water have been reported. Therefore, this range of As ions has been used to test the synthesized adsorbent. The results in Table 4 show the potential of the synthesized BNNSs-Fe$_3$O$_4$ nanocomposite as an adsorbent for As levels well above the WHO guideline. Further, it has been demonstrated that the higher concentrations of As(III) can be brought to the drinking level by increasing the temperature. At room temperature (25 °C), low concentrations of As(III) starting from 68.79 to 134.13 ppb can be successfully reduced to 2.65 and 2.67 ppb, respectively by applying the synthesized nanocomposite. However, it fails to bring it down to the safe drinking limit at initial concentrations of 351.30 ppb and
higher. By increasing the temperature from 25 to 35 °C, the nanocomposite can bring down 347.05 and 566.42 ppb to 5.95 and 10.29 ppb, respectively, after adsorption. To assess the potential of the synthesized nanocomposite, its adsorption capacity was compared to other adsorbents used for As(III) adsorption. Table 5 shows the adsorption capacities of different adsorbents used for As(III) adsorption. As can be seen, the synthesized nanocomposite is better than the
magnetic nanoparticle-functionalized graphene and graphene oxide and showed better adsorption capacity than most of the adsorbents. There are a few studies that have reported a higher adsorption capacity than the current study. However, they have not reported about the regeneration and separation property of the adsorbents. Some of the other studies report a high adsorption capacity at a high initial concentration range, i.e., 1−250 ppm, of As(III). However, this concentration range of As(III) is not practically available in many parts of the world. The As(III) contamination is found to be below 1 ppm in the majority of the cases. Therefore, it is also important to study the adsorption behavior of the adsorbent at this concentration range, which has been done in this study. In sum, this study demonstrates the potential of BNNS-Fe₃O₄ nanocomposites as novel adsorbents for As(III) removal from water.

4. CONCLUSIONS

This study presented the synthesis of BNNSs and BNNS-Fe₃O₄ nanocomposite with SBET values of BNNSs and BNNS-Fe₃O₄ of 1801.9 and 179.5 m² g⁻¹, respectively. Further, their performance as adsorbents for As(III) removal from contaminated water was studied with various adsorption parameters that included pH, adsorption time, dosage rate, and the effect of the initial concentration of As(III). It was found through the pH study that the maximum adsorption could be achieved at pH = 8. The thermodynamic study showed the exothermic and endothermic nature of BNNSs and BNNS-Fe₃O₄ nanocomposite, respectively. Additionally, the kinetic analysis showed that the As(III) adsorption on both of them followed the PSO kinetic model. The adsorption isotherms of BNNSs fitted well with the Freundlich model, while it correlated well with the Langmuir model in the case of BNNS-Fe₃O₄. The maximum adsorption capacity of BNNSs was found to be 8.5 mg g⁻¹, while it was 30.3 mg g⁻¹ in the case of BNNS-Fe₃O₄. This nearly 4-fold increase in the adsorption capacity is mainly due to the enhanced binding affinity of As(OH), on the BNNS-Fe₃O₄ nanocomposite, as revealed by the DFT calculations. The synthesized BNNS-Fe₃O₄ nanocomposite was able to reduce 134 ppb of As(III) to 2.67 ppb at room temperature (25 °C). With an increase in the temperature to 35 °C, the synthesized nanocomposite could decrease the level of As(III) from up to 556 to 10.29 ppb that is very close to the limit recommended by WHO. Since the nanocomposite exhibited superparamagnetic behavior at room temperature, its separation from water was achieved quite easily. Moreover, the synthesized adsorbent showed regeneration behavior. Hence, the synthesized nanocomposite

Figure 16. Plot of Gibb’s free-energy change (ΔG°) versus temperature for exothermic (BNNSs) and endothermic (BNNS-Fe₃O₄) processes.

Figure 17. (a) Regeneration and (b) recycling results of As(III)-adsorbed samples.

Table 3. Thermodynamic Parameters for the Adsorption of As(III) on BNNSs and BNNS-Fe₃O₄

| temp. (K) | ΔG° (kJ mol⁻¹) | ΔH° (kJ mol⁻¹) | ΔS° (J mol⁻¹ K⁻¹) | ΔG° (kJ mol⁻¹) | ΔH° (kJ mol⁻¹) | ΔS° (J mol⁻¹ K⁻¹) |
|----------|----------------|----------------|-------------------|----------------|----------------|-------------------|
| 298      | −12.47         | −13.099        | 1708              | −15.35         | 7.999          | −78               |
| 308      | −10.17         | －             |                   | −15.99         | －             |                   |
| 318      | −9.05          | －             |                   | −16.92         | －             |                   |

Table 4. As(III) Concentration after Adsorption on BNNSs-Fe₃O₄ (Experimental Conditions: pH, 8.0; Dose of Adsorbent, 0.4 g l⁻¹; Temp, 25 and 35 °C)

| temp. (°C) | C₀ (before adsorption, ppb) | Cₑ (after adsorption, ppb) | C₀ (before adsorption, ppb) | Cₑ (after adsorption, ppb) |
|-----------|-------------------------------|----------------------------|----------------------------|----------------------------|
| 25         | 68.79                         | 2.65                       | 140.18                     | 2.05                       |
| 35         | 134.13                        | 2.67                       | 165.05                     | 2.16                       |
|            | 351.30                        | 19.63                      | 347.05                     | 5.95                       |
|            | 567.86                        | 46.48                      | 566.42                     | 10.29                      |

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demonstrates its suitability as a promising candidate for the treatment of As(III) ions from polluted water.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04295.

FESEM, BET images; \( N_2 \) adsorption–desorption isotherm; and pore size distribution of BNNSs and BNNS-Fe\(_3\)O\(_4\) (PDF)

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Notes

The authors declare no competing financial interest.

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Table 5. Comparison of Maximum As(III) Adsorption Capacities Reported by Different Adsorbents

| adsorbent | pH | initial conc./conc. range (ppm) | adsorption capacity (mg g\(^{-1}\)) | regeneration | magnetic separation | refs |
|-----------|----|-------------------------------|----------------------------------|--------------|---------------------|-----|
| magnetite-reduced graphene oxide composites | 7.0 | 3–7 | 13.10 | not reported | reported | 18 |
| mesoporous silica coated with Fe and Al oxides | 8.0 | 0–50 | 13.30 | not reported | not reported | 21 |
| magnetic activated carbon nanotubes | 5.5 | 0.5–11 | 8.13 | not reported | not reported | 20 |
| cupric oxide nanoparticles | 8.0 | 0.1–100 | 26.90 | not reported | not reported | 62 |
| graphene aerogels decorated with \( \alpha \)-FeOOH nanoparticles | 9.0 | 1–16 | 13.42 | not reported | not reported | 22 |
| magnetic CuO–Fe\(_3\)O\(_4\) nanoparticles | 7.0 | 0.1–50 | 118.11 | not reported | reported | 60 |
| magnetic ordered mesoporous Fe/Ce bimetal oxides (OMICs) | 7.0 | 1–150 | 281.34 | not reported | reported | 16 |
| microscale dialdehyde cellulose–cystine (MDAC–cys) fiber | 7.0 | 50–250 | 344.82 | not reported | not reported | 13 |
| nanoscale dialdehyde cellulose–cystine (NDAC–cys) fiber | 7.0 | 50–250 | 357.14 | not reported | not reported | 62 |
| iron oxide–multiwalled carbon nanotube hybrid | 4.0 | NA | 1.70 | not reported | not reported | 19 |
| nano zero-valent iron on activated carbon | 6.5 | NA | 18.19 | not reported | not reported | 49 |
| functionalized synthetic graphite | 7.5–8.0 | 0.1 to 50 | 18.80 | not reported | not reported | 63 |
| ZMA (Sonora) | 4.0 | 0.1–4 | 0.01 | not reported | not reported | 64 |
| manganese-incorporated iron(III) oxide–graphene nanocomposite | 7.0 | | 14.42 | not reported | reported | 65 |
| Fe\(_2\)O\(_3\)@C | | | | | | |
| Fe/Mn-HDTMA kaolin | 6.5 ± 0.2 | 0.2–30 | 29.40 | not reported | reported | 66 |
| MBC | 7.0 | 1–12 | 7.99 | not reported | not reported | 67 |
| MNP-PCP | 8.0 | 25–150 | 13.86 | not reported | reported | 69 |
| Fe/Cu nanoparticles | 7.0 | 0.1–5 | 19.68 | not reported | not reported | 70 |
| surfactant modified kaolin clay | 6.0 ± 0.5 | 1–30 | 2.33 | not reported | not reported | 71 |
| iron nanoparticle-modified | 3.0 | 50–250 | 24.2 | not reported | not reported | 72 |
| humic acid-grafted MNPs | 6.6 | 0.1–10 | 12.2 | not reported | reported | 15 |
| magnetite nanoparticles | 5.0 | 3.75–75 | 16.6 | not reported | reported | 73 |
| BNNS-Fe\(_3\)O\(_4\) | 8.0 | 6–70 | 30.30 | not reported | reported | this study |
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