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Insights into the single and binary adsorption of copper(II) and nickel(II) on hexagonal boron nitride: Performance and mechanistic studies

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Graphical abstract

Highlights

- A series of *h*-BN was developed for Cu(II) and Ni(II) adsorption
- Multilayer adsorption occurred at higher Cu(II)/Ni(II) concentration
- Cu(II) and Ni(II) adsorbed on the same active sites
- Affinity of Cu(II) for *h*-BN adsorption was higher than that of Ni(II)
- The oxygen functional groups played a critical role in Cu(II) and Ni(II) adsorption

Abstract: A series of hexagonal boron nitrides (*h*-BNs) was developed using a facile method involving pyrolysis of urea and boric acid mixture at different temperatures. The as-prepared *h*-BNs were characterized using XRD, FESEM, FTIR, BET and XPS and the results indicated that the as-prepared *h*-BNs consist of microparticle structures with BET specific surface area between 12-18 m² g⁻¹. The *h*-BN prepared at 750°C (BN-750) displayed excellent adsorption capacities for both Cu(II) and Ni(II) (up to 200 and 95 mg g⁻¹, respectively) compared to those prepared at other temperatures. At higher metal ion concentrations (>250 mg L⁻¹), multilayer adsorption was observed. The equilibrium adsorption modelling study indicated that the adsorption process was best fitted to the Langmuir ($R^2 > 0.97$) and Sips ($R^2 > 0.98$) isotherm

models. The binary adsorption of Cu(II) and Ni(II) was also investigated and the results revealed that the BN-750 has higher adsorption affinity for Cu(II) compared to Ni(II). Detailed analyses of the spent adsorbent using XPS and FTIR indicated that the oxygen functional groups of BN-750 played an important role in facilitating the electrostatic attraction and complexation of heavy metal during adsorption process. Furthermore, the results confirmed that Cu(II) and Ni(II) occupied the same active sites on BN-750. The results of this study revealed insights into the adsorption mechanism of Cu(II) and Ni(II) on BN-750 and demonstrated that the as-prepared *h*-BN is a promising adsorbent for efficient heavy metal removal in aqueous system.

Keywords: Adsorption; Boron nitride; Copper(II); Nickel(II); Oxygen functional groups; Mechanism

1. Introduction

Environmental pollution by heavy metals such as Cu(II), Ni(II) and Cr(IV) is increasing due to the rapid development of key industrial and agricultural sectors [1]. Heavy metals are not biodegradable and can bioaccumulate in living organisms, leading to heavy metal poisoning [2]. Specifically, heavy metals such as Cu(II) and Ni(II) are known to induce deleterious effect on respiratory tract, liver and kidneys [3-5]. The World Health Organization stipulated that the Cu(II) and Ni(II) concentrations in drinking water should not exceed 2 mg L^{-1} and 0.07 mg L^{-1} , respectively [6]. Considering the severity of heavy metal toxicity to living organisms, it is crucial to remove the heavy metal from contaminated wastewater prior to its discharge.

Various heavy metal removal techniques including adsorption, chemical precipitation, reverse osmosis membrane separation and use of ion exchanger have been evaluated [7]. Among these techniques, adsorption is considered as eco-friendly and effective in removing heavy metals from polluted aqueous systems. Meanwhile, other techniques such as chemical precipitation, reverse osmosis membrane separation and use of ion exchanger are either relatively more expensive or have higher chemical footprint compared to the adsorption process. For instance, chemical precipitation requires constant chemical addition and produces toxic sludge while membrane separation may require higher power consumption and leads to toxic brine effluent [7, 8]. The adsorption process is a surface phenomenon where the heavy metal is attracted to the adsorbent through electrostatic interactions or complexation on the surface functional groups [9]. After adsorption, the spent adsorbent can be recovered for safe disposal or heavy metal recovery[10]. To date, many types of adsorbent have been developed for heavy metal removal including activated carbons, low-cost biosorbents (developed from industrial and agricultural wastes), and inorganic materials. However, the adsorption performance of activated carbon and low-cost biosorbents are generally poor as most of them have relatively low heavy metal adsorption capacity ($< 50 \text{ mg g}^{-1}$) [11].

Recently, hexagonal boron nitride (*h*-BN) has emerged as a promising adsorbent for water treatment. As a two-dimensional material with graphite-like structure, *h*-BN consists of periodic stacking of B-N hexagons [12]. It has a relatively high thermal and chemical stabilities, low intrinsic toxicity and good adsorption capacity for heavy metals and organics compounds [13]. Various forms of *h*-BN nanostructures have been developed for metal ions removal. For instant, Wang et al. [14] developed *h*-BN with urchin-like structure for Pb(II) and Cu(II) removal (adsorption capacities at 115.07 mg g⁻¹ and 92.85 mg g⁻¹, respectively). Meanwhile, *h*-BN nanosheets prepared via two-step roasting method possessed adsorption capacity of up to 819 mg g⁻¹ [15]. However, the reported preparation methods for these *h*-BN can be relatively tedious and energy extensive because they involved either more than one step, require auxiliary chemicals during synthesis, or high energy demand (calcination $T \geq 1400^{\circ}\text{C}$). The investigation of the surface chemistry change of *h*-BN during heavy metal adsorption was also not conducted. The *h*-BN surface consists of many functional groups which can induce various surface interactions including electrostatic, ion exchange and complexation interactions with heavy metal [16]. The study of surface chemistry change of the adsorbent during adsorption will provide useful insights into the adsorption mechanism and *h*-BN-metal interactions, allowing better understanding and control of the adsorption process.

In this study, *h*-BN was developed using a facile, one-step synthesis method and optimized for Cu(II) and Ni(II) adsorption. The effects of various operational parameters including pH, initial Cu(II)/Ni(II) concentration, and adsorbent dosage on the adsorption of Cu(II) and Ni(II) by *h*-BN were also studied. Finally, we analysed the surface chemical changes and identified the mechanism of Cu(II) and Ni(II) adsorption by *h*-BN in aqueous system.

2. Experimental

2.1. Chemicals

The following chemicals were used in this study: boric acid (H_3BO_3 , Sigma-Aldrich), urea ($\text{CO}(\text{NH}_2)_2$, Merck), copper sulfate hexahydrate ($\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Sigma-Aldrich), nitric acid (HNO_3 , Merck) and sodium hydroxide (NaOH , Alfa Aesar). All the experiments were conducted using deionized (DI) water.

2.2. Synthesis of adsorbent

In this study, *h*-BN was synthesis using a facile technique involving pyrolysis of urea and boric acid mixture [17, 18]. In a typical synthesis procedure, exactly 4.50 g of urea was weighed using an analytical balance (Kern ABS, ± 0.3 mg) and mixed with 0.93 g of boric acid. The mixture was grounded in a mortar until homogeneous fine particles were obtained. Then, the urea-boric acid mixture was loaded onto a quartz boat and placed in a horizontal tubular furnace operated under nitrogen atmosphere at 250 mL min^{-1} . The tubular furnace was gradually heated at the heating rate of $10^\circ\text{C min}^{-1}$ until the desired temperature (750°C , 900°C or 1050°C) was achieved after which the temperature was maintained for 4 h. After the heating process, the tubular furnace was cooled to room temperature (25°C), and the adsorbent (denoted as BN-750, BN-900 and BN-1050 corresponding to the synthesis temperature of 750°C , 900°C or 1050°C , respectively) was collected, washed with DI water and dried in an oven at 60°C for 24 h.

2.3. Characterization techniques

The crystal structure and mineralogical information were investigated by obtaining the X-ray diffraction (XRD) patterns of the adsorbents using an X-ray diffractometer (Bruker AXS D8 Advance). The X-ray diffractometer was equipped with high-intensity monochromatic $\text{Cu-K}\alpha$ source ($\lambda = 1.5218 \text{ \AA}$) and operated at the scan rate and 2θ range of $0.02^\circ \text{ s}^{-1}$ and $10\text{--}70^\circ$, respectively. The secondary electron micrographs and elemental maps (B and N) of the

adsorbents were obtained using the field emission scanning electron microscope (FESEM, JEOL 7600F) equipped with energy dispersive spectroscopy (EDX, Oxford Xmax80 LN₂ Free). The bonding configuration and surface chemistry were investigated using the X-ray photoelectron spectrometer (XPS, Kratos Axis Supra spectrometer). The surface functional groups were determined from the Fourier transform infrared (FTIR) spectra obtained using the attenuated total reflectance coupled- FTIR spectrometer (Frontier ATR-FTIR, Perkin Elmer). The specific surface area was calculated from the nitrogen adsorption-desorption isotherm derived from a surface area analyser (77 K, Quantachrome Autosorb-1 Analyzer).

The point of zero charge was determined using the pH drift method [19]. Briefly, a series of solution in a sealed vessel containing 30 mL of 0.01 M NaCl was prepared. Then, the solution was adjusted to between pH 2 to 12 using 1 M NaOH and 1 M HCl. Exactly 0.9 g of *h*-BN was introduced into the solution and the initial pH was recorded. After 48 h, the pH of the solution was measured (denoted as pH_{final}) and the point of zero charge (where pH_{initial} = pH_{final}) was calculated from the intercept of Δ pH against pH_{initial} plot.

2.4. Adsorption study

The performance of various *h*-BNs as adsorbent for Cu(II) and Ni(II) removal was evaluated by comparing their Cu(II) and Ni(II) adsorption capacities in a batch system. A higher heavy metal adsorption capacity indicates better adsorption performance. In a typical batch adsorption study, exactly 0.20 g of *h*-BN was placed in a 50-mL reaction vessel. The reaction vessel was then filled with 20 mL of desired concentration of heavy metal solution (30 – 700 mg L⁻¹ of Cu(II) or Ni(II)) and agitated at 500 rpm and 25°C using an orbital shaker. At selected time intervals, exactly 1 mL of the suspension was drawn out using a syringe and the suspension was centrifuged to separate the adsorbent from the aliquot. Then, the heavy metal concentration in the aliquot was determined using an inductively coupled plasma optical

emission spectroscopy (ICP-OES, Perkin Elmer Optima, 2000 DV). The amount of heavy metal adsorbed (q_t , mg g⁻¹) at time t was calculated using the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where C_o and C_t are the heavy metal concentrations at $t=0$ and time t , respectively, V is the volume of the solution and m is the mass of adsorbent. The sampling process was carried out in the same reaction vessel and destructive sampling was not carried out to minimize the error due to fluctuation in the adsorbent dosage (0.20 g). To ensure that the results are reproducible, the contact time experiments were conducted in triplicate. The batch adsorption experiments were also conducted at different pH levels (3-8) and adsorbent dosages (0.1 – 0.4 g). The binary adsorption of Cu(II) and Ni(II) was also investigated. The binary component adsorption experiments were carried out using the same procedure as the single component system, except that additional heavy metal (either Cu(II) or Ni(II)) was added (at the concentration of either 30, 100 or 300 mg L⁻¹). The surface chemical changes and mechanism of adsorption of Cu(II) and Ni(II) by *h*-BN were investigated by comparing the XPS and FTIR spectra of the pristine and spent *h*-BN. Furthermore, the adsorbent regeneration study was also conducted to investigate the reusability of the adsorbent. In general, *h*-BN was loaded with excess heavy metal concentration (3000 mg L⁻¹). The heavy metal-loaded *h*-BN was immersed in 10 mL of 0.1 mol L⁻¹ HNO₃. After 24 h, the regenerated *h*-BN was separated from the supernatant by centrifugation and dried in an oven at 60°C. The regenerated *h*-BN was reimmersed into the heavy metal (3000 mg L⁻¹) solution and the concentration of heavy metal was determined. The amount of heavy metal adsorbed was calculated using Eq. (1). Each of the adsorption experiments involving equilibrium adsorption was conducted in duplicate.

2.5. Adsorption isotherm

The Langmuir, Freundlich and Sips adsorption isotherms were employed to study the equilibrium adsorption process. The Langmuir adsorption isotherm can be expressed by the following equation [20]:

$$q_e = \frac{Q_m C_e}{1 + K_L C_e} \quad (2)$$

where q_e (mg g⁻¹) is the amount of metal adsorbed at equilibrium, C_e (mg L⁻¹) is the metal concentration at equilibrium, Q_m (mg g⁻¹) is the calculated maximum monolayer coverage, and K_L (L mg⁻¹) is the Langmuir constant related to the adsorption energy. The basic assumptions of the Langmuir isotherm are (1) monolayer adsorption, (2) no lateral interactions between the adsorbed metals, and (3) homogeneous adsorption surface. The Langmuir isotherm is useful to estimate the monolayer capacity of BN-750. The Freundlich isotherm is an empirical model which can be presented by the following equation [21]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where K_F (mg g⁻¹ (L mg⁻¹)^{1/n}) is the Freundlich constant related to the adsorption capacity while n is the heterogeneity factor. The Freundlich isotherm can be employed to describe the multilayer adsorption process [22, 23]. Meanwhile, Sips isotherm is a three-parameters hybrid isotherm model related to the Langmuir and Freundlich isotherms, but without their limitations [24, 25]. The Sips isotherm can be presented by the following equation:

$$q_e = \frac{K_S C_e^b}{1 + a_S C_e^b} \quad (4)$$

where K_S (L g⁻¹), b and a_S (L mg⁻¹) are the Sips isotherm constants.

The results of the isotherm modelling are presented in **Table S1** and **Fig. 3d**. Considering the Langmuir isotherm is formulated based on the monolayer adsorption process, the data was fitted only up to where the first monolayer saturation was observed (at ~250 mg L⁻¹ for Cu(II) and Ni(II)). Meanwhile, the Freundlich and Sips isotherms were fitted up to $[Me]_0 = 700$ mg

L^{-1} . Compared to the Freundlich isotherm ($R^2 > 0.86$), the results show that the Langmuir ($R^2 > 0.97$) and Sips ($R^2 > 0.98$) models gave better fitting to the experimental data.

3. Results and discussion

3.1 Characteristics of adsorbent

The XRD patterns of *h*-BN synthesized at different temperatures (BN-750, BN-900, and BN-1050) are presented in **Fig. 1a**. In all the XRD patterns, two distinctive graphite-like peaks at $2\theta = 26^\circ$ and 42° are observed, corresponding to the (002) and (100) planes of *h*-BN (JCPDS card no. 34-0421), respectively [26]. For the XRD patterns of BN-750 and BN-900, several peaks, particularly those at 16° and 27° , are also present and they can be assigned to the diffraction peaks of B_2O_3 phase. Based on the presence of B_2O_3 phase at lower synthesis temperature, this suggests that the formation of *h*-BN began with the decomposition of boric acid and polycondensation of urea to B_2O_3 and melamine, respectively, followed by subsequent fusion to form *h*-BN [27, 28].

The characteristics of the as-prepared *h*-BNs were further investigated by obtaining the FTIR spectra (**Fig. 1b**). In all the *h*-BNs, the FTIR spectra indicate the presence of various peaks at 3400, 3250, 1670, 1310, 1180, 1000, 900, and 860 corresponding to B-OH, B-NH₂ stretching vibration, C=O, in-plane B-N stretching vibration, B-N-O, C-O, B-N-O, and B-N-B bending vibration, respectively [29, 30]. The scanning electron micrograph and elemental mapping (B and N) of BN-750 are shown in **Fig. 1c**. The BN-750 consists of microparticle morphology with homogeneous distribution of B and N at the atomic ratio of 2.6:1. The BET specific surface areas of BN-750, BN-900 and BN-1050 are calculated to be 12.2, 13.4, 17.5 m² g⁻¹,

respectively. The improvement in specific surface area from 12.2 to 17.5 m² g⁻¹ could be attributed to the emergence of *h*-BN which has a rougher surface texture.

To further characterize the surface chemistry of *h*-BN, survey scan and high resolution XPS spectra of BN-750 and BN-1050 at the O 1s, B 1s and N 1s regions were obtained. Apparently, the XPS survey scans show that the amount of surface oxygen is higher in BN-750 (44.9 at.%) than BN-1050 (32.3 at.%). The XPS spectra at O1s region of BN-750 and BN-1050 indicate that the dominant oxygen configuration is B-O (532.3 eV). The B-O bonding configuration could exist predominantly as surface B-OH group or B₂O₃ [31, 32]. Comparison of the B 1s XPS spectra of BN-750 and BN-1050 show that the at.% of B-O (~190.4 eV) is significantly higher in BN-750 compared to that of BN-1050 due to (i) the presence of B₂O₃ phase, and (ii) decomposition of oxygen functional groups at higher synthesis temperature. Several peaks at binding energies of ~398.4 eV, ~400.1 eV, and ~401.9 eV corresponding to the B-N, O-N, and N-H, respectively, can be observed in the high-resolution N 1s XPS spectra of BN-750 and BN-1050 [33]. The peak associated with B-N increased dramatically with increasing synthesis temperature due to complete formation of B-N at 1050°C. The BN-750, BN-900 and BN-1050 were employed as adsorbents for Cu(II) and Ni(II) removal.

3.2. Performance and reusability

3.2.1. Single component system

Comparison of *h*-BNs prepared at different temperatures showed that BN-750 presented the highest adsorption capacity for Cu(II) and Ni(II) adsorption (BN-750>BN-900>BN-1050, where the adsorption capacities of BN-750 for Cu(II) and Ni(II) adsorption were at least 14% and 40% higher than that for BN-1050, respectively) and hence, it was selected as the primary adsorbent in this study. The better performance of BN-750 is due to the higher density of surface oxygen functional groups (as oxygen-containing organics and surface

hydroxyl groups) in BN-750 which plays a pivotal role in facilitating heavy metal adsorption [34]. The promotional role of surface oxygen groups has also been observed in other two-dimensional materials including graphene oxide and graphite oxide [35, 36].

The adsorption of Cu(II) and Ni(II) at different initial concentrations and various time intervals by BN-750 are compared and presented in **Fig. 3a and b**, respectively. The Cu(II) and Ni(II) adsorption increased with increasing contact time and attained adsorption equilibrium (<5% change in metal concentration) at $t > 30$ min. To ensure that the adsorption equilibrium was fully attained, the contact time was fixed at $t = 120$ min. At all concentrations, the adsorption capacity for Cu(II) was consistently higher (~1.4 times) than that of Ni(II) indicating that the BN-750 has higher selectivity for Cu(II). Surprisingly, the results showed that as the initial metal concentration increased, the q_e of the respective heavy metal increased proportionally (up to 3 g L^{-1} of Cu(II) and Ni(II), where the q_e are 200 and 95 mg g^{-1} , respectively). The empirical relationships between the $q_{e,Me}$ and initial Cu(II) and Ni(II) concentrations can be described by Eqs. (8) and (9), respectively (**Fig. 3c**).

$$q_{e,Cu(II)} (\text{mg g}^{-1}) = 0.0926[\text{Cu(II)}] \quad (8)$$

$$q_{e,Ni(II)} (\text{mg g}^{-1}) = 0.0677[\text{Ni(II)}] \quad (9)$$

This suggests that the adsorption process is not confined within the monolayer coverage.

To further evaluate the Cu(II) and Ni(II) adsorption by BN-750, the adsorption data was fitted with the Langmuir, Freundlich, and Sips isotherm models. The results of the isotherm modelling are presented in **Table S1** and **Fig. 3d**. The coefficient of determination (R^2), normalized deviation (ND) and normalized standard deviation (NSD) were used to evaluate the goodness of fit [37]. Considering the Langmuir isotherm is formulated based on the monolayer adsorption process, the data was fitted only up to where the first monolayer saturation was observed (at $\sim 250 \text{ mg L}^{-1}$ for Cu(II) and Ni(II)). Meanwhile, the Freundlich and Sips isotherms were fitted up to $[\text{Me}]_0 = 700 \text{ mg L}^{-1}$. Compared to the Freundlich isotherm

($R^2 > 0.86$, $ND < 11.8$, $NSD < 25.7$), the results show that the Langmuir ($R^2 > 0.97$, $ND < 10.3$, $NSD < 24.2$) and Sips ($R^2 > 0.98$, $ND < 10.1$, $NSD < 23.7$) models gave consistently better fitting to the experimental data. As expected from the experimental results, the calculated Langmuir maximum adsorption capacity for monolayer saturation of Cu(II) (42.4 mg g^{-1}) is higher than that for Ni(II) (33.1 mg g^{-1}). The K_L values (between $0.0262 - 0.0289 \text{ L mg}^{-1}$) indicate that the adsorption affinities of Cu(II) and Ni(II) during the formation of monolayer are comparable. The trend of adsorption capacity (Cu(II) > Ni(II)) predicted by the Sips model is similar to that predicted by the Langmuir model. Meanwhile, the K_F and n_F values of Cu(II) calculated from the Freundlich isotherm are marginally higher than those obtained for Ni(II) indicating that the adsorption of Cu(II) is marginally more favourable than Ni(II).

Fig. 4a and b shows the effects of BN-750 dosage and pH on the adsorption of Cu(II) and Ni(II), respectively. The q_e decreased by at least 68% with increasing BN-750 dosage from 0.10 to 0.40 g attributed to the lower metal:BN-750 ratio. At higher BN-750 dosage (and constant heavy metal concentration), larger quantity of surface active sites is available for metal adsorption, leading to more unoccupied active sites and lower q_e . The effects of initial pH on adsorption were also studied by varying the initial pH from pH 3 to 6. Above pH 6, precipitation of the metal could occur due to the formation of metal hydroxide (K_{sp} for Cu(II) and Ni(II) are 1.6×10^{-19} and 1.6×10^{-16} , respectively), leading to the difficulty to distinguish between the adsorption and precipitation processes [38]. In general, the results indicate that for both Cu(II) and Ni(II), the q_e increased gradually with increasing pH up to pH 5-6. This trend can be explained based on the widely-reported heavy metal removal mechanisms, namely the electrostatic attraction and complexation processes, which are strongly dependent on the solution pH [35]. Considering the point of zero charge of BN-750 is pH 3.7, the surface charge of BN-750 is dominated by negatively-charged species at pH > 3.7. The electrostatic attraction and complexation reactions between the positively-charged heavy metals with the negatively-

charged BN-750 surface becomes more favourable with increasing pH (>3.7), leading to higher adsorption capacity. **Fig. 4c** shows the adsorption capacity of BN-750 for Cu(II) and Ni(II) after regeneration with 0.1 M nitric acid. After the first cycle, the adsorption capacity decreased by ~65% due to adsorption irreversibility. The adsorption irreversibility could be induced by the direct interaction of metal and active site, forming strong electrostatic and coordination bonds. The interactions and mechanisms of heavy metal adsorption are further evaluated using XPS and FTIR and discussed in **Section 3.3**.

3.2.2. Binary component adsorption

Fig. 5 shows the binary Cu(II) and Ni(II) adsorption by BN-750. In general, the Cu(II) adsorption is not significantly affected by Ni(II) up to 100 mg L^{-1} where Ni(II) occupied only about 10% of the overall adsorption active sites ($\sim 2\text{-}5 \text{ mg g}^{-1}$). At 300 mg L^{-1} Ni(II), only about 20% of the overall adsorption active sites was occupied by Ni(II). On the other hand, the Ni(II) adsorption was affected at a higher quantum in the presence of Cu(II). The Cu(II) at the concentrations of $30 - 300 \text{ mg g}^{-1}$ occupied 20-40% of the overall adsorption capacity of BN-750 regardless of the Ni(II) concentration. Comparison of the extent of adsorption in the binary system also indicates that the adsorption affinity for Cu(II) is higher than that of Ni(II). The better adsorption affinity of Cu(II) over Ni(II) was also observed by other researchers and this is due to several factors including (i) lower solubility of Cu(II) over Ni(II) which promotes better adsorption, and (ii) more positive electrode potential of Cu(II), favouring better electrostatic attraction [39-41].

3.3 Mechanism of adsorption

The mechanism of adsorption was further investigated by obtaining the FTIR spectra and XPS (survey scan, O 1s, Cu 2p and Ni 2p regions) of the Cu- and Ni-loaded *h*-BN and the results are presented in **Figs. 6 and 7**, respectively. The FTIR spectra in **Fig. 6** shows that the

peak at 3200-3400 cm^{-1} region became more apparent after adsorption due to possible formation of Me hydroxide on the BN-750 surface [42]. A new peak emerged due to the formation of organometallic complexes and overlap with the peak at $\sim 1670 \text{ cm}^{-1}$. The FTIR spectra also show that the peaks below 1000 cm^{-1} became less intense and eventually disappear due to excessive coverage of Me on the surface, shielding the functional groups.

The XPS survey scan (**Fig. 7a**) confirmed the presence of Cu(II) and Ni(II) on the surface of spent BN-750. The at.% of Cu(II) and Ni(II) calculated from the XPS survey scan are proportional to the Me loading concentration. It is observed that the B-O peak in the XPS O 1s spectra (**Fig. 7b**) was split into two main peaks at the binding energies of 532.3 eV and 531.9 eV, which can be assigned to B-O^{BN} and B-O^{Me} , respectively. The intensity of the B-O^{Me} peak was higher with increasing Me loading. Based on this observation, it can be construed that the emergence of B-O^{Me} peak occurs due to the formation of stable complex species during Me adsorption, which occupies the oxygen functional groups (B-O), leading to the observed shift in binding energy of the B-O peak. The O 1s XPS spectra of spent BN-750 for the binary adsorption system was also obtained (**Fig. S1**) and similarly, only two types of B-O bonding configurations can be identified (B-O^{BN} and B-O^{Me}). This shows that the Cu(II) and Ni(II) occupied the same active site on the BN-750 surface. The Cu 2p XPS spectra of spent *h*-BN confirmed the presence of several characteristic Cu-O peaks at the binding energies of 955.1 eV (Cu 2p_{1/2}) and 935.3 eV (Cu 2p_{3/2}) with shakeup satellite peaks at 963.0 eV and 943.3 eV, respectively [43]. Similarly, the presence of Ni-O was also evidenced in the Ni 2p XPS spectra where the characteristic Ni-O peaks are detected at the binding energies of 855.8 eV (Ni 2p_{3/2}) and 873.4 eV (Ni 2p_{1/2}) [44]. These results clearly indicate that the B-O group plays a pivotal role as binding site for Me adsorption, reaffirming that the Me adsorption is facilitated by the electrostatic attraction and complexation of the Me species with oxygen containing groups.

4. Conclusions

In this work, three *h*-BNs were prepared by pyrolysis of urea and boric acid mixture at different temperatures (750, 900 and 1050°C) for the adsorption of Cu(II) and Ni(II) in aqueous system. The characteristics of the adsorbents were investigated, and the results indicated that the adsorbents have microparticle morphology with BET specific surface area between 12-18 m² g⁻¹. The best *h*-BN was BN-750 (prepared at temperature of 750°C) and it was selected for further study. The adsorption process was well-described by the Langmuir ($R^2 > 0.97$) and Sips isotherm ($R^2 > 0.98$) models. The changes in surface chemistry of BN-750 after adsorption were studied using FTIR and XPS. It was revealed that the surface oxygen functional groups (particularly B-O) played an important role in facilitating the electrostatic attraction and complexation of Cu(II) and Ni(II) during adsorption process. The Cu(II) and Ni(II) competed for the same active sites for adsorption. The results of this study provide insights into the mechanism of Cu(II) and Ni(II) adsorption on *h*-BN-based materials.

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