Adsorptive properties of Fe₃O₄/Ni/NiₓB nanocomposite coated nutshell for the removal of arsenic(III) and arsenic(V) from waters

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Adsorptive properties of $\text{Fe}_3\text{O}_4/\text{Ni/Ni}_x\text{B}$ nanocomposite coated nutshell for the removal of arsenic(iii) and arsenic(V) from waters

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Abstract: A novel adsorbent $\text{Fe}_3\text{O}_4/\text{Ni/Ni}_x\text{B}$-nanocomposite coated nutshell was synthesized and used for the identification of the adsorption characteristics for both As(III) and As(V). The point of zero charge of pH of the adsorbent was determined as 8.0. The adsorption of arsenic on the adsorbent was optimum at pH 7.5. The Langmuir isotherm well fitted to the equilibrium data with a maximum adsorption capacity of 3.6 and 2.6 mg/g for As(III) and As(V), respectively. The separation factor, $R_L$, calculated from the Langmuir isotherm and the parameter, $n$, calculated from the Freundlich isotherm showed that the adsorption of both As(III) and As(V) on $\text{Fe}_3\text{O}_4/\text{Ni/Ni}_x\text{B}$ nanocomposite coated nutshell was favorable. The D–R isotherm showed that the adsorption was chemical in nature. The kinetic data followed the pseudo-second-order model which supported that the adsorption mechanism was chemical. The adsorption method was applied to real samples with a column. The removal efficiencies were about 100%. The adsorbent effectively reduced the concentration of arsenic species in water sample from 100 μg/L to the level below 10 μg/L (the recommended limit of arsenic in drinking water). The regeneration of the spent adsorbent was successfully done with 3% NaCl + 2% NaOH solution. The adsorption and the regeneration cycle were repeated for three times without loss efficiency.

ABOUT THE AUTHOR

Tülin Deniz Çiftçi, PhD, is a research assistant of Chemistry at the Department of Analytical Chemistry, Ege University, Izmir, Turkey. She completed PhD in 2010. The author studies on the determination and removal of heavy metals especially arsenic.

Her group previously clarified the mechanism of nickel interference in the hydride generation atomic absorption spectrometric determination of arsenic and antimony (Henden E, İşlek Y, Kavas M, Aksuner N, Yayayürük O, Çiftçi TD et al. 2011. Spectrochim Acta Part B 66:793–798. doi:10.1016/j.sab.2011.10.001). The study showed that Ni/Ni,B nanoparticles adsorbed arsenic and antimony with high efficiencies. This manuscript builds on our prior study to obtain a magnetic-based adsorbent. A novel adsorbent, magnetite/nickel/nickel boride nanocomposite ($\text{Fe}_3\text{O}_4/\text{Ni/Ni}_x\text{B}$)-coated nutshell was developed for the first time in the literature and used for the adsorption of As(III) and As(V) from water samples. The adsorbents were found to be very effective.

PUBLIC INTEREST STATEMENT

A novel magnetic adsorbent $\text{Fe}_3\text{O}_4/\text{Ni/Ni}_x\text{B}$ nanocomposite-coated nutshell was synthesized for the removal of arsenic species from waters. The adsorbent is very effective for the adsorption of both As(III) and As(V). The adsorbent is easily separated from the solution using a magnet. The article submitted is original and we believe that opening a promising area for the removal, adsorption, or preconcentration of heavy metals.
1. Introduction

Arsenic is a metalloid that is toxic to humans, animals, and environment (World Health Organization [WHO], 2011b). In natural waters, As(III) and As(V) species are common. As(III) is more toxic than As(V) where the inorganic species are more toxic than monomethylarsonic acid and dimethylarsinic acid, arsenobetaine, arsencolcholines, arsenu-sugars, arsenolipids which are the organic species of arsenic (Jain & Ali, 2000). Many toxic effects such as skin lesions, cancers of lung, bladder, kidney, and liver have occurred and arsenic is classified as a Group 1 carcinogen (International Agency for Research on Cancer, 2012). The WHO (2011b) and the United States Environmental Protection Agency (2001) reported the guideline value as 10 μg/L for arsenic in drinking water. The source of arsenic in the environment may be natural as well as anthropogenic. Arsenic is currently and historically used in pharmaceuticals, pigments, wood preservatives, agricultural chemicals, and applications in the metallurgical, glass-making, and semiconductor industries (Jain & Ali, 2000). Elevated arsenic concentrations in ground waters were determined in countries around the world (Abdullah et al., 2010; Chen et al., 1994; Çiftçi & Henden, 2016; Mandal & Suzuki, 2002; Niccoli, Suriano, Gomez Peral, Ferzozzori, & Baleani, 1989; Smith, Lingas, & Rahman, 2000). Oxidation, coprecipitation, membrane filtration, ion exchange, coagulation/filtration, and adsorption techniques are preferred for the removal of arsenic according to composition of waters. The adsorption method comes into prominence with easy handling, high capacity, low cost, and regenerability properties (Henden & Çiftçi, 2016). Iron, aluminum, manganese, titanium, cerium, zirconium, nickel, and copper-based materials have been most commonly used. Especially, iron and iron compounds such as granular ferric hydroxide (Thirunavukkarasu, Viraraghavan, & Subramanian, 2003), nano zero valent iron (Lackovic, Nikolaides, & Dobbs, 2000), natural iron ores (Zhang, Singh, Paling, & Delides, 2004), and iron(III) (hydr)oxides (hematite, goethite, akagaenite ...) are used for the adsorption of arsenic. Sand (Hsu, Lin, Liao, & Chen, 2008), zeolite (Jeon, Baek, Park, Oh, & Lee, 2009), pumice (Far, Souri, Heidari, & Khoshnavazi, 2012), silicagel (Çiftçi, Yayayürük, & Henden, 2011), pottery (Dong, Zinin, Cowen, & Ming, 2009), alumina (Kim, Kim, Choi, Rengaraj, & Yi, 2004), and resin (Çiftçi & Henden, 2015) were used as the support material to make particles suitable for column studies. Because of higher surface area, nanomaterials have high adsorption capacity and, therefore, are promising adsorbents.

In our previous studies (Henden et al., 2011), during the determination of arsenic and antimony by the hydride generation atomic absorption spectrometric method, a nickel interference was observed. After an elaborate study, we clarified the mechanism of nickel interference. We assumed that the interference is not due to the sorption or catalytic decomposition of the generated arsine and stibine. Arsenite, arsenate, and antimonite species in the solution are adsorbed by the nanoscale Ni/Ni/B sorbent generated by the reduction of Ni^{2+} with sodium tetrahydroborate(III). Also our other study (İşlek Coşkun, Çiftçi & Henden, 2016) showed that the adsorption capacity of Ni/Ni,B nanoparticles for As(III) and As(V) was extremely high (2,500 mg/g).

This manuscript builds on our prior study to obtain a magnetic-based and highly efficient adsorbent. In this study, magnetite/nickel/nickel boride nanocomposite (Fe_{3}O_{4}/Ni/Ni,B)-coated nutshell was prepared and used for the As(III) and As(V) removal. Since the Fe_{3}O_{4}/Ni/Ni,B nanocomposite contained magnetite in the structure, the adsorbent had magnetic property which makes the adsorbent separable from the solution by a magnet. Point of zero charge of pH, effect of pH and adsorbent dose, equilibrium and kinetic parameters of the adsorbent were determined. Real sample application and regeneration study were also done.
2. Materials and methods

2.1. Equipment

A Moulinex AR1105 model grinder was used for grinding nutshell. An atomic absorption spectrometer (Varian 220FS model) equipped with an automated continuous hydride generation system (GBC HG3000 model) was used for the determination of inorganic arsenic. The measurements of arsenic were done at 193.7 nm to isolate the line of arsenic. A scanning electron microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDX) (JEOL, JSM-6610 model) was used for the analysis of the adsorbent morphology. pH measurements were done with a Mettler Toledo FG2 model pH meter. pH 4, 7, and 10 buffers were used for the calibration of the pH meter before use. Biosan OS-10 model shaker was used for batch type adsorption studies.

2.2. Reagents

All the reagents were analytical grade. FeCl$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, NiSO$_4$·6H$_2$O, and NaBH$_4$ solids were purchased from Merck (Germany) for the preparation of the Fe$_3$O$_4$/Ni/NixB nanocomposite. As(III) and As(V) solutions (1,000 mg/L) were prepared from As$_2$O$_3$ (Merck, Germany) and Na$_2$HAsO$_4$·7H$_2$O (Merck, Germany) solids, respectively. The required amounts were dissolved in concentrated HCl and diluted with distilled water. Just before the experiment, more diluted standard solutions were prepared daily. KI (Merck, Germany) was used to reduce As(V) to As(III) in acidic media. Ascorbic acid (Merck, Germany) was used to reduce the iodine (formed during the reduction of As(V) to As(III) by KI) to iodide. NaCl (Merck, Germany), NaOH (Merck, Germany), conc. HCl (Merck, Germany) and conc. HNO$_3$ (Merck, Germany) were used for the preparation of NaCl, NaOH, HCl, and HNO$_3$ solutions, respectively. Commercially bottled drinking water was used as real water sample.

2.3. Preparation of the adsorbent

Required amounts of FeCl$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, and NiSO$_4$·6H$_2$O was weighed and placed in a beaker. 1.25 mL of 2 M HCl and required amount of distilled water was added for dissolving the solid. The solution was diluted to 250 mL. The final concentrations of Fe(II), Fe(III) and Ni(II) in the solution were 0.05, 0.1, and 0.15 M, respectively.

The raw hazelnuts were purchased from a market. The nutshell was separated from the hazelnut and grinded. The sizes were adjusted using 250–355 μm mesh sieves. 2.5 g of nutshell was conditioned by heating with 0.1 M HCl for one hour. Then, the nutshell was thoroughly washed with distilled water until giving no reaction with AgNO$_3$ and dried at 70°C. 1.0 g of the conditioned nutshell particles to be coated was weighed and added to a 50 mL falcon tube. Twenty milliliters of Ni(II)/Fe(III)/Fe(II) mix solution were added onto the particles and the mixture was shaken at 25°C for 24 h. The solution then decanted and 20 mL of 4% (w/v) NaBH$_4$ solution was added. Black Fe$_3$O$_4$/Ni/NixB layer coated the surface and the pores of the nutshell. The final adsorbent was thoroughly washed again with distilled water and dried at 70°C.

2.4. Characterization

2.4.1. SEM and EDX

The characterization of the adsorbent was performed using a scanning electron microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDX). Twenty-five milliliters of 100 mg/L As(III) or As(V) solutions at pH 7.5 were added onto 0.2 g of adsorbent and shaken at 25°C for 24 h. The supernatant solution was decanted and the adsorbent was washed with distilled water. The adsorbent was dried at 70°C and analyzed by SEM-EDX. Adsorbent without arsenic adsorption process was also analyzed by SEM-EDX. SEM images of the adsorbent were obtained at ×100, ×500, and ×10,000 magnifications. EDX was used for element mapping.
2.4.2. The point of zero charge

Either HNO₃ or NaOH solution was added to the 0.1 M NaNO₃ solution for adjusting pH. The solutions at different pHs were added to the particles and shaken at 25°C for 24 h. The equilibrium pHs were measured and ΔpH values were calculated by taking difference of equilibrium and initial pHs. pH(PZC) was the point of ΔpH = 0 determined from the curve of ΔpH vs. initial pH.

2.5. Adsorption

Batch experiments were used for investigation of relation of adsorbate and adsorbents. Unless otherwise stated, the adsorption study was done with 0.05 g of particles. The adsorbents were placed in a falcon tube (50 mL volume) and 25 mL of 100 μg/L (for the removal efficiency study) or 100 mg/L (for the uptake study) of As(III) or As(V) solution at pH 7.5 added and the mixtures were shaken (at 300 rpm) at 25°C for 24 h. Since the Fe₃O₄/Ni/NixB nanocomposite had magnetic property, particles were separated from the solution by a magnet. All the studies were conducted at least in duplicate.

The effects of adsorbent dose (0.4–8.0 g/L), pH of the solution (2–12), initial concentration of arsenic (0.1–100 mg/L), and contact time (5–1,440 min) were investigated. Isotherm and kinetic models were also used for the validation of equilibrium and kinetics of the adsorption.

2.5.1. Effect of conditioning

The effect of acidic, neutral, and alkaline conditioning on arsenic uptake was determined. Ground and sieved nutshell particles were heated for one hour with 0.1 M HCl, distilled water, and 0.1 M NaOH. Then the particles were washed with distilled water and each of the conditioned nutshell particles were divided into two groups. The first group prepared as previously described. For comparison, the second group was not coated by Fe₃O₄/Ni/NixB nanocomposite. The adsorption procedure was applied to two groups.

2.5.2. Adsorption isotherms

Twenty-five milliliters of As(III) or As(V) solutions at various concentrations (0.1–100 mg/L) were added onto 0.05 g of adsorbent and shaken at 25°C for 24 h. Remaining arsenic was determined by HGAAS. Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were fitted to the adsorption data. The units and the definitions of the abbreviations of the isotherms are listed in Table 1.

The Langmuir isotherm model (Langmuir, 1918) describes that monolayer adsorption occurs on homogenous surfaces and there is no any interaction between adsorbate. The linearized equation is:

\[ \frac{C_e}{q_e} = \frac{1}{bQ_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \]  \hspace{1cm} (1)

The separation factor, \( R_L \), obtained from the Langmuir isotherm determines the favorability of the adsorption (Worch, 2012) and is calculated from the Equation (2):

\[ R_L = \frac{1}{1 + bC_0} \]  \hspace{1cm} (2)

The value of \( R_L \) above 1 indicates an unfavorable adsorption, where the value in the range of 0 and 1 indicates a favorable adsorption. The adsorption type is defined as irreversible if the value is 0.

The Freundlich isotherm model (Freundlich, 1906) describes a heterogeneous adsorption. The linearized form of the Freundlich isotherm is:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  \hspace{1cm} (3)
The Dubinin Radushkevich (D–R) model (Hazzaa & Hussein, 2015) is used for the identification of the nature of the adsorption. The equation of the D–R isotherm is:

\[
\ln Q = \ln Q_m - ke^2
\]  

(4)

where \( e \) is Polany potential and calculated from the Equation (5).

\[
e = RT \ln \left(1 + \frac{1}{C_m}\right)
\]  

(5)

The mean adsorption energy is calculated from the Equation (6).

\[
E = \frac{1}{\sqrt{-2k}}
\]  

(6)

\( E \) value determines the type of the adsorption. The adsorption type is chemical in nature if \( E \) values are in the range between 8 and 16 kJ/mol. \( E \) values below 8 kJ/mol point out a physical adsorption due to van der Waals interactions (Inglezakis & Zorpas, 2012).
2.5.3. Kinetic studies
One hundred and twenty-five milliliters of 100 μg/L As(III) or As(V) solution were added to 0.3 g adsorbent and shaken at 25°C for various times (5, 30, 90, 150, 240, 500 and 1,440 min). Remaining arsenic was determined by HGAAS. The validation of the adsorption kinetics was evaluated using three kinetic models. The pseudo-first-order (PFO Equation (7)) (Laguerre, 1898), pseudo-second-order (PSO Equation (8)) (Ho & McKay, 1999), and intraparticle diffusion (Equation (9)) (Weber & Morris, 1963) kinetic models were commonly used kinetic models and fitted to the kinetic data. The units and the definitions of the abbreviations are listed in Table 1.

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  

\[ \frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \text{ where } h = k_2 q_e^2 \]  

\[ q_t = K_{int} t^{0.5} + I \]

2.5.4. Column studies
Column experiments were done for application to real sample and regeneration studies. Commercially bottled drinking water was used as real water sample. Also arsenic-spiked real water sample was used to test Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell. 1.0 mL of 10 mg/L As(III) or As(V) solution was transferred to a 100 mL volumetric flask and diluted to volume with real water sample. The final concentration of arsenic in water sample was 100 μg/L. 0.5 g of the adsorbent was filled to a 30-cm height and 1-cm i.d. column. Glass wool was placed to the bottom and top of the column. Water samples were passed through the column at a 1.7 ml/min flow rate.

For the regeneration studies, 25 mL of 100 μg/L As(III) or As(V) solution was passed through the column. Then 25 mL of 2% NaOH + 3% NaCl mix solution was passed for the elution of arsenic. The adsorption and regeneration cycles were repeated three times using the same adsorbent.

2.6. Arsenic analysis
Inorganic arsenic (As(III) + As(V)) in the solution was determined by automated hydride generation atomic absorption spectrometer (HGAAS). Since only As(III) species reacts with NaBH₄ to form arsine gas, first, As(V) species reduced to As(III) species. One milliliter of concentrated HCl (12.06 M) was added to 9 mL of arsenic contained solution. Two milliliters of 50% (w/v) KI solution were then added and waited for 15 min for completing the reduction. A small amount (tip of a small spatula) of ascorbic acid was added to the solution for reducing the iodine formed during As(V) reducing to As(III) by KI. The solution was ready for the determination with HGAAS. With the automated system, the solution was acidified with 10.2 M HCl and reacted with 0.6% (w/v) NaBH₄ in 0.6% (w/v) NaOH. The flow rates of the solution, the acid, and NaBH₄ was 8.0, 2.0, and 2.0 ml/min, respectively. The generated arsine gas was carried to AAS by nitrogen.

3. Results and discussion
3.1. Characterization
Porosity of the nutshell is shown at ×100 and ×500 magnifications in Figure 1(a) and (b), respectively. Fe₃O₄/Ni/NiₓB nanocomposite particles at nanosize in the pores of the nutshell are shown in Figure 1(c). Agglomeration of the nanoparticles is also seen in Figure 1(c). From the EDX analysis, the mean component (70.8%) of the adsorbent is found to be carbon because of the organic structure of nutshell. Also EDX spectrum confirmed the arsenic adsorption on the adsorbent. Arsenic peaks with carbon, iron, and nickel peaks are presented in Figure 1(d).
3.2. Effect of conditioning

Adsorption of both As(III) and As(V) was greatest with HCl conditioning (Figure 2). Coating with Fe₃O₄/Ni/NiₓB nanocomposite improved the adsorptive capacity of the nutshell. The uptake values of Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell was almost two times and 3.5 times higher than the raw nutshell for As(III) and As(V), respectively.
The concentration of nickel in the supernatant solution after the adsorption was determined as <0.02 mg/L (Limit of Detection) using flame AAS.

3.3. Effect of pH on the removal of As(III) and As(V)

The pH of the solution and the surface charge of the adsorbent play a very important role for adsorption studies. The point of zero charge of pH (pH\text{PZC}) was determined as pH 8.0 (Figure 3). The adsorbent surface will be positively charged under pH\text{PZC} where it will be negatively charged at higher pH levels than 8.0. At higher pH levels than 9.2, arsenic species As(III) and As(V) also become predominant as $\text{H}_2\text{AsO}_3^-$ and $\text{HAsO}_2^-$, respectively. The decrease (Figure 4) in the removal efficiency can be explained by the electrostatic repulsion. At pH levels under pH\text{PZC}, the positively charged adsorbent exhibits high affinity for arsenate anions. As(III) and As(V) removal efficiencies were ≥75% at pH 5.5–9.5. Maximum removal efficiency was obtained at about pH 7.5 (Figure 4), which was just below the pH\text{PZC} (8.0). Kumari, Sharma, Srivastava, and Srivastava (2006) similarly reported maximum As(III) adsorption at pH 7.5 for Lamarck seed powder (Kumari et al., 2006).

3.4. Effect of adsorbent dose

Since the adsorption sites increase and the surface area gets larger by the rise in the adsorbent dose, the removal efficiencies increase. A rapid increase was observed with an increase in the adsorbent dose from 0 to 1.0 g/L as shown in Figure 5. The removal efficiencies reached a plateau above 2.0 g/L adsorbent doses.
3.5. Adsorption isotherms

All the parameters calculated and determined from the plots of the isotherms are shown in Table 2. The Langmuir isotherm plot of $C_e/q_e$ vs. $C_e$ is shown in Figure 6(a). The maximum adsorption capacities ($Q_{\text{max}}$) for As(III) and As(V) were determined as 3.6 and 2.6 mg/g, respectively.

The plot of separation factor, $R_L$ values vs. $C_0$ is shown in Figure 6(b). The values of the separation factor were ranged between 0 and 1 which indicated that the adsorption of both As(III) and As(V) on the Fe$_3$O$_4$/Ni/Ni$_x$B nanocomposite-coated nutshell was favorable.

$n$ values obtained from the Freundlich isotherm graph (Figure 6(c)) were greater than 1 (Table 2) also indicated a favorable adsorption (Worch, 2012).

The D–R isotherm plot of ln $Q$ vs. $\varepsilon^2$ is shown in Figure 6(d). The mean adsorption energy (E) for the adsorption of As(III) and As(V) on the Fe$_3$O$_4$/Ni/Ni$_x$B nanocomposite-coated nutshell which determined the type of the adsorption was calculated from the Equation (6) as 9.3 and 9.7 kJ/mol.

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**Table 2. The parameters of the equilibrium studies**

|                  | Langmuir isotherm | Freundlich isotherm | DR isotherm |
|------------------|-------------------|---------------------|-------------|
|                  | $Q_{\text{max}}$ (mg/g) | $b$ (L/mg) | $R^2$ | $n$ | $K_f$ (mg/g) | $R^2$ | $E$ (kJ/mol) | $k$ (mol$^2$/kJ$^2$) | $R^2$ |
| As(III)          | 3.6               | 0.09               | 0.999 | 1.31 | 0.20 | 0.959 | 9.3     | 0.006 | 0.988 |
| As(V)            | 2.6               | 0.16               | 0.999 | 1.51 | 0.23 | 0.948 | 9.7     | 0.005 | 0.982 |
The values indicated that the adsorption processes were driven by a chemical ion exchange mechanism.

3.6. Kinetic studies
A rapid increase in the uptake of arsenic was observed in first 240 min for both As(III) and As(V). Within 500 min, arsenic concentration decreased from 100 μg/L to below 10 μg/L (maximum contamination level for arsenic in drinking water (WHO, 2011a)) (Figure 7(a)).

Theoretical $q_e$ values based on the PFO model differed greatly from experimental value (41.7 μg/g) for adsorption of As(III) and As(V) but were much closer for the PSO model, which had much higher $R^2$ values (Figure 7(b) and (c), Table 3).

The Weber Morris model is used for the definition of the rate-determining step. The plot of the intraparticle diffusion model (Figure 7(d)) was not linear and did not pass through zero which means that the intra-particle diffusion was not the only rate-determining step (Önal, Akmil-Başar, & Sorici-Ozdemir, 2007). There are two stages in the plots of the intraparticle diffusion model for both As(III) and As(V). The first stage indicated the external adsorption (macropore and mesopore diffusion) of arsenic on the adsorbent surface. The second phase is the gradual adsorption stage (micropore diffusion) with controlling intra-particle diffusion.

3.7. Test using drinking water
The adsorption of As(III) and As(V) in real samples by the Fe$_3$O$_4$/Ni/NixB nanocomposite-coated nutshell using a column was investigated. Because the concentration of arsenic in water sample was below 0.5 μg/L (the limit of detection), As(III) or As(V) were spiked to the drinking water at 100 μg/L. As shown in Table 4, As(III) and As(V) in the real sample waters were effectively removed by the Fe$_3$O$_4$/Ni/NixB nanocomposite-coated nutshell.

![Figure 7](image.png)

The Weber Morris model is used for the definition of the rate-determining step. The plot of the intraparticle diffusion model (Figure 7(d)) was not linear and did not pass through zero which means that the intra-particle diffusion was not the only rate-determining step (Önal, Akmil-Başar, & Sorici-Ozdemir, 2007). There are two stages in the plots of the intraparticle diffusion model for both As(III) and As(V). The first stage indicated the external adsorption (macropore and mesopore diffusion) of arsenic on the adsorbent surface. The second phase is the gradual adsorption stage (micropore diffusion) with controlling intra-particle diffusion.

![Table 3](image.png)

**Table 3. The parameters of the kinetic studies**

| Pseudo-first-order | Pseudo-second-order | Intraparticle diffusion |
|--------------------|---------------------|-------------------------|
| $q_e$ (μg/g) | $k_1$ (L/min) | $R^2$ | $q_e$ (μg/g) | $k_2$ (g/μg min) | $R^2$ | $I$ | Kint (μg/g min$^{0.5}$) | $R^2$ | $I$ | Kint (μg/g min$^{0.5}$) | $R^2$ |
| As(III) | 32.9 | 0.0012 | 0.7378 | 43.9 | 3.05 × 10$^{-4}$ | 0.9954 | 2.6 | 1.90 | 0.9620 | 35.4 | 0.17 | 1 |
| As(V) | 31.1 | 0.0012 | 0.7051 | 43.3 | 3.85 × 10$^{-4}$ | 0.9974 | 3.5 | 1.99 | 0.9561 | 35.9 | 0.15 | 1 |
Table 4. Test of Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell using commercially bottled drinking water

| Sample water               | Spiked arsenic (μg/L) | Remaining arsenic (μg/L) | Removal efficiency (%) |
|----------------------------|-----------------------|--------------------------|------------------------|
| Drinking water             | BLD                   | BLD                      | BLD                    |
| Drinking water + As(III)   | 100                   | –                        | 1.8 ± 0.06             | 98.2 ± 3.3             |
| Drinking water + As(V)     | –                     | 100                      | 2.0 ± 0.07             | 98.0 ± 3.2             |

Note: BLD: Below the limit of detection, that is 0.5 μg/L.

Figure 8. Removal and desorption efficiencies vs. the cycle number (2% NaOH + 3% NaCl was used for the desorption).

Table 5. Comparison of the adsorbents reported in the literature

| Adsorbent                             | Species          | pH   | Initial conc. (mg/L) | Qₘₐₓ (mg/g) | Isotherm model            | Kinetic model | Reference                                |
|---------------------------------------|------------------|------|----------------------|-------------|---------------------------|---------------|------------------------------------------|
| Raw and magnetite-doped AC            | As(V)            | 4    | 2                    | 0.50–4.16   | Langmuir/Freundlich       | PSO           | Zhang, Li, and Chen (2010)               |
| Moroccan clays                        | As(V)            | 7    | 0.1–50               | 0.561–1.076 | Langmuir/Freundlich       | –             | Bentahar, Hurel, Drooui, Khairoun, and Marmier (2016) |
| Iron oxide coated fungal biomass      | As(III)          | 6    | 0.100                | 0.880       | Langmuir                  | PSO           | Pokhrel and Viraraghavan (2008)         |
|                                       | As(V)            | 6    | 0.100                | 1.08        | Langmuir                  | PSO           |                                        |
| Lamarck seed powder                   | As(III)          | 7.5  | 1.0–100              | 1.59        | Langmuir                  | PFO           | Kumari et al. (2006)                    |
|                                       | As(V)            | 2.5  | 1.0–100              | 2.16        | Langmuir                  | PFO           |                                        |
| Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell | As(III)       | 7.5  | 0.1–100              | 3.6         | Langmuir                  | PSO           | This study                              |
|                                       | As(V)            | 7.5  | 0.1–100              | 2.6         | Langmuir                  | PSO           | This study                              |
| MnO-coated rice husk                  | As(V)            | 3    | 2–150                | 10          | Langmuir                  | PSO           | Ouédraogo et al. (2016)                 |
| MnO coated rice straw                 | As(V)            | 3    | 2–150                | 12          | Langmuir                  | PSO           | Ouédraogo et al. (2016)                 |
3.8. Regeneration study
Reuse potential is an important property in terms of cost. The spend adsorbent was effectively regenerated by the mixture of 2% NaOH + 3% NaCl and reused at least three times without loss of efficiency (Figure 8).

3.9. Comparison
Some of the natural and semi-natural (inorganic + organic) adsorbents reported for the removal of arsenic were compared with the Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell. The maximum adsorption capacities, the fitted isotherm and kinetic models, the initial concentrations, and the studied pH of the adsorbents are summarized in Table 5. The adsorbents were sorted according to the maximum adsorption capacities. The maximum adsorption capacities of the Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell for As(III) and As(V) were higher than nearly all of the others compared. Most of the adsorbents exhibited Langmuir monolayer adsorption and, with the exception of the Lamarcck seed powder, followed a pseudo-second-order model.

4. Conclusion
A novel semi-natural adsorbent Fe₃O₄/Ni/NiₓB nanocomposite-coated nutshell was prepared and used for the removal of inorganic arsenic species from water. The supporting material (nutshell) is a natural sorbent combined with Fe₃O₄/Ni/NiₓB to produce a nanocomposite adsorbent. pH_{PZC} of the adsorbent was found to be 8.0. Equilibrium and kinetic parameters of the adsorbent were determined. The adsorption processes of both species on the adsorbent were favorable and driven by a chemical ion exchange mechanism. The adsorbent was found to be very effective for the removal of both As(III) and As(V) from water samples. High reuse potential is another advantageous property of the adsorbent.
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