Enhanced Single and Simultaneous As(III) Adsorption in Pearl River Delta Water by Hexylamine Functionalized Vermiculite

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Abstract: Enhanced As(III) removal (>99.7) was achieved by a novel organoclay (HEX-VER) adsorbent in Pearl River Delta water. Single and simultaneous As(III) removal in the presence of Cd(II) and/or Pb(II) by batch adsorption tests was analyzed. Spectroscopic, spectrometric, microscopic, and potentiometric techniques were used for characterization of the adsorbents. The parameters affecting As(III) adsorption, including pH, kinetic, isotherm, thermodynamic, and co-existing ions (Cl\(^-\), F\(^-\), NO\(_3\)\(^-\), CO\(_3^{2-}\), SO\(_4^{2-}\), Ca\(^{2+}\) and Mg\(^{2+}\)) were also investigated. The results showed that HEX-VER owned different morphology and larger average pore diameter after functionalization, resulting in an improvement of As (III) adsorption capacity. Further analysis confirmed that adsorption was of the monomolecular layer, well-described by the Langmuir isotherm model. The dominant mechanisms for As(III) removal were ion-exchange and complexation. Moreover, HEX-VER was regenerated for five consecutive cycles, and the removal ratio was ≈ 92%, showing its great regeneration potential. These findings suggest that the proposed inexpensive adsorbent has potential for practical applications of As(III) removal from river water.

Keywords: As(III); simultaneous adsorption; Pearl River Delta (PRD); Hexylamine; Vermiculite

1. Introduction

The Pearl River Delta (PRD) is a densely urbanized and heavily industrialized region in South China. Since the late 1990s, there has been fast industrialization, economic growth, and a significant rise in population, which has caused some severe environmental concerns to emerge in PRD, especially toxic metals pollution [1,2]. As(III) is one of the highly carcinogenic and toxic heavy metals [3–5]. The source of arsenic in the environment are geogenic (weathering rock or minerals) and anthropogenic, which include mining, agricultural (wood preservation and pesticides/herbicides), and industrial (tannery and paint) processes [6,7]. Arsenic may enter the body by drinking contaminated water or by food chain if crops or vegetation are grown in arsenic-contaminated soil [8]. Long-term exposure
to arsenic can cause health hazards and results in arsenicism (arsenic poisoning) and death, even at trace levels [9–11]. The World Health Organization (WHO) has set a limit on arsenic concentration in drinking water as \( \leq 10 \mu g \cdot L^{-1} \) [12], likewise, China has set a limit of maximum arsenic concentration in groundwater (10 \( \mu g \cdot L^{-1} \) for Class III; 50 \( \mu g \cdot L^{-1} \) for Class IV and V), surface water (50 \( \mu g \cdot L^{-1} \) for Class I, II and III), and soil (20–40 mg·Kg\(^{-1}\) for agriculture) while a high arsenic concentration (>300 \( \mu g \cdot L^{-1} \)) exceeding the national limits were reported in PRD as per previous studies [13–15]. Lead pollution in the environment is of significant concern [16] since excess lead consumption can cause carcinogenicity, mutagenicity, and teratogenicity [17]. Cadmium is one of the most toxic metals for living beings, even at trace levels [18]. Cadmium causes irreversible multiple organ damage on kidneys, skeletal, cardiovascular, reproductive system, central and peripheral nervous system, and lungs. Moreover, it is highly carcinogenic [19]. Therefore, effluents containing toxic metals have to be treated before discharging into river bodies.

Heavy metals cannot be destroyed [20], and common techniques to remove them from water include precipitation, electrochemical, membrane separation, adsorption, ion exchange and biological processes. However, adsorption is regarded as a promising technique due to its simplicity, low cost, efficiency and adsorbent reusability [21,22]. Recently, perovskite [23], and phyllosilicates, including sepiolite [24], montmorillonite [25], zeolite [26], and other clay minerals [27] have also been used to remove the toxic metals from wastewater. Using clay minerals as an adsorbent may have many advantages over the other adsorbents, such as low cost, abundant availability, non-toxic, high surface area, excellent adsorbent properties, reusability, and massive potential for ion exchange [28].

In this work, vermiculite (VER) was chosen as an adsorbent since it is an inexpensive and naturally abundant aluminosilicate clay mineral which contains hydrated exchangeable cations, primarily Ca\(^{2+}\) and Mg\(^{2+}\) in the interlayer [29,30]. VER has a higher exchange capacity which makes it a more feasible material for higher adsorption results [31] and has stimulated many studies for toxic metals removal [32–35].

Studies reveal that clay minerals can be easily modified for enhanced adsorption results [36]. Adsorbent-pollutant interactions can be improved by the basic chemical functions in materials such as -OH and amine groups and, correspondingly, enhanced adsorption results of amine-enriched materials towards toxic metals in water have been reported in previous studies [37–40]. Therefore, in this study, hexylamine (HEX) \([\text{CH}_3(\text{CH}_2)_5\text{NH}_2]\) was chosen as a modifier. HEX is a primary amine of six carbons, which is a water-white colored liquid with an amine-like odor and it is used as a food additive in industries [41].

To the best of our knowledge, there is little information about practical As(III) removal by VER, especially in real river water. Arsenic is not the only metalloid present in water, but it coexists with other metal ions in most cases. Cadmium and lead exist as common heavy metal ions in water effluents, and developing a suitable adsorbent capable of removing As(III) in the presence of other heavy metals would be fascinating. Therefore, it was anticipated that HEX might alter VER and get enhanced As(III) removal results in Pearl River Delta water. In this work, we functionalized VER with HEX and produced HEX-VER. The specific objectives of this study were: (i) to investigate and analyze the structure and properties of HEX-VER by using different characterization techniques; (ii) to investigate various factors affecting As(III) adsorption on HEX-VER, and find out optimum conditions for individual and simultaneous adsorption systems; (iii) to use HEX-VER to remove As(III) from PRD water, (iv) to elucidate the adsorption mechanism of As(III) on HEX-VER. This study provides a new perspective for As(III) removal and reveals the application potential of HEX-VER adsorbent for individual and simultaneous removal of As(III) from river water.

2. Experimental Section

2.1. Materials and Chemicals

VER was acquired from Sigma Aldrich, with cation exchange capacity (CEC) of 0.853 meq g\(^{-1}\), it had <3% mica impurities, and its chemical composition as per XRF data is
presented in (Table S1). Hexylamine surfactant was also purchased from Sigma-Aldrich; its molecular structure is presented in (Figure S1). Sodium arsenite (NaAsO₂) was purchased from Sigma-Aldrich. Other analytical grade reagents, including Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ were purchased from Guangzhou Chemical Reagent Factory (Guangdong province, China). The stock solution of Pb(II), Cd(II), and As(III) were prepared by adding an adequate amount of Pb(NO₃)₂, Cd(NO₃)₂·4H₂O and NaAsO₂ to deionized (DI) water, respectively.

2.2. Preparation of Functionalized Materials

HEX-VER was prepared by the following method:

VER clay was washed rigorously by DI water and was oven-dried at 60 °C. 1 M HCl was added in 1.5 L DI water. Later, 5 g of washed VER, and HEX with equivalent CEC of VER was mixed in. The mixture was stirred at 80 °C for 1 h. The ionization of HEX took place in the presence of HCl, as in (Equation (1)).

\[
\text{C}_6\text{H}_{15}\text{N}^+ + \text{HCl} \rightarrow \text{C}_6\text{H}_{15}\text{N.HCl} \rightarrow \text{C}_6\text{H}_{15}\text{NH}^+ + \text{Cl}^- \quad (1)
\]

While Cl⁻ were removed by 0.1 M AgNO₃, as in (Equation (2)), where X represents the adsorbent.

\[
\text{AgNO}_3 + \text{X.Cl} \rightarrow \text{X} + \text{NO}_3^- + \text{AgCl} \quad (2)
\]

Mg²⁺ ions present in VER were replaced by hexylamine, and the modified version of VER was formed, as in (Equation (3)).

\[
\text{VER} - \text{Mg}^{2+} + \text{C}_6\text{H}_{15}\text{NH}^+ \rightarrow \text{VER} - \text{C}_6\text{H}_{15}\text{NH}^+ + \text{Mg}^{2+} \quad (3)
\]

White precipitates were skimmed, and adsorbent was washed 3 times with DI water and 2 times with ethanol and collected by centrifuge. Finally, HEX-VER was dried at 60 °C in a desiccator for 48 h, pulverized, and stored at room temperature for further experiments.

2.3. Characterization and Equipment

Pellet KBr technique was used to produce Fourier transform infrared (FTIR) spectra in the range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹ using a (PerkinElmer 1725X) FTIR spectrometer. The structure of the materials was determined using X-ray diffraction (XRD, Eindhoven, The Netherlands). Scanning electron microscope (SEM, Carl Zeiss, Oberkochen, Germany) was used to examine the surface morphology. The thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC/PG equipment. A ζ-potential analyzer (Zetasizer 2000; Malvern, England) was used to determine the ζ-potential of samples in the pH range (2–11). The chemical compositions of the samples were examined using a PANalytical PW-4400 X-ray fluorescence (XRF) spectrometer, and the states of elements on the surface of adsorbents were explored using X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo, Waltham, MA, USA) To determine pH, a pH meter (PHS-2, Three Letters Instrument Factory, Shanghai, China) was used. A Micrometric ASAP 2020 analyzer was used to determine the specific surface area. The metal concentration was measured by inductively coupled plasma atomic emission spectroscopy (Agilent 730 ICP-OES, Foster, CA, USA).

2.4. Potentiometric Titration Experiment

Methodology of potentiometric titration experiments including point of zero charge (pzc), and surface charge density are presented in (Supplementary Data, Experimental Section).

2.5. Adsorption and Desorption Experiments

The adsorption batch experiments for As(III) removal were conducted in 50 mL centrifuge tubes filled with 20 mL of As(III)@30 mg·L⁻¹ metal ions solution and simultaneous experiments were performed with Pb(II):Cd(II):As(III) ratio (10:5:3) concentration, respectively. Adsorbent dose experiments were carried out in the range of 0.2–8 g·L⁻¹. Influence
of pH on metal ions adsorption was performed in the 2–10 pH range, and the adsorbent used was 1 g·L⁻¹ (i.e., 0.02 g). Solution pH was adjusted with 0.1 M NaOH and HCl and measured by pH meter. Adsorption isotherm experiments were performed with varying initial concentrations of As(III) (9–90 mg·L⁻¹) and in simultaneous experiments [Pb(II) (30–300 mg·L⁻¹) and Cd(II) (15–150 mg·L⁻¹)] with Pb(II):Cd(II):As(III) ratio (10:5:3), respectively. Thermodynamics adsorption experiments were conducted at three temperatures (303, 313, and 323 K). Adsorption kinetic experiments were conducted at a time interval (5–1440 min). The desorption was performed by placing already used adsorbent in 100 mL of 0.1 mol·L⁻¹ NaOH solution, shaking at 180 rpm at 298 K for 4 h, then recovered by filtration and washed with DI water several times, dried at 333 K under vacuum overnight then used for next adsorption trial. Effect of co-existing ions (Cl⁻, F⁻, NO₃⁻, CO₃²⁻, SO₄²⁻, Ca²⁺ and Mg²⁺) was evaluated at 1 g·L⁻¹ adsorbent dose, As(III) initial concentration 3 mg·L⁻¹, and co-existing ions initial concentration of 5 mg·L⁻¹. The practical applicability test was carried out in spiked water of Pearl River (Zhujiang, Guangzhou, China) at spiked concentration of As(III)@2000 µg·L⁻¹, Cd(II) and/or Pb(II) @4000 µg·L⁻¹. A thermostatic oscillator was used at 150 rpm at a controlled temperature (as per requirements) for placing tubes. Tubes containing adsorbent and the metal ions were centrifuged at 8 k rpm for 10 min; plastic syringes were used to collect supernatant. The supernatants were passed through a fiber membrane (0.45 µm) and analyzed by ICP-OES. All the related parameters regarding specific experiments have been mentioned in the respective figures’ captions; however, the formulas and models information regarding kinetic, isotherm and thermodynamic models are explained in (Table S2).

3. Results and Discussion
3.1. Characterization Results
3.1.1. Spectroscopy

The FTIR spectra of VER, as well as modified HEX-VER along with relative surfactant (HEX), are presented in (Figure 1a). A strong and sharp band at 461 cm⁻¹ was associated with bending vibrations of Si-O-Si, indicating siloxane group as the principal constituent of the sample’s structure. Further, two bands at 680 and 1003 cm⁻¹ were associated with Si-O-M (M=Al, Fe, Mg) bending vibrations and Si-O stretching vibrations, respectively [42,43]. An absorption band at 1642 cm⁻¹ was attributed to -OH bending vibrations due to water molecules hydration [44]. The broad band at 3428 cm⁻¹ and a small band at 3720 cm⁻¹ were attributed to stretching vibrations of -OH related to water molecules in the interlayer and Si-OH, respectively [32], and these peaks were associated with VER structural characteristics. The spectra of HEX having typical peaks at 1379 and 1464 cm⁻¹ were allocated to C-H group wagging vibrations and C-N stretching vibrations, respectively [45,46]. Further two typical peaks at 2929 and 2959 cm⁻¹ were associated to asymmetric stretching vibrations of sp₃ alkane -CH₂ and -CH₃ groups of ammonium [47]. Peaks observed at 2857 cm⁻¹ were due to C-H bending group of hexylamine [48]. Noted that these peaks were not visible in VER sample but after modification they were emerged, unveiling that surfactant had been successfully intercalated into interlayer and/or on the VER surface.
Figure 1. FTIR (a), XRD pattern (b), and zeta (c)/electrical potential (e) of VER and HEX–VER.

The XRD was performed to analyze crystalline (phase) structure of VER and HEX-VER, as shown in (Figure 1b). The characteristic diffraction peak (0 0 2) of VER was observed at 2θ = 6.27° with a typical basal-spacing (d002) of 1.44 nm. VER showing two split diffraction peaks at 2θ = 7.15° and 2θ = 7.51° were commensurate to mica and hydrobiotite, respectively [49,50]. All of the characteristic peaks of VER were in good agreement with standard vermiculite JCPDS file (JCPDS No. 16-0613) [51]. After modification, a decrease in the (0 0 2) facet intensity was observed in HEX-VER, due to interactions between VER and HEX. The characteristic diffraction peak of VER (2θ = 6.27°) was sifted at 2θ = 5.16° in HEX-VER sample, which was due to macrostrain of planar stress caused by the bulkier head group of HEX [52]. The electrostatic attraction between positively charged HEX head group and negatively charged VER surface rendered the interlayer space more crowded. The d-spacing d002 value of VER was increased from 1.45 nm to 1.87 nm after modification due to increased distance between parallel planes of atoms. These results indicated successful grafting of HEX on VER.

As shown in (Figure 1c), the zeta potential of VER and HEX-VER remained consistently negative throughout the pH range 2–11 and respectively reduced from (−8 to −34 mV for VER) and (−18 to −39 mV for HEX-VER), with no isoelectric point (IEP). The detailed results of zeta potential are presented in (Figure S2). Sim et al. reported that the zeta
potential of vermiculite varies between $-15 \text{ mV}$ to $-35 \text{ mV}$ in the pH range of 2–12, and no IEP was observed [53], which was in correspondence with our results. The surface charge or zeta potential depends on the quantity of SiO$_2$, MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ in the sample, which were the main constituents of VER. The zeta potential of samples decreased as the pH was increased till pH 6, later, a small rise and then a drop in zeta potential was observed in HEX-VER, at higher pH due to rise in alkalinity in solution [54]. HEX-VER compared to VER showed more negative charges in all the pH range (2–11). The absolute value of zeta potential is directly proportional to the stability of particles in a tested system [55]. These results verified that HEX-VER was a more stable adsorbent material compared to VER.

3.1.2. BET Analysis and Surface Morphology

The N$_2$ adsorption-desorption isotherm was performed to evaluate the textural properties of adsorbents (Figure S3a). The Brunauer-Emmett-Teller (BET) method was used for the calculation of specific surface areas [56]. The Density Function Theory (DFT) method was used for pore size distribution (PSD), which was determined using the Barrett Joyner Halenda (BJH) technique from the desorption branch of isotherms [57]. According to BJH desorption, the mean pore diameter was between 2 and 50 nm, which indicated mesoporous structure (Figure S3b). The obtained textural parameters results are compared in (Table S3).

Nonetheless, both VER and HEX-VER maintained type-II isotherm and mesoporous adsorption, the point B at isotherms’s linear middle section (Figure S3a) indicated monolayer coverage has been completed and the multilayer adsorption has begun [58,59], while lack of hysteresis showed that pores were easily accessible. After functionalization by HEX, the VER pore volume (0.0306 cm$^3$·g$^{-1}$) and specific surface area (11.297 m$^2$·g$^{-1}$) were reduced due to the blocking of the pores by HEX [60,61].

The SEM results for VER and HEX are presented in (Figure S4a,d), along with an insight look through zoomed imaging in (Figure S4b,e), respectively. VER surface with tightly stacking and uniform thickness distribution (Figure S4a), turned rougher after modifying with HEX (Figure S4d), which was conducive for enhanced adsorption of heavy metal ions, due to the increase of pore diameter and active sites [38], which was in accordance with BET analysis results. Brighter areas on the surface indicate the compact and typical arrangement of aluminosilicates scattered on surface with small fragments. After modification, crimped edges and rough agglomerates could be observed due to irregular nano flakes stacks or preferential orientation, which indicated that the surfactant (HEX) accumulated either in broken edges and interlayer or on surface after the modification. Furthermore, abundance of specific elements of VER and HEX-VER were determined by EDS, detailed results are presented in (Table S4), while major elements (as per EDS data) present in the respective samples are depicted in (Figure S4c,f), respectively.

After modification, an increase in carbon (C) was observed, indicating that HEX was successfully introduced into VER. The reduction of magnesium (Mg) was associated to the leaching of octahedral cations of VER due to HEX treatment [62]. As SiO$_4^+$ in tetrahedron is an exchangeable cation, therefore reduction in Si was observed after modification with HEX [63]. A minor change was observed in Al, Ca, K, Ti, and Fe after modification. Elemental mapping results are presented in (Figure S5).

3.1.3. Thermogravimetric Analysis (TGA)

TGA was performed to analyze the thermal stability of VER and HEX-VER. TG mass loss (%) and its derivative (DTG) with respect to temperature were plotted to monitor the difference (Figure S6a,b). In the first stage (25–150 °C), the mass loss for VER and HEX-VER was 3.03% and 7.00%, respectively. The DTG peaks of VER at 70.8 °C and HEX-VER at 78 °C were due to the removal of absorbed hydrogen-bonded water molecules or OH– groups. Whereas in the second stage (150–300 °C), the mass loss observed for VER and HEX-VER was 0.92 and 0.79 %, respectively. Finally, in the third stage (300–800 °C), the mass loss for VER and HEX-VER was 2.08 and 2.27%, respectively, and The internal
structural de-hydroxylation was linked to DTG peaks at 624 and 617 °C for VER and HEX-VER, respectively. The overall mass loss of VER (6.03%) was lower while HEX-VER (10.06%) showed a higher mass loss, which could be explained by the bulkier head group of HEX, which rendered the interlayer space more crowded.

3.1.4. Potentiometric Analysis

Potentiometric titration was conducted in pH range 2–11, and the resulting titration curves of VER and HEX-VER are depicted in (Figure 2a,b), respectively. The pzc (an equal charge balance of +ve and -ve charge planes) for VER and HEX-VER was observed at pH 4.5 and 6.1, respectively. The proton charge of VER and HEX-VER was calculated by acid-base potentiometric titration method, resulting curves are shown in (Figure 2c,d), respectively. The average pHZP for VER and HEX-VER was observed in the range between 9.4–9.8 and 8.4–8.7, respectively. With the increase of pH, the decrease in surface proton charge was observed due to deprotonation of surface sites; the same results were observed in previous studies [64,65]. Some studies claim that clay minerals show a common intersection point (CIP) in charge potential curve [66,67], but our results did not show any CIP at varying ionic strengths; hence titration at more ionic strength values should be performed to ascertain a CIP exist or not. The surface charge density was +ve at pH < pHpzc due to protonation, and -ve at pH > pHpzc due to deprotonation of surface densities at edge sites [68]. The surface charge is determined by the amount of SiO\(_2\), MgO, Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) in the sample and so the specific surface area (SSA).

Figure 2. The potentiometric titration curves of pH\(_{pzc}\) for VER (a), and HEX–VER (b) in the pH range (2–11) at ionic concentration of 0.1, 0.01 and 0.001 M of NaCl; surface proton density/Surface charge of the VER (c), and HEX–VER (d) in the pH range (2.7–10.4) at ionic concentration of 0.1, 0.01 and 0.001 M of NaOH; Temp 25 °C. Surface proton density of VER (c) and HEX–VER (d) at 0.1, 0.01 and 0.001 M NaOH ionic concentrations; temperature: 25 °C; pH: (2.7–10.4).
3.2. Adsorption Results

3.2.1. The Effect of Dose and pH

The effect of VER and HEX-VER adsorbent dose on As(III) uptake was investigated in a dose range (0.2–8 g·L⁻¹). When the adsorbent dosage was increased, the adsorption efficiency increased due to higher adsorbent dose possessed more functional groups. The adsorption capacity for As(III) reached ≈ 99% at the 6 g·L⁻¹ dose (Figure 3a). N-containing functional groups like amines and -OH groups in clay minerals are more capable for heavy metals adsorption. Typically Cd(II) and Pb(II) have more adsorption capacity compared to As(III), and as our further experiments were simultaneous, therefore we chose 1 g·L⁻¹ dose. HEX-VER showed 17.1% of As(III) uptake at 1 g·L⁻¹ dose (Figure 3b).

**Figure 3.** Effect of VER and HEX–VER dose at pH 5 on As(III) at 0.2–8 mg·L⁻¹ (a); Adsorption at 1 g·L⁻¹ dose from molar perspective for As(III) (b); Effect of pH in the range of pH 2–10 for As(III) (c); all above experiments at As(III) Cᵢ = 30 mg·L⁻¹; contact time, 1440 min; temperature, 30 °C; pH, (2–10).

- As(III)ₘₘₙₒ₁·g⁻¹: (HEX-VER, 6.84 × 10⁻⁵) > (VER, 4.72 × 10⁻⁵)

The difference in metals uptake was due to the formation of stable metal aminocomplexes (due to HEX) on vermiculite.

The pH has significant importance in adsorption since it influences adsorbents surface charge and adsorbates speciation [69]. Therefore, the influence of pH on As(III) removal was studied (Figure 3c). The As(III) removal was higher at intermediate pH (4–8), and lower at extreme acidic or alkaline conditions. This behaviour of As(III) removal at varying pH was due to adsorbent surface charges and arsenic speciation at varying pH. The
pHpzc of the VER and HEX-VER evaluated using titration was found to be 9.4–9.8 and 8.4–8.7, respectively.

Lee and his coworkers observed that, at lower pH, As(III) exists as the neutrally charged H3AsO3, while at higher pH values, the solution is predominated by negatively charged species (H2AsO−3, HAsO32−, and AsO33−) [70]. At lower pH, the H⁺ dominates the adsorbent surface, resulting in decreased As(III) absorption due to suppressed deprotonation of neutrally charged H3AsO3 (Equation (4)) [71]. While at moderate pH, the low charge density on adsorbent surface, promotes the Van der Waal attraction forces, which results in optimum As(III) uptake (Equation (5)). Moreover, at extreme alkaline pH, both the As(III) and adsorbent surface have negative charges, which create a strong repulsion forces, resulting in a poor As(III) adsorption (Equations (6) and (7)) [72].

$$\equiv \text{Si} - \text{OH}^+ + \text{H}_3\text{AsO}_3 \rightarrow \equiv \text{Si} - \text{OH} - \text{H}_2\text{AsO}_3 + \text{H}_2\text{O} \quad (4)$$

$$\equiv \text{Si} - \text{OH}^+ + \text{H}_3\text{As}^- \rightarrow \equiv \text{Si} - \text{HAsO}_3^- + \text{H}_2\text{O} + \text{H}^+ \quad (5)$$

$$\equiv \text{Si} - \text{OH}^- + \text{H}_3\text{As}_2^- \rightarrow \equiv \text{Si} - \text{HAsO}_3^- + \text{H}_2\text{O} + \text{H}^+ \quad (6)$$

$$\equiv \text{Si} - \text{OH}^- + \text{As}_3^- \rightarrow \equiv \text{Si} - \text{AsO}_3^- + \text{H}_2\text{O} + \text{H}^+ \quad (7)$$

### 3.2.2. Adsorption Isotherm Experiments

In order to interpret the interactions between adsorbate (As(III)) and other adsorbents (VER and HEX-VER), adsorption isotherms were performed (Figure 4). Langmuir and Freundlich isotherm models were applied, and results were summarized in (Table S5). All of the adsorption systems matched the Langmuir model better, suggesting the development of a monolayer adsorption [32]. In a singular As(III) adsorption system, maximum adsorption capacities for HEX-VER were improved from 11.89 to 13.52 mg·g⁻¹, while in the presence of Cd(II) and Pb(II) from 6.12 to 10.33 mg·g⁻¹, respectively.

![Figure 4](image_url)

**Figure 4.** Effect of initial concentration and adsorption isotherms study of As(III) singular (a), in the presence of Cd(II) (b), in the presence of Pb(II) (c), and in the presence of Cd(II)/Pb(II) (d) on VER and HEX–VER; contact time, 1440 min; temperature, 30 °C; pH, 5.
3.2.3. Adsorption Kinetics

Interaction of As(III) and adsorbents was evaluated by kinetic studies (Figure S7). A rapid As(III) adsorption was observed till 180 min since abundant sites of the adsorbent reacted with As(III). Then a slow increase was observed before equilibrium since empty sites were occupied gradually. Pseudo-first-order (PFO), and pseudo-second-order (PSO) models were used to analyze kinetic data, the equations for these models are given in Table S2. Kinetic results were in better agreement with PSO model with higher R² values in all systems, suggesting chemisorption process [38]. Fitting parameters are summarized in Table S6. Intraparticle diffusion, which is usually a rate-limiting step in many adsorption processes, in which the adsorbate species are carried from the bulk solution into the solid phase. Therefore, the intraparticle diffusion kinetic model was used to investigate the possibility of intraparticle diffusion [73]. The obtained results are presented in Figure S8 and rate constants in Table S7, respectively.

On the basis of x-axis values (time), the adsorption process curve of As(III) on HEX-VER can be split into three linear parts, representing three corresponding stages i.e., surface diffusion, intraparticle diffusion, and ultimate adsorption equilibrium, respectively [74]. However, the As(III) adsorption curve on VER could only be divided into stages of surface diffusion and adsorption equilibrium, these different fitting modes indicating a disparate adsorption process. After loading HEX on the surface of VER, the structure of adsorbent changed from two-dimensional to a three-dimensional hierarchical structure, resulting in the process of intraparticle diffusion generated in the fitted intraparticle diffusion model of HEX-VER. After modification of VER, the intraparticle diffusion stage has also been reported in previous studies [75]. These results were also consistent with the variation of morphology.

3.2.4. Adsorption Thermodynamics

The temperature effect on As(III) adsorption was analyzed, as shown in (Figure S9). The temperatures selected were (303, 313, and 323 K). The study of adsorption thermodynamics system showed an improved adsorption capacity with the increase in temperature. The values of thermodynamic parameters (ΔG°, ΔH°, and ΔS°), which were calculated from the slope and intercept of linear fit using origin Lab software, are presented in (Table S8). The value of ΔG°, which decides the feasibility of reaction, was found to be negative, indicating that the reaction was spontaneous. The positive ΔH value revealed an endothermic adsorption system, which was confirmed from the calculated thermodynamic parameters. The positive ΔS values showed randomness of solid-liquid interaction [22].

3.3. XPS Analysis

XPS analysis was performed for quantitative analysis of the adsorbents. The spectra of survey showing Mg 1 s, O 1 s, C 1 s, and Si 2p peaks which were the main elements of the samples, as shown in (Figure 5a), these results matched with SEM and EDS data. Moreover, XPS was used to identify the elements before and after the metal ions adsorption, while newly emerged peaks can be observed in (Figure 5b–d) allocated to As 3d, Cd 3d, and Pb 4f, confirming the presence of As(III), Cd(II), and Pb(II), respectively. The As 3d peaks before and after As(III) adsorption are shown in (Figure 5b). the As 3d binding energy (BE) at 44.3 eV was ascribed to As(III) [76]. Cd 3d spectrum was divided into two peaks located at 406.2 eV (3d_{5/2}) and 412.5 eV (3d_{3/2}), indicating formation of Cd-OH group (Figure 5c). Pb 4f spectrum showed two characteristic peaks at BE 139.1(4f_{7/2}) eV and 143.9 eV (4f_{5/2}) were BE of Pb(NO₃)₂ with a significant shift of lower BE, indicated Pb-O binding mechanism between Pb(II) and HEX-VER (Figure 5d), the obtained results were consistent with the previous study [32].
3.4. Effect of Co-Existing Ions

The groundwater naturally contains salts, while river water has high concentrations of ions (depending on the source), which affect the efficacy of As(III) removal to some extent [77,78]. Therefore, we evaluated the influence of co-existing ions on As(III) removal in the presence of Cl\(^-\), F\(^-\), NO\(_3\)\(^-\), CO\(_3\)\(^2-\), and SO\(_4\)\(^2-\) anions, as they are commonly present in river water and some of which were confirmed by analyzing the Pearl River water (Table S10), while Ca\(^{2+}\) and Mg\(^{2+}\) cations were selected as they were the constituents of HEX-VER sorbent. The obtained results for co-existing ions effect on As(III) removal are presented in (Figure 6). The removal of As(III) was hardly influenced by the presence of Cl\(^-\), F\(^-\) and NO\(_3\)\(^-\). However, a much decreased As(III) adsorption capacity was observed in the presence of CO\(_3\)\(^2-\) and SO\(_4\)\(^2-\), which suggested that these anions compete with As(III), leading to its decreased removal efficacy [72] On the other hand, As(III) removal rate was increased in the presence of Ca\(^{2+}\) and Mg\(^{2+}\) cations. The As(III) removal rate, in the presence of Ca\(^{2+}\) cation, increased from 80.9% to 92.5% and 75.8% to 87.3% with HEX-VER and VER, respectively. However, in the presence of Mg\(^{2+}\) cations, the removal rate increased from 80.9% to 96.85% with HEX-VER, and 75.8% to 91.4% with VER, respectively, as shown in (Figure 6b). The obtained results concluded that Ca\(^{2+}\) and Mg\(^{2+}\) cations enhanced the
positive charges and created more active sites on the adsorbent surface, which led to higher sorption of As(III). Similar results have been reported in previous studies [72,79].

![Graph showing adsorption of As(III) with and without co-existing ions](image)

**Figure 6.** The effect of co-existing ions on adsorption of As(III) singular (a), and in the presence of Cd(II)/Pb(II) (b) on VER and HEX–VER; adsorbent dosage: 1.0 g·L\(^{-1}\); contact time: 1440 min; temperature: 30 °C; ionic strength 5 mg·L\(^{-1}\).

### 3.5. Pearl River (ZhuJiang) Water Adsorption Test

River water is more complex as compared to deionized water, as it contains different types of organic and inorganic particles [5]. The practical application for removal of As(III) by HEX-VER was tested in spiked river water (Peal River, Guangdong, China). The spiked concentration of As(III) was 2000 µg·L\(^{-1}\), while 4000 µg·L\(^{-1}\) for both Cd(II) and Pb(II), other quality parameters are described in (Table S10). The obtained results are presented in (Figure 7). The HEX-VER successfully removed the As(III) in single and simultaneous adsorption systems. The As(III) residual concentration was 5.08 µg·L\(^{-1}\) in single adsorption system while in the presence of Cd(II), Pb(II) and Cd(II)/Pb(II), it was observed 8.04, 9.57, and 10.13 µg·L\(^{-1}\), respectively, after 4 h of adsorption. These results proved the potential of HEX-VER for practical applications of As(III) removal from water.

### 3.6. Desorption

The management of the used adsorbent and metal ions recovery is one of the most important aspects. However, only a limited number of studies considered the fate of spent adsorbents before disposal [80]. To elute adsorbed As(III) from surface of adsorbents, 0.1 M NaOH was used as a desorbent. The desorption took place due to competition of binding-sites between heavy metals and protons introduced by NaOH [32]. The adsorption capacity of materials was decreased slightly with the increased numbers of regeneration cycles, and five cycles were performed. After five cycles, HEX-VER recovery rate for singular As(III) was 92.6%, while in the presence of Cd(II) and Pb(II) was 91%, respectively (Figure S10). Before and after desorption, XRD results were compared to know whether our selected desorbent (NaOH) would have any pickling or other effect on HEX-VER or not. The results (Figure S11) revealed no significant effects only d spacing was reduced from 1.87 nm to 1.81 nm. Therefore, it was concluded that HEX-VER possessed potential properties of regeneration.
Figure 7. Effect of contact time and kinetic study of As(III) singular (a), in the presence of Cd(II) (b), in the presence of Pb(II) (c), and in the presence of Cd(II)/Pb(II) (d) on VER and HEX–VER in Pearl River delta water (As(III) at $C_i = 2000 \mu g\cdot L^{-1}$; Cd(II) and Pb(II) both $C_i = 4000 \mu g\cdot L^{-1}$; contact time: 240 min; temperature: 30 $^\circ$C; pH: 7.26 (natural as it was); adsorbent dosage: 1.0 g L$^{-1}$).

3.7. Adsorption Mechanism Overview

The characterization results of N$_2$ adsorption-desorption indicated that SSA of HEX-VER was less than VER, but on the other hand, HEX-VER showed improved As(III) adsorption capacity. This phenomenon indicated that the adsorption performance of HEX-VER was dependent not only on the textural properties but also on the surface charge [81]. The negatively charged adsorbent surface (surfactant head group) and positively charged arsenic ions favored the As(III) adsorption. Further analysis showed that three places could be possible for As(III) adsorption, as demonstrated in (Figure S12). Firstly, zeta potential of HEX-VER was throughout negative in the pH range (2~11) since tetrahedral and octahedral sheets were deprotonated and formed SO$^-$ group, and As(III) was adsorbed on SO$^-$ sites by surface complexation. Second, a portion of As(III) might be adsorbed on both inner or outer layers of clay due to ion-exchange as metal cations were exchanged, and Mg$^{2+}$ and Ca$^{2+}$ were releases from clay surface into solution [82]. The O 1s spectrum was deconvoluted into two peaks at BE of 530.08 eV and 531.7 eV (for HEX-VER), which were attributed to the lattice oxygen in -OH and adsorbed water, respectively [5,32], as shown in (Figure 8a). After adsorption, peaks of O 1 s shifted to a higher BE, from 530.08 to 530.18 eV and from 531.7 to 531.91 eV, respectively. Moreover, the intensity of H$_2$O spectra increased, and a significant decrease in -OH spectra was observed. The peak area ratio of -OH group was
decreased from 82.71% to 75.92% (As(III)) and 73.38% (As(III)+Cd(II)/Pb(II)), respectively. This phenomenon indicated that metal ions were bound onto oxygen atoms; therefore, electron density towards the oxygen atoms was decreased [32]. As a result, several -OH were replaced by As(III) or Cd(II)/Pb(II) during the adsorption process, and inner-sphere surface complexes were formed subsequently. Third, negatively charged headgroup (-NH3) of HEX associated with positively charged metal ions, for which XPS of N 1 s before and after adsorption was analyzed (Figure 8b). The XPS spectrum of N 1 s (HEX-VER) was fitted into two peaks of functional groups and overlapping each other at 397.98 (assigned to -NH2) and 400.33 eV (assigned to -NH3+), respectively [32]. After As(III) uptake, the BEs of both N 1 s peaks shifted to higher energy (398.04 and 400.27 eV for HEX-VER+As(III)), and (398.02 and 400.15 eV for HEX-VER+As(III)/Cd(II)/Pb(II)). This phenomenon was likely due to the formation of R-NH2-M (Equation (8)) (M denotes As(III) or Cd(II)/Pb(II)) and R-NH3+-M(Equation (9)) complexes [32]. This happened since a lone pair of the amino group’s nitrogen atom (hexylamine) was donated to form a shared bond between metal ions and the N atoms. As a result, the nitrogen’s electron cloud density was reduced, and peak was shifted at a higher BE [32,38]. Hence, the chelation between -NH2 or -NH3+ groups and metal ions was identified as one of the adsorption mechanisms.

\[
R-\text{NH}_2 + M \rightarrow R-\text{NH}_2M \quad (8)
\]

\[
R-\text{NH}_3^+ + M \rightarrow R-\text{NH}_2M + H^+ \quad (9)
\]

**Figure 8.** High-resolution spectra of O 1 s (a); and N 1 s (b) for before and after adsorption of As(III) and As(III)+Cd(II)/Pb(II) onto HEX–VER.

After analyzing the pH, zeta potential, XPS, and effect of co-existing ions results thoroughly, it was revealed that ion-exchange and complexation were the dominant mechanisms. The hypothetic simulation of As(III) adsorption on HEX-VER is illustrated in (Figure S12).
4. Conclusions

Multimetal contamination, especially in water, has been a significant concern, and developing a suitable adsorbent capable of removing As(III) in the presence of other heavy metals is a huge challenge. Here, a novel material (HEX-VER) was prepared by functionalization of hexylamine on vermiculite. HEX was deposited well on the vermiculite surface, confirmed by XRD, FTIR, BET, EDS, and XPS analyses. Compared to VER; HEX-VER showed an improved As(III) uptake from 11.89 to 13.52 mg·g⁻¹ in the singular system, and from 6.12 to 10.33 mg·g⁻¹ in the presence of Cd(II) and Pb(II), respectively. Adsorption was homogenous and the monolayer is described-well by the Langmuir isotherm model and PSO. Results revealed that pH conditions and co-existing ions significantly affect the adsorption rate. The As(III) removal in spiked water (Pearl River Delta water) test was (> 99.7) and As(III) was reduced from 2000 to 5.08 µg.L⁻¹. Before and after adsorption analyses revealed the dominant mechanisms for As(III) removal were ion-exchange and complexation. HEX-VER showed excellent regeneration performance. This study provides a new strategy for adsorption of As(III) in the presence of other heavy metals, and HEX-VER could be practically used in heavy metal removal applications from water.

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