Efficient Removal of Antimony(III) in Aqueous Phase by Nano-Fe₃O₄ Modified High-Iron Red Mud: Study on Its Performance and Mechanism

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Abstract: The resource utilization of excess red mud produced from aluminum production is a current research focus. In this study, novel nano-Fe₃O₄ modified high-iron red mud material (HRM@nFe₃O₄) was fabricated using the method of co-precipitation to remove Sb(III) from the aqueous phase. The HRM@nFe₃O₄ at a nFe₃O₄:HRM mass ratio of 1:1 had optimal adsorbing performance on Sb(III) in water. Compared with others, the synthetic HRM@nFe₃O₄ sorbent had a superior maximum Sb(III) adsorption capacity of 98.03 mg g⁻¹, as calculated by the Langmuir model, and a higher specific surface area of 171.63 m² g⁻¹, measured using the Brunauer-Emmett-Teller measurement. The adsorption process was stable at an ambient pH range, and negligibly limited by temperature the coexisting anions, except for silicate and phosphate, suggesting the high selectivity toward Sb(III). HRM@nFe₃O₄ retained more than 60% of the initial adsorption efficiency after the fifth adsorption-desorption cycle. The kinetic data fitted by the pseudo-second-order model illustrated the existence of a chemical adsorption process in the adsorption of Sb(III). Further mechanism analysis results indicated that the complexation reaction played a major role in Sb(III) adsorption by HRM@nFe₃O₄. This HRM@nFe₃O₄ adsorbent provides an effective method for the removal of Sb(III) in wastewater treatment and is valuable in the reclamation of red mud.

Keywords: high-iron red mud; nano-Fe₃O₄; Sb(III); kinetics and isotherms; mechanism

1. Introduction

Antimony (Sb) is a heavy metal with high toxicity, which may result in harm to humans [1]. This element is widely found in the environment on account of rock weathering, mining and smelting activities, coal combustion, antimony product release, etc. [2]. Sb mainly exists in the forms of Sb(III) and Sb(V) in water. The species of Sb(III) are dependent on pH value: when the pH is less than 2.0, positive ionic groups play a dominant role in Sb(III), such as Sb³⁺, SbO²⁺, and Sb(OH)²⁺, while neutral species of Sb(OH)³⁻ and H₂SbO₃⁻ are predominant within the pH range from 2.0 to 10.0, and when the pH of the solution is higher than 10.0, only one species of SbO²⁻ exists [3,4]. It is reported that the toxicity of Sb(III) is 10 times higher than Sb(V) [5]. Long-term ingestion of excessive Sb can cause immune system impairment, lung injury, liver damage, and even cancer [6]. Antimony and antimonious compounds have been categorized as priority pollutants by the United States Environmental Protection Agency (US EPA). The concentration of Sb in drinking water is limited to below 5 µg L⁻¹ in the European Union and 6 µg L⁻¹ by the US EPA [7,8]. Thus, effective technologies for Sb removal from aqueous solutions are of great significance to ensure the health of both the environment and human beings. Various technologies have
been applied to remove Sb from wastewater, such as coagulation or flocculation [9,10], ion-exchange [11], membrane separation [12], oxidation [13], electrochemical deposition [14], bioremediation [15] and adsorption [16]. Adsorption has attracted great attention among those technologies, with advantages such as simple operation, easy application and low cost [17].

Red mud is solid waste generated from the common process of aluminum production [18,19]. Various forms of iron and aluminum oxides are the essential ingredient of red mud, and others contain titanium dioxide, calcium carbonate, quartz, sodium aluminum silicates, etc. [20]. In 2019, the global stock of red mud was estimated to be near 4 billion tons, and the annual production amount was 0.15 billion tons [21]. According to the amount of iron, red mud can be classified into two categories: high-iron red mud, with more than 30% iron content, and low-iron red mud, with less than 30%. The high-iron red mud is more difficult to dispose of than low-iron red mud because it does greater harm to environment [22]. Due to its features of high alkalinity (pH of 10.5–12.5), complex constituents, massive generation and random disposal, it poses a great threat to ecosystems and the environment. Several leakage events caused by the random disposal of red mud have attracted much attention around the world [23,24]. Thus, the treatment of red mud is an international problem. Therefore the utilization of red mud has been explored in many fields, such as building materials, mineral extraction, catalyst and environmental remediation materials, etc. [25,26]. Red mud, with a fine porous structure and rich functional groups, has great potential to be applied as a novel absorbent to remove harmful components in wastewater [27–29]. A large amount of modified red mud was applied in the field of heavy metal pollution treatment in previous studies. For example, red-mud-modified biochar was used to adsorb As(III) and As(V) in water [30]. Functionalized material synthesized by red mud, lignin, and carbon dioxide showed good removal efficiency for the removal of Cr [31]. Fe(III)-modified, heat-treated and acid-activated red mud were utilized to remove the Mn(II) from acid wastewater [32]. However, the performance and reusability of red-mud-based materials for heavy metal removal are still unsatisfactory. Moreover, there is a lack of research reports about the removal of antimony using red mud.

Very recently, iron oxide composite adsorption materials have been regarded as promising adsorbents for heavy metal removal due to their abundant functional groups and excellent dispersibility [33,34]. In particular, Fe₃O₄ and Fe(0), which can be separated from liquid by an external magnetic field, have been widely utilized in wastewater treatment research [35,36]. At present, several innovative adsorbents based on Fe₃O₄ have been investigated to remove antimony; these include Ce(III)-doped Fe₃O₄ magnetic particles [37]; Fe₃O₄ magnetic nanoparticles coated with cationic surfactants [8]; Fe₃O₄@TA@UiO-66 developed via in situ crystal growth of UiO-66 around the magnetic Fe₃O₄ modified by Tannic Acid (TA) [38]; Fe₃O₄ crosslinked by 3-aminopropyltriethoxysilane (APTES) and nitrilotriacetic acid (NTA) [39]; core-shell Fe₃O₄@Ce-Zr binary oxide [40]. Hence, nFe₃O₄ modification as a kind of mature technology could be a feasible method to improve the adsorption performance and recycling of red mud.

In this study, we aim to use the waste resources of high-iron red mud (HRM) to prepare a novel magnetic adsorbent (HRM@nFe₃O₄). This could not only remove Sb(III) from water effectively but also realize red mud reclamation and reuse. We focus on the following: (1) synthetic composition and characterization of nFe₃O₄-HRM; (2) adsorption performance of Sb(III) from aqueous solution by HRM@nFe₃O₄, including equilibrium time, maximum adsorption capacity, effects of pH, reaction temperature, initial concentration, coexisting anions and reusability; (3) the potential adsorption mechanism of Sb(III) by HRM@nFe₃O₄ via the adsorption kinetics, isotherms, functional groups analysis and binding energy analysis. This new absorbent of HRM@nFe₃O₄, with the properties of low cost and easy industrial production, could provide unique performance for Sb pollution control.
2. Materials and Methods

2.1. Materials and Reagents

The high-iron red mud was collected from the Jiaozuo alumina refinery of Aluminum Corporation of China Limited (Zhengzhou, China). The compositional matrix of the red mud used in this study is provided in Table S1. Prior to use, the red mud was dried to a constant weight in an oven at 85 °C, sieved through 100-mesh screen, and then stored in a desiccator.

Ferrous sulfate (FeSO$_4$·7H$_2$O), ferric chloride (FeCl$_3$), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethyl alcohol (CH$_3$CH$_2$OH), and all other analytical grade chemical reagents were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ultrapure water obtained by a ZOOMAC-L system (China) was used in all experiments. An Sb(III) stock solution of 1000 mg L$^{-1}$ was premade from dissolving potassium antimonyl tartrate trihydrate ($C_8H_4K_2O_12Sb_2·3H_2O$) in ultrapure water. The preparation of working solutions was made in real time by diluting the stock solution with ultrapure water. An antimony standard solution containing 2% nitric acid (HNO$_3$) was obtained from Merck Millipore Co. Ltd. (Hong Kong, China).

2.2. Preparation of HRM@nFe$_3$O$_4$

A series of HRM@nFe$_3$O$_4$ adsorbents was synthesized at 0:1, 1:2, 1:1, 2:1 and 1:0 nFe$_3$O$_4$:HRM mass ratios using the following modified method of co-precipitation; the mass ratios of 0:1 and 1:0 were pure HRM and nFe$_3$O$_4$, respectively [37,41]. First, 5.56 g FeSO$_4$·7H$_2$O and 10.80 g FeCl$_3$·6H$_2$O were dissolved in 150 mL oxygen-free water, which was prepared by filling N$_2$ into ultrapure water for 30–60 min. Second, under the nitrogen atmosphere, dried HRM was distributed into a 500 mL three-necked flask, which contained 200 mL oxygen-free water, and agitated for 30 min over a water bath at 60 °C. Third, in the condition of magnetic stirring and N$_2$ protection, the FeSO$_4$·7H$_2$O and FeCl$_3$·6H$_2$O mixed solution was added into the three-necked flask, followed by the addition of 1 mol L$^{-1}$ NaOH solution, drop-wise, until alkaline, and then aged at 60 °C for 2 h. Fourth, after cooling down to room temperature, the composites were further separated from the liquid phase by filtration, then purified by decanting and rewashing with oxygen-free water and ethanol (purged of N$_2$ for 30 min before use) until neutral. Finally, after vacuum drying at 95 °C for 24 h, the dried mixtures were ground into ultrafine powder and passed through a 100-mesh sieve. Additionally, nucleation and growth from the supersaturated solution was guaranteed through temperature control of the synthetic process, which could influence the size of synthesized product.

2.3. Characterization of HRM@nFe$_3$O$_4$

The surface area, pore volume and pore size of the adsorbents were measured using Brunauer-Emmett-Teller (BET) isotherms (ASAP 2460, Micromeritics, Norcross, GA, USA). The morphology and crystallinity of HRM@nFe$_3$O$_4$ were observed using a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) (Merlin Company, ZEISS, Forchtingen, Germany) and transmission electron microscopy (TEM) (Tecnai G2 F3, FEI, USA). The functional group(s) of nFe$_3$O$_4$-HRM were identified by Fourier transform infrared spectroscopy (FT-IR) in a spectra range from 400 to 4000 cm$^{-1}$ wavenumber (Nicolet iS, Thermo Fisher, Waltham, MA, USA). X-ray photo-electron spectroscopy (XPS) was used to analyze the chemical states of elements on the surface of HRM@nFe$_3$O$_4$ through analysis with a spectrometer (Nexsa, Thermo Fisher, USA). The X-ray diffraction (XRD) patterns to identify the compounds contained in HRM@nFe$_3$O$_4$ were obtained from a diffractometer (Smartlab 9kW, Rigaku, Japan). The magnetic characterization of HRM@nFe$_3$O$_4$ was measured using a vibrating sample magnetometer (VSM) in the Physical Property Measurement System (PPMS) (DynaCoo, Quantum, USA). The zeta
potential of HRM@nFe₃O₄ was obtained using a zeta potential analyzer (Nano ZS90, Malvern, UK).

2.4. Batch Experiments
2.4.1. Effect of nFe₃O₄/HRM Mass Ratio

The optimized mass ratio of materials (nFe₃O₄:HRM with different mass ratios of 0:1, 1:2, 1:1, 2:1 and 1:0) was acquired by comparing their adsorption capacities at 298 K with the concentration of 10 mg·L⁻¹ Sb(III) solution at pH 4.6 ± 0.2. Then most efficient HRM@nFe₃O₄ was selected to apply to subsequent experiments.

2.4.2. Adsorption Isotherm and Kinetics

The adsorption isotherms of HRM@nFe₃O₄ were set at 298 K, 308 K and 318 K in the different initial Sb(III) concentrations of 5–80 mg·L⁻¹. The adsorption kinetics were conducted by sampling at the specified time under 298 K and at a pH of 4.6 ± 0.2, and the initial concentration of Sb(III) was 5, 10, and 20 mg·L⁻¹.

2.4.3. The Influence of Solution PH and Coexisting Ions

The influence of pH was adjusted to 1.6–11.6 using 1 mol·L⁻¹ NaOH or HCl solution with the most efficient HRM@nFe₃O₄ at 298 K. The influences of common coexisting anions (SO₄²⁻, SiO₃²⁻, CO₃²⁻, PO₄³⁻ and Cl⁻) and cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) on the removal of Sb(III) were researched at pH 4.6 ± 0.2. The concentration range of these ions was 0.1–10 mmol·L⁻¹.

2.4.4. Adsorption and Desorption Tests

To evaluate the reusability of the desired HRM@nFe₃O₄, five cycles of adsorption-desorption experiments were conducted sequentially [42]. For the adsorption experiment, 0.2 g of HRM@nFe₃O₄ was added into 1 L polyethylene bottles, which contained 1 L of 10 mg·L⁻¹ Sb(III) solution at pH 4.6 ± 0.2. The solution was stirred for 4 h, and then the HRM@nFe₃O₄ after adsorption was separated from the solution by a magnet. The residual solution was sampled for the antimony concentration test. For the desorption experiment, the HRM@nFe₃O₄, which had absorbed antimony, was added into 0.5 mol·L⁻¹ HCl solution and 0.5 mol·L⁻¹ NaOH solution at a dosage of 4 g·L⁻¹. After agitating for 4 h, the regenerated HRM@nFe₃O₄ was separated and collected from the eluent, washed several times, dried, and prepared for the next sorption-desorption cycle.

The dose of adsorbent for all batch experiments was 0.2 g·L⁻¹. All polyethylene bottles containing mixed solution were constantly agitated at 150 rpm. At regular time intervals (10–300 min), the samples of 5 mL were immediately filtered through a 0.45 μm pore size membrane. The adsorption capacity of Sb(III) at specified time (t) was calculated by the following equation:

\[ q_t = \frac{(C_0 - C_t)V}{W}, \]

where, \( q_t \) is the adsorption capacity (mg·g⁻¹), \( C_0 \) is the initial concentration of Sb(III) (mg·L⁻¹), \( C_t \) is the concentration of Sb(III) at specified time (t), \( V \) is the volume of the solution (L) and \( W \) is the dose of sorbent used (g).

2.5. Analytical Methods

All batch experiments were performed in the dark and repeated in triplicate. Then the concentration of residual Sb(III) in solution was analyzed using an atomic fluorescence spectrometer (AFS6500, HAIGUANG INSTRUMENT, Beijing, China). It was coupled with a hollow double cathode antimony lamp. Thiourea was used as a pre-reducing agent. The working solution was prepared with 10% HCl (GR) as the carrier solution and a mixture of 0.5% KOH and 2% KBH₄ as the reducing solution. The main current of the antimony lamp was set at 40 mA. In addition, the negative high voltage for antimony analysis was set 300 V. Argon (99.999%) was used as the shielding gas and the carrier gas, and the flow rates were
set to 800 mL·min⁻¹ and 300 mL·min⁻¹, respectively. The flow rate of the liquid phase pump and the speed of the peristaltic pump were set at 1.5 mL·min⁻¹ and 120 r·min⁻¹, respectively. All samples were stored in a mobile phase solution and filtered through a 0.45 μm microporous membrane. All samples were analyzed within 24 h after collection.

3. Results and Discussion

3.1. Structure, Morphology and Surface Properties of HRM@nFe₃O₄

The morphologies of HRM and HRM@nFe₃O₄ in 1:1 mass ratio were confirmed by TEM images, as seen in Figure 1. Many nanoparticles were aggregated on the surface of HRM@nFe₃O₄, with a particle size of 5 nm to 30 nm, which was much smaller than HRM. This irregular spherical shape could create porous structure and rough surface, which was the essential condition of a desired absorbent. The SEM-EDS analysis results are illustrated in Figure S1. As shown in the mapping image, Fe was evenly distributed on the surface of HRM@nFe₃O₄, and the iron content of HRM@nFe₃O₄ increased significantly compared to that of HRM. The energy image further demonstrated that the Fe mass ratio on the surface of HRM@nFe₃O₄ was about 51.93%, which was 3.7 times that of HRM. Above all, Fe was successfully loaded onto the surface of HRM in the form of small nanosized particles with non-uniform shapes [43].

![Figure 1. TEM images of HRM and HRM@nFe₃O₄: (a,b) TEM images of HRM; (c,d) TEM images of HRM@nFe₃O₄.](image-url)

Figure 2 shows the XRD patterns of HRM, HRM@nFe₃O₄ and nFe₃O₄ (HRM: nFe₃O₄ with mass ratios of 1:0, 1:1 and 0:1). The pattern of HRM exhibited an unordered structure with the peaks at 24.22°, 33.22°, 35.78°, 49.62°, 54.18°, 62.66° and 64.29°, which represented the Bragg reflections from the (110), (121), (−110), (220), (132), (130) and (−211) planes, respectively, typical of Fe₂O₃ phase (Reference code: 85-0599). The HRM used in this study is rich in Fe₂O₃, and the result is identifiable to the XRF. For the synthetic nFe₃O₄, the high-intensity peaks were observed at 2θ = 30.36°, 35.76°, 43.47°, 57.51°, and 63.17° in the XRD pattern, which represented the Bragg reflections from the (220), (311), (400), (511), and (440) planes, respectively (Reference code: 75-0449). This means nFe₃O₄ was successfully loaded by the synthetic method in this study. Although some peaks could be found at 10° to 45° in the XRD pattern of the HRM@nFe₃O₄, it was difficult to distinguish the Fe₂O₃ and Fe₂O₄. In addition, there was no distinct peak at 2θ ranging from 45° to 80°, illustrating that the
original spinel structure of HRM was changed by adding nFe₃O₄, and the HRM@nFe₃O₄ was the amorphous phase. Notably, the non-crystal phase of HRM@nFe₃O₄ might result from the vigorous stirring and low-temperature drying in the synthesis procedure [44]. The performance of adsorption of HRM@nFe₃O₄ might be dependent on its amorphous structure and various functional groups on the surface. The adsorbability and surface activity of amorphous ferric oxide to antimony were demonstrated to be much stronger than that of crystalline goethite, according to the previous research [45].

The N₂ adsorption-desorption isotherms of HRM@nFe₃O₄ are shown in Figure S2a. They did not reach an equilibrium state at the high stage of P/P₀ and presented an H3 hysteresis loop matched to type IV in isotherms classification by International Union of Pure and Applied Chemistry IUPAC. It was indicated that the existence of a slit hole structure was attributed to particle accumulation, and this material might be mesoporous adsorbent [40,46]. The BET results of HRM and HRM@nFe₃O₄ were obtained by analyzing the sorption data through the Barrett-Joyner-Halenda (BJH) model. As it showed, the HRM@nFe₃O₄ had a high specific surface area of 171.63 m²·g⁻¹, average pore width of 7.62 nm and pore volume of 0.31 cm³·g⁻¹, which was in the scope of mesoporous dimension and suitable for use as an absorbent. The HRM had a BET specific surface area of 15.49 m²·g⁻¹, average pore width of 22.76 nm and pore volume of 0.06 cm³·g⁻¹. It is well-known that larger specific surface area provides more adsorption sites, while smaller particle size promotes the diffusion of small molecules from the aqueous phase onto the surface active sites [47,48].

Figure S2b illustrates the comparison of magnetic field-dependent behaviors between HRM and HRM@nFe₃O₄ in an applied magnetic field from −20 to 20 k Oe. HRM@nFe₃O₄, a kind of ferromagnetic material, showed typical hysteresis loops in magnetic behavior, with a magnetic coercivity of about 45.18 Oe, suggesting that HRM@nFe₃O₄ could be categorized as magnetically soft and possessing ferrimagnetic rather than the superparamagnetic properties. Relatively lower coercivity of HRM@nFe₃O₄ indicated a better dispersibility in the aqueous phase, because residual magnetic attraction disappeared when the external magnetic field was removed. This provided a basis for HRM@nFe₃O₄ to be a good adsorbent [37]. Apparently, the magnetic induction intensity of HRM@nFe₃O₄ was higher than that of HRM, which meant that loading nFe₃O₄ could promote the magnetiza-
tion of HRM, and the HRM@nFe₃O₄ could separate more quickly from water than HRM under an external magnetic field.

3.2. Effect of Mass Ratio of nFe₃O₄/HRM on Sb(III) Adsorption

To examine the best mass ratio of nFe₃O₄/HRM on Sb(III) adsorption, several HRM@nFe₃O₄ sorbents with different nFe₃O₄:HRM mass ratios of 0:1, 1:2, 1:1, 2:1 and 1:0 were used in Sb(III) adsorption tests. As shown in Figure 3, the adsorption capacities of various types of synthetic HRM@nFe₃O₄ were all higher than pure HRM. When the mass ratio was 1:1, the adsorption capacity was the largest, at approximately 33 mg·g⁻¹. Hence, the nFe₃O₄ with an HRM mass ratio of 1:1 was selected as a feasible HRM@nFe₃O₄ material and applied to the following tests.

Figure 3. Effect of HRM/nFe₃O₄ mass ratio on Sb(III): initial Sb(III) concentration = 10 mg·L⁻¹, sorbent dose = 0.2 g·L⁻¹, pH = 4.6 ± 0.1 and T = 298 K.

3.3. Adsorption Behavior

3.3.1. Effect of Solution pH

To know the influence of electrostatic interaction on Sb(III) adsorption by HRM@nFe₃O₄, the relation between pH values and adsorption capacity was investigated, and the zeta potentials of HRM@nFe₃O₄ before and after reaction were detected. As shown in Figure 4, little effect of pH was observed on the adsorption of Sb(III) [49]. The adsorption capacity was approximately constant in the pH range from 2.6 to 11.6. It was demonstrated that there is no electrostatic attraction during the adsorption process. This is mainly due to the fact that Sb(III) exists as largely uncharged Sb(OH)₅ over a large pH range, from 2.0 to 10.0 [50–52], suggesting that Sb(III) could tightly bound on the surface sites via the formation of surface complexes [48]. Similar results of pH independence of Sb(III) adsorption have been reported previously for goethite and amorphous Fe hydroxides as sorbents [51,53]. The pH value results for Sb(III) solution after adsorption are illustrated in Figure 4a. It could be found that the pH value of Sb(III) solution after adsorption moved towards a pH value of 7, except for the conditions of strong acid or alkaline. This was ascribed to the idea that the corrosion of nFe₃O₄ in acid might consume H⁺, while the formation of iron hydroxides in alkaline might consume OH⁻ [43]. The zeta potentials of HRM@nFe₃O₄ before and after reaction are shown in Figure 4b. The point of zero charge (PZC) of HRM@nFe₃O₄ shifted from 5.2 to approximately 4.8 upon Sb(III) adsorp-
tion, indicating the formation of negatively charged inner-sphere Sb(III) complexes on HRM@nFe₃O₄ [50]. Though the predominant species of aqueous Sb(III) exist as Sb(OH)₃ in the pH range of 2–11, the deprotonation of Sb species is likely to occur [54], as well as As [55], becoming more suitable for binding Sb(III) species present as H₅SbO₂ and Sb(OH)₃ when adsorbed onto the surface of metal oxides (e.g., the deprotonated form Fe₅SbO(OH) for Sb(III) [51,56]). The influence of pH on the sorption of Sb(III) onto HRM@nFe₃O₄ may be explained by the two following complexation mechanisms: (i) ligand exchange at the Sb center and release of hydroxides [56] and (ii) formation of a negatively charged complex [57].

![Figure 4](image-url)

**Figure 4.** Sb(III) removal by HRM@nFe₃O₄ as a function of pH values and the zeta potential: (a) the pH value after adsorption and the adsorption capacity at different pH levels; (b) zeta potential before and after adsorption. Initial Sb(III) concentration = 10 mg·L⁻¹, sorbent dose = 0.2 g·L⁻¹, and T = 298 K.

### 3.3.2. Influences of Coexisting Ions on Sb(III) Adsorption

Due to the fact that actual wastewater generally contains a variety of ions, it was necessary to understand the influence of coexisting ions on the adsorption of Sb(III) by HRM@nFe₃O₄. The influence of coexisting cations of Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺ are shown in Figure 5a, which exhibited negligible changes on Sb(III) adsorption. The reason may be that, because Sb(III) could bind tightly to surface sites by complexation [48], Sb(III) could resist these cations during the adsorption by HRM@nFe₃O₄ [58]. It is well known that the anti-interference performance of an adsorbent is owing to the hydration radius of interference ions and the target adsorbate. The closer the hydration radius was, the stronger the competing adsorption. In this study, the hydration radius of Sb(III) was quite different from these interference cations, indicating that little adsorption process competition occurred among them [59]. The adsorption capacity of Sb(III) by HRM@nFe₃O₄ was further studied to investigate the influence of common anions of SO₄²⁻, CO₃²⁻, SiO₂²⁻, PO₄³⁻, and Cl⁻. As shown in Figure 5b, there was no significant effect on the absorption of Sb(III) for the anion of SO₄²⁻ and Cl⁻ because Sb(III) was chemisorbed onto the absorbent, whereas sulfate and chloride were mainly removed by electrostatic interaction [60]. There was no negative impact on the adsorption of Sb(III) under low anion concentrations; a slight increase was actually observed in the presence of SiO₂²⁻ and PO₄³⁻. Similar observations have been reported in other studies, such as the removal of Sb(III) by chitosan modified iron nanosheet [48]. However, the adsorption of Sb(III) was inhibited by ions of SiO₂²⁻ and PO₄³⁻ at the concentration of 10 mmol·L⁻¹. This was because elements P and Sb are in the same main group of elements in the periodic table and have similar physicochemical properties, and thus they compete for same adsorption sites on surfaces of adsorbents [61]. It was reported in a previous study that phosphate has a huge inhibiting effect on Sb(III) adsorption [16,60]. Nevertheless, SiO₂²⁻ was anticipated to accumulate on hydrous ferric
oxides, and it was thought that the competitive adsorption with Sb(III) on HRM@nFe3O4 would happen [16,62,63]. On the contrary, carbonate promoted the adsorption of Sb(III), which probably can be attributed to the association between the specific adsorption of antimony on carbonate surfaces. There was significant correlation between calcium carbonate and antimony in a previous study, suggesting surface adsorption or ligand exchange with the carbonate group [64]. Furthermore, it is worth mentioning that the concentration of interference ions added in this study (10 mmol·L⁻¹) was higher than most existing in surface waters. Therefore, the adverse effects of these anions would be not seriously limit the application of HRM@nFe3O4.

3.3.3. Regeneration and Reusability of HRM@nFe3O4

Reusability is one of the important indexes for evaluating the potential of an adsorbent. Therefore the recycling property of HRM@nFe3O4 on Sb(III) removal was studied using the adsorption capacities and the numbers of desorption cycling. The regeneration of HRM@nFe3O4 was desorbed after each adsorption with two different eluent of 0.5 mol·L⁻¹ NaOH and 0.5 mol·L⁻¹ HCl [48,65,66]. As shown in Figure S3, HRM@nFe3O4 retained more than 60% of the initial adsorption efficiency after the fifth adsorption–desorption cycle using NaOH as eluent, which proves the good regenerability of HRM@nFe3O4. The performance of NaOH was better than HCl as the eluent of HRM@nFe3O4. This was because NaOH might promote the oxidation of Sb(III) to Sb(V). There was still a large number of adsorption sites that could be regenerated by the ion exchange process between OH⁻ and [Sb(OH)₆]⁶⁻ on the HRM@nFe3O4 surface [42]. The oxidation reaction was completed within seconds, and the Sb(V) oxyanion oligomers tended to be hydrolyzed to more readily desorbed monomers [67]. There was no iron leaching at pH > 3.0, while the iron release concentration gradually increased when pH decreased to below 3.0 [39,56]. Therefore, using HCl as eluent could result in the dissolution of precipitated iron oxide during regeneration, and the procedures of solid-liquid separation inevitably cause some loss during the recovery processes. In addition, due to the adsorbed Sb(III) on materials that were not desorbed completely in previous cycles, the adsorption capacity was reduced gradually in subsequent cycles [62]. It is crucial for future studies to focus on improving the recovery rate of HRM@nFe3O4 for the better application of Sb(III) in wastewater treatment.

3.4. Mechanism of Sb(III) Removal by HRM@nFe3O4

3.4.1. Adsorption Kinetics

The kinetics of Sb(III) removal in water were investigated by batch experiments in order to acquire the adsorption rate and appropriate contact time of HRM@nFe3O4 in order.
to understand the possible absorbed mechanism. As illustrated in Figure 6a,b, the removal of Sb(III) was very fast initially, within 60 min, reaching a plateau with 80% of Sb(III) adsorption. Over 97% of equilibrium adsorption capacity was reached after a reaction time of 240 min. The initial rapid reaction was attributed to the strong affinity sites or the precipitation of adsorbate on the surface of adsorbent [37]. The intraparticle diffusion played a dominant role in the following period [37].

![Image of adsorption kinetics](image_url)

**Figure 6.** (a) The pseudo-first-order kinetic of Sb(III) sorption on HRM@nFe3O4 and (b) the pseudo-second-order kinetic of Sb(III) sorption on HRM@nFe3O4. Initial Sb(III) concentration = 10 g·L⁻¹, sorbent dose = 0.2 mg·L⁻¹, pH = 4.6 ± 0.1 and T = 298 K.

The kinetic data was fitted using the pseudo-first-order kinetic model equation, as follows:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t$$  \hspace{1cm} (2)

The pseudo-second-order kinetic model equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (3)

where \(q_e\) is the adsorption capacity (mg·g⁻¹) of the adsorbent at equilibrium, \(q_t\) is the sorption capacity (mg·g⁻¹) at pre-selected time \(t\) (min), \(k_1\) (min⁻¹) is the pseudo-first-order rate constant for the absorption process, and \(k_2\) (mg·g·min⁻¹) is the pseudo-second-order rate constant. The related parameters are shown in Table 1.

| Sb (mg·L⁻¹) | \(C_0\) (mg·g⁻¹) | \(q_e\) (mg·g⁻¹) | \(k_1\) (min⁻¹) | \(R^2\) | \(q_e\) (mg·g⁻¹) | \(k_2\) (mg·g·min⁻¹) \(R^2\) |
|-------------|-----------------|-----------------|-----------------|--------|-----------------|-----------------|
| 5           | 22.0170         | 0.0214          | 0.9838          |        | 25.4863         | 0.0004          | 0.9930          |
| 10          | 31.0136         | 0.1013          | 0.9473          |        | 33.1181         | 0.0022          | 0.9909          |
| 20          | 60.8113         | 0.0175          | 0.9688          |        | 72.2033         | 0.0001          | 0.9831          |

The above two models were employed to study the adsorption behaviors of HRM@nFe3O4 on Sb(III) adsorption at different initial concentrations. It was found that the pseudo-first-order model and the pseudo-second-order model were both suitable for illustrating the adsorption process of Sb(III) on HRM@nFe3O4. A higher correlation coefficient value (0.99) was observed using the pseudo-second model. This demonstrates that the adsorption process of Sb(III) by HRM@nFe3O4 was related to chemical adsorption and physical adsorption [44] and that chemisorption might play a major role in the reaction process [8].
The pseudo-second order kinetic model also presented a better fitting degree at lower Sb(III) concentration. This indicates that the process of removing Sb(III) by HRM@nFe$_3$O$_4$ resulted from a multi-mechanism synergy [43].

3.4.2. Adsorption Isotherms

The two classical Langmuir and Freundlich models were employed to study the adsorption isotherms and calculate the maximum adsorption capacities of the materials at 298 K, 308 K and 318 K. The resulting data were analyzed with the Langmuir equation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m k_L},$$

(4)

and the Freundlich equation:

$$\log q_e = \frac{1}{n} \log c_e + \log k_F,$$

(5)

where $c_e$ (mg·L$^{-1}$) is the concentration of Sb(III) at equilibrium, $q_e$ (mg·g$^{-1}$) is the equilibrium adsorption capacity of Sb(III), $q_m$ (mg·g$^{-1}$) is the maximum absorption amount of the Sb(III), $k_L$ (L·mg$^{-1}$) is the Langmuir equilibrium sorption constant, $k_F$ (L·mg$^{-1}$) is the Freundlich characteristic constant, which is proportional to the equilibrium constant, and $n$ is the index of adsorption strength, where a lower value indicates more homogeneous surfaces.

Adsorption isotherm data explored by nonlinear fitting of the Langmuir model and Freundlich model is shown in Figure 7a,b. Related isotherm parameters that were calculated are summarized in Table 2. Better correlation coefficients ($R^2$ values of 0.9967, 0.9948 and 0.9946) fitted using the Langmuir model were obtained in this work. On the basis of the Langmuir model, the adsorbent surface was homogeneous, which was in connection with uniform monolayer adsorption onto the surface of the adsorbent, including a limited number of adsorption sites. Meanwhile, maximum adsorption capacity was obtained when all adsorption sites on the adsorbent were occupied as single layer [41]. The maximum adsorption capacity of Sb(III) on HRM@nFe$_3$O$_4$ was 98.03 mg·g$^{-1}$ at 308 K, in theory, according to the nonlinear Langmuir model. Normally, the adsorptive action occurs easily when $n$ is larger than 2.0, while it is unlikely to occur when $n$ is below 0.5 [68]. The values of $n$ were 3.16, 3.24 and 3.56, as seen in Table 2, indicating that Sb(III) was easily adsorbed on HRM@nFe$_3$O$_4$, which was attributed to the large number of adsorption sites on the surface. The performance comparison between HRM@nFe$_3$O$_4$ and various adsorbents for the removal of Sb(III) is shown in the Table S2. As can be seen, the maximum adsorption capacity was larger than carbon nanofibers decorated with ZrO$_2$ (ZrO$_2$ -MWCNT) [4] and a zirconium metal-organic framework modified amino (UiO-66(NH$_2$)) [69], the dosage of HRM@nFe$_3$O$_4$ was lower than Fe(0)-Zeolite [70], Praphene was modified with polyamide composite sorbent (PAG) [66] and three-dimensional Cu(II)-specific metallogels (Cu-MG) [49], and the pH range was wider. Furthermore, the equilibration time of HRM@nFe$_3$O$_4$ was shorter than polyacrylonitrile modified by an ultrahigh percentage of amidozone groups (UAPAN) [68] and NU-1000 [52]. It can be found that HRM@nFe$_3$O$_4$ is superior to many published adsorbents.
3.4.4. Adsorption Mechanism Reconstruction

The chemical compositions of HRM and HRM@nFe$_3$O$_4$ before and after Sb(III) sorption were further examined by XPS. As displayed in XPS survey spectra in Figure 8a, the HRM@nFe$_3$O$_4$ after Sb(III) adsorption presented the characteristic peaks of C1s, O1s, Fe2p, Sb3d3 and Sb4d, while HRM and HRM@nFe$_3$O$_4$ only showed the characteristic peaks of C1s, O1s and Fe2p. The emergence of Sb3d3 and Sb4d peaks were observed after Sb(III) adsorption, suggesting the successful attachment of Sb(III) on the surface of HRM@nFe$_3$O$_4$. The intensity of Fe2p peaks was much weaker in HRM than that in HRM@nFe$_3$O$_4$ because of the lower Fe content, which was in agreement with EDS results. The C1s spectrum of HRM@nFe$_3$O$_4$ was differentiated into three peaks at binding energies of 284.8, 286.4 and 288.4 eV, corresponding to C=C, C=O and C=O bonds, respectively [4]. As shown in Figure 8b, the peaks of carbon were hardly shifted after modification by nFe$_3$O$_4$, but the
peak area ratio of C-O and C=O was increased. This proved that the chemical environment around carbon was changed after adding nFe3O4 [62].

According to the binding energy for different species of oxygen with metal (M), the O1s and Sb3p spectrum was used to study the changes of components specifically. As shown in Figure 8c, the peaks at 532.6 eV, 531.3 eV, 529.5 eV and 539.9 eV corresponded to the H-O-H, M-OH, M-O and Sb-O bonds, respectively [4,43]. Because HRM contains many metal oxides, M-O and M-OH did not carry out peak separation specifically. However, due to the high iron content of HRM, it could be inferred that Fe-O-Fe and Fe-OH played the leading role in M-O and M-OH. The percentages of M-O, M-OH and H-O-H in HRM were 17.91%, 64.38% and 17.71%, respectively. After loading nFe3O4, the content of M-O in HRM@nFe3O4 increased to 70.64%, and M-OH to 29.36%, but H-O-H disappeared. However, the adsorbed H2O did not participate in the reaction between absorption [4,75]. This could indicate that the nFe3O4 was synthesized successfully with some byproducts of M-OH, such as FeOOH. After adsorption of Sb(III), the contents of M-O increased to 35.28%, whereas that of M-OH decreased to 56.99%, because M-OH and Sb formed M-O-Sb complexes by surface complexation [45,47,56,76]. Furthermore, the peaks of the M-OH shifted to higher binding energies after Sb(III) adsorption, which could also demonstrate the interaction between M-OH and Sb(III) [40]. This was consistent with the result obtained by FT-IR. Moreover, the fitted characteristic peak for O1s at 539.9 eV corresponded to Sb(III)-O after reaction, which provided supportive evidence for the attachment of Sb(III) on HRM@nFe3O4 [52,62,63]. Meanwhile, the -OH group on HRM@nFe3O4 might be partially substituted by Sb species during the antimony adsorption process, thus leading to the formation of inner-sphere surface complexes.

Figure 8. XPS spectra of HRM, HRM@nFe3O4 and HRM@nFe3O4 after Sb(III) sorption: (a) the XPS survey spectra, (b) C 1s spectra, (c) O1s spectra and (d) Fe2p spectra.
As illustrated in Figure 8d, the binding energy of Fe2p3/2 at 712.4–712.7 eV and that of Fe2p1/2 at 726.2–726.3 eV were ascribed to FeO(OH) [77]. The binding energy at 710.6–710.8 eV and 724.3–724.4 eV were characteristic of Fe3O4 [48,78]. Extra Fe(III) double peaks were observed at 714.5–714.8 eV and 726.0–726.3 eV, which were attributed to Fe2TiO5 [79,80]. Because FeO is known to be extremely unstable, the peaks at 709.6–709.9 eV and 723.1–723.4 eV might belong to the Fe(II) oxidation state in Fe3O4. Moreover, there were two satellite peaks located at 718.7–718.8 eV and 732.7–733.2 eV. The binding energy and peak shape of Fe2p were almost unchanged after the adsorption, implying that the chemical valence of Fe stayed the same [45]. Fe3O4 was the main iron compound in HRM, with tiny amounts of FeO(OH) and Fe3O4. After the modification of loading nFe3O4, the content of FeO was increased from about 1.2% to 27.3%, and FeO(OH) was raised from 20.3% to 27.4%, but Fe3O4 decreased from 61.4% to 38.7%, and Fe2TiO5 decreased from 17.2% to 6.5%. This indicated that nFe3O4 was successfully loaded on the surface of HRM, and the by-product of nFe3O4 synthesized by this method was FeO(OH). This may indicate compounds whose chemical formula is likely to be 3Fe2O3·FeO(OH)-4H2O [81]. The instability of amorphous ferrihydrite drove it into highly stable and crystalline goethite and lepidocrocite [45]. Comparing the before and after adsorption, it was found that the rate of Fe2TiO5 changed negligibly, the rate of FeO(OH) decreased to 23.1% and Fe2O3 decreased to 37.9%, while the rate of FeO increased to 32.5% after the sorption of Sb(III). This phenomenon can be explained by the fact that there was a certain loss of HRM during the magnetic recovery process due to its nonmagnetic and hydrophilic ingredients. In addition, the reduction of FeO(OH) was not only a result of the loss of HRM@nFe3O4 but also due to the strong interactions between FeO(OH) and Sb(III), which is consistent with previous results [62].

Accordingly, the generation of nFe3O4 and its iron-compound by-products were determined as detailed in the following equations:

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{H}_2\text{O}^{\text{OH}} & \rightarrow \text{FeO(OH)} + 3\text{H}^+ \\
\text{Fe}^{2+} + \text{Fe}^{3+} + 5\text{OH}^- & \rightarrow \text{Fe(OH)}_2 + \text{Fe(OH)}_3 \\
4\text{Fe(OH)}_2 + \text{O}_2 & \rightarrow \text{FeO(OH)} + 2\text{H}_2\text{O} \\
\text{Fe(OH)}_2 + 3\text{Fe(OH)}_3 & \rightarrow \text{FeO(OH)} + \text{Fe}_3\text{O}_4 + 5\text{H}_2\text{O} \\
4\text{Fe}_3\text{O}_4 + 6\text{H}_2\text{O} + \text{O}_2 & \rightarrow 12\text{FeO(OH)}
\end{align*}
\]

The formation of FeO(OH) could be attributed mainly to hydrolysis of FeCl3 [82,83], the complexation of Fe(OH)2 with Fe(OH)3, as well as the oxidation of Fe(OH)2 and Fe3O4 [32]. Hence, abundant surface groups and active sites were available after modification by nFe3O4. The potential adsorption mechanisms between Sb(III) and HRM@nFe3O4 are shown in Figure 9. It is obvious that Sb was chemically bonded with Fe from the XPS analysis, which was coincident with the results of sorption isotherms and sorption kinetics. Additionally, the larger specific surface area (SBET) on HRM@nFe3O4 indicated that there were more active sites and better antimony adsorption performance. Furthermore, surface complexation reaction between Sb(III) and amorphous ferric oxide, including nFe3O4 and its by-products FeO(OH) and Fe(OH)3, played an indispensable role in the removal of Sb(III) by HRM@nFe3O4. Hydrogen bonds between hydroxyl groups on HRM@nFe3O4 and antimony molecules were also conductive to the removal of Sb(III) [37,43]. Moreover, a small number of corrosion products of HRM@nFe3O4 produced by Fe3+ could remove Sb(III) from the aqueous phase by co-precipitation [43,84]. It is reasonable to speculate that the loading of nFe3O4 changed the surface structure and the functional groups such that the adsorption capacity was improved eventually.
Figure 9. Proposed mechanisms for the adsorption of Sb(III) onto HRM@nFe₃O₄.

4. Conclusions

In this work, the HRM functionalized with nFe₃O₄ was synthesized by the co-precipitation method, which showed favorable physical and chemical characteristics and adsorption performance. The adsorption capacity of HRM@nFe₃O₄ was significantly improved compared with HRM. The adsorption of Sb(III) was not limited by the solution pH. Most of coexisting cations and anions showed negligible interference on Sb(III) removal. The XRD, TEM, SEM, BET, FTIR and XPS analysis demonstrated that nFe₃O₄ particles were loaded on the surface of HRM successfully. The addition of nFe₃O₄ endowed HRM@nFe₃O₄ with magnetic performance, enhancing the efficiency of solid-liquid separation. After loading nFe₃O₄, the generation of iron oxides and hydroxides played a significant role in the Sb(III) removal. According to the results of batch experiments and characterization analysis, the major mechanisms of removing Sb(III) were complexation and co-precipitation. The great Sb(III) adsorption performance illustrated that the novel HRM functionalized nFe₃O₄ shows great potential in the wastewater treatment field, with the properties of high efficiency, simple fabrication, wide suitability range of pH, good recyclability and low cost.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/6/809/s1, Figure S1: SEM-EDS spectrum and Fe-mapping images of HRM and HRM@nFe₃O₄; (a) Fe-mapping images of HRM, (b) Fe-mapping images of HRM@nFe₃O₄, (c) EDS spectrum images of HRM and (d) SEM-EDS spectrum images of HRM@nFe₃O₄; Figure S2: (a) N₂ adsorption-desorption isotherms of HRM@nFe₃O₄ and (b) magnetization versus applied magnetic field for HRM and HRM@nFe₃O₄; Figure S3: Sb(III) sorption and desorption in five consecutive cycles for HRM@nFe₃O₄. Sorption conditions: initial Sb(III) concentration = 10 mg·L⁻¹, sorbent dose = 0.2 g·L⁻¹, pH = 4.6 ± 0.1, T = 298 K and contact time = 4 h. Desorption conditions: regenerant = 0.5 mol·L⁻¹ HCl or NaOH, dose = 4 g·L⁻¹, T = 298 K and contact time = 4 h; Figure S4: FTIR spectra of initial HRM, HRM@nFe₃O₄ and HRM@nFe₃O₄ after Sb(III) sorption; Table S1: Compositional matrix of the red mud (X-ray fluorescence data); Table S2: Comparison of adsorption capacity of Sb(III) by the synthesized HRM@nFe₃O₄ sorbent with different sorbents.

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