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Limonite as a Natural Adsorbent for the Removal of Antimony(III) from an Aqueous Solution

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Abstract: Natural limonite, which contains mainly nano-sized iron and manganese oxides, is widely distributed worldwide. This study investigated the kinetics, thermodynamics, and the effects of pH, ion strength, and anions on the adsorption of Sb(III) via limonites sampled from Xinqiao and Yeshan (Tongling, China). Results show that adsorption equilibrium is achieved after 24 h for all experiments. Under initial Sb(III) = 200 mg/L, pH = 3.0, and temperature = 25 °C, Sb adsorption quantities for X1 (Mn-free limonite from Xinqiao), X2 (Mn-containing limonite from Xinqiao), Y1 (Mn-free limonite from Yeshan), and Y2 (Mn-containing limonite from Yeshan) are 10.92, 12.97, 27.12, and 89.34 mg/g, respectively. Manganese oxides in limonites promote Sb removal through oxidizing Sb(III) to Sb(V). The adsorption processes for all four limonites are fitted with a pseudo-second-order model. All adsorptions except for X1 fit with the Freundlich model; for X1, the Langmuir adsorption model is better. All adsorptions except for Y1 are spontaneous reactions (ΔG < 0). All adsorptions except for Y1 are exothermic reactions (ΔH > 0). Antimony adsorption is independent of solution pH for Mn-free limonites but is negatively related to solution pH for Mn-containing limonites. Generally, ion strength has a weak positive effect on Sb adsorption. The effects of anions on Sb adsorption are grouped into three types: weak negative (NO$_3^-$ and SO$_4^{2-}$), negative (CO$_3^{2-}$, SiO$_4^{4-}$, and PO$_4^{3-}$), and equivocal (humic acid). This study indicates that due to a much higher surface area, Yeshan (124.8 m$^2$/g for X1 and 171.7 m$^2$/g for X2) rather than Xinqiao (13.7 m$^2$/g for Y1 and 12.8 m$^2$/g for Y2) limonites are better materials for Sb(III) removal in an aqueous solution. The key factors for the better use of limonite as an Sb(III) treatment material include temperature, pH, ion strength, and Mn content.

Keywords: limonite; antimony(III); iron oxide; manganese oxide; adsorption; oxidation

1. Introduction

Antimony (Sb) is a 15-group metalloid in the periodic table of elements. It has extensive applications in alloy, flame-retarding additives, batteries, chemicals, ceramics, glass, therapeutic agents, and other fields [1]. On the other side, excessive Sb exposure may cause severe health problems, such as respiratory irritation, pneumoconiosis, gastrointestinal symptoms, and antimony spots on the skin [1,2]. Thus, Sb intake is strictly controlled in many countries and regions. For example, China, the USA, and the European Union have confined respective Sb upper limits of 5, 6, and 10 µg/L in drinking water [1,3].

Although high-Sb geological settings are scarce because Sb abundance in the Earth’s crust is very low (~0.3 mg/kg) [4], anthropogenic activities can exceptionally concentrate Sb; in a mining environment, it can even reach 22,000 mg/kg in the sediment and 6384 µg/L in the water [5,6]. Mining and smelting wastes, coal and fossil fuel combustion residuals, and shooting-range soils are now recognized as typical secondary Sb sources and sinks [2,7–10]. Thus, monitoring and treatment of Sb in such solid and aquatic systems are
becoming important environmental tasks. In China, such tasks are especially formidable, not only because they contribute about 78% of global Sb production [11] but also because they are important contributors to global anthropogenic Sb emissions [9,12].

Antimonate (Sb(V)) and antimonite (Sb(III)) are the two main Sb species in the Earth’s surficial environment [1]. Low-valent Sb(III) is more stable than high-valent Sb(V) under relatively reducing conditions [13,14] and is 10 times more toxic than Sb(V) [15–18]. Many oxidants and adsorbents have been developed to remove aqueous Sb(III). Low-cost iron and manganese oxides are especially favored. Numerous batch and flow experiments have been explored to study the thermodynamics, the kinetics, and the influencing factors of Sb(III) adsorption and oxidation via Fe and Mn oxides [19–27]. Generally, Mn oxides have a much stronger Sb(III) oxidation ability than Fe oxides [28–31], while Fe oxides have stronger Sb(III) and Sb(V) adsorption ability [32,33]. Alternatively, some high-performance Fe–Mn binary composites and Fe-doped Mn oxides have been developed to achieve the aim of synchronous Sb(III) detoxification and removal [18,27,32,34,35]. It was found that Mn(IV) and Fe(III) oxides in such materials are responsible for Sb oxidation and adsorption, respectively [32,34].

Limonite is a special Fe ore derived from sulfide and/or carbonate ores weathering. Goethite (α-FeOOH) and hematite (α-Fe₂O₃) are usually its two main phases. Additionally, Mn oxides and Mn-containing Fe oxides are often present if limonite is derived from Mn-containing ores [36]. Although the mineralogical property of limonite indicates it to be a potential low-cost natural material for Sb(III) adsorption and oxidation, hitherto, little concern has been paid to this topic, and the potential of Sb(III) removal via limonite is not very clear. In this study, we conducted batch experiments to investigate the efficiency, thermodynamics, kinetics, and influencing factors of Sb(III) adsorption via some natural limonites. We discussed the possibility of using the Mn-containing limonite as a low-cost Sb(III) treatment material.

2. Materials and Methods

2.1. Materials and Chemicals

Limonites used for experiments were sampled from Xinqiao and Yeshan iron deposits in the Tongling polymetallic mineralization cluster in China. For detailed geological settings of the two deposits, please see Liu et al. [37] and Chen et al. [36], respectively. Limonites sampled from both deposits were divided into types I and II in terms of color, where type I limonites (labeled as X1 for Xinqiao limonite and Y1 for Yeshan limonite, respectively) are brownish yellow and are weathering products of Mn-lack hematite or sulfides, and type II limonites (labeled as X2 for Xinqiao limonite and Y2 for Yeshan limonite, respectively) are brownish black and are weathering products of Mn-lack hematite or sulfides, and type II limonites (labeled as X2 for Xinqiao limonite and Y2 for Yeshan limonite, respectively) are brownish black and are weathering products of Mn-containing siderite (FeCO₃) and silicates (Figure 1a,d). A scanning electron microscopy (SEM) observation showed that goethite particles are sub-micrometer-sized in Xinqiao limonites (Figure 1b,c) while they are nano-sized in Yeshan limonites (Figure 1e,f). Chemical compositions were measured using the X-ray fluorescence (XRF-1800, Shimadzu, Kyoto, Japan) method. Results show that both X2 and Y2 have considerable Mn content (Table 1). X-ray diffraction and transmission electron microscopy (TEM) analyses show that limonites are composed mainly of Fe- and Mn-oxides in X2 and Y2 ([36,37], and this work).

Before the experiments, natural limonites were crushed, ground, and sieved to obtain powders with a particle size below 200 mesh (<75 μm in diameter) (Figure 2). The powders were then washed with deionized water to remove soluble impurities and dried naturally. Specific surface areas were measured using a surface area analyzer (Nova 3000e, Quantachrome Instruments, Boynton Beach, FL, USA). Results (Table 1) show that Yeshan limonites have a much higher surface area than Xinqiao limonites. Surface potentials of limonite powders were analyzed on a Zetasizer Nano ZS90 (Malvern Instruments, Malvern, WR14 1XZ, UK) zeta potential analyzer. Results (Table 1) show obvious decreases in surface potential in the presence of Mn minerals.
Table 1. Chemistry (wt%) and mineralogy of limonites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>pHₚZC</th>
<th>SA</th>
<th>Mineral Assemblage</th>
</tr>
</thead>
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<tr>
<td>X1</td>
<td>83.79</td>
<td>2.39</td>
<td>1.42</td>
<td>-</td>
<td>6.9</td>
<td>13.7</td>
<td>goethite, hematite, and quartz</td>
</tr>
<tr>
<td>X2</td>
<td>66.26</td>
<td>19.01</td>
<td>5.47</td>
<td>3.56</td>
<td>4.0</td>
<td>12.8</td>
<td>goethite, hematite, quartz, illite, and pyrolusite</td>
</tr>
<tr>
<td>Y1</td>
<td>80.01</td>
<td>1.75</td>
<td>1.73</td>
<td>0.49</td>
<td>7.1</td>
<td>124.8</td>
<td>goethite, hematite, and amorphous silica</td>
</tr>
<tr>
<td>Y2</td>
<td>68.08</td>
<td>7.02</td>
<td>2.33</td>
<td>19.24</td>
<td>4.1</td>
<td>171.7</td>
<td>goethite, hematite, Mn-goethite, groutite, ramsdellite, pyrolusite, quartz, and residual ivalite</td>
</tr>
</tbody>
</table>

* below detection; ** point of zero charge; ³ surface area (m²/g).

Figure 1. Macroscopic and microscopic (observed using SEM) morphologies of limonite ores collected from Xinqiao (a–c) and Yeshan (d–f). Xinqiao limonite ores contain mainly yellow goethite (Gt) and black to red hematite (Hm) (a). Goethite is the product of hematite hydration (a) and siderite (Sd) weathering (b). Sub-micron goethite particles in Xinqiao limonites show a spindle shape (c). The hand specimen shows the coexistence of yellow goethite and black pyrolusite (Pyr) in Yeshan limonite (d). Goethite in Yeshan limonite shows cluster (e) and flocculent (f) shapes.

Figure 2. Limonite powders used for Sb adsorption.
2.2. Adsorption Experiments

2.2.1. Adsorption Kinetics

The adsorption kinetics experiment was conducted in a 2 L glass beaker containing a 1 L Sb(III) solution (2 mg/L), which was prepared with an analytical pure antimony potassium tartrate (C₈H₄K₂O₁₂Sb₂) solution. Limonite was added to the beaker to create a mineral concentration of 0.6 g/L. Sodium chloride was selected to adjust the solution’s ionic strength to 0.01 M. The solution’s pH was adjusted to 3.0 using 0.1 M HCl and NaOH. Beakers were placed in a 25 °C constant-temperature oscillator, running for 24 h. Solutions were extracted at 0, 5, 10, 20, and 40 min, and 1, 1.5, 2, 3, 4, 6, 8, 10, 12, and 24 h. Clear solutions were obtained through centrifuging and filtrating. Residual Sb concentrations in the clear solutions were measured using an AFS-820 (Titan, Zhuhai, China) atomic fluorescence spectrophotometer (AFS), and the adsorption capacities were calculated. All experiments were performed in triplicate. Without special notification, initial conditions such as ionic strength, pH, and temperature were the same as in the subsequent experiments.

2.2.2. Adsorption Thermodynamics

This experiment was conducted in a 100 mL polyethylene vessel containing a 50 mL Sb(III) solution and 0.03 g limonite. In order to obtain the saturated Sb(III) adsorption of limonite at different temperatures, initial Sb(III) concentrations were set to 2, 5, 10, 20, 40, 80, 100, and 200 mg/L, and the adsorption temperatures were set to 25, 35, and 45 °C, respectively. After adsorption, limonites in experiments with an initial Sb(III) concentration of 200 mg/L were washed with deionized water, freeze-dried, and stored under low-temperature conditions before X-ray photoelectron spectroscopy (XPS) analyses.

2.2.3. Effect of pH on Sb(III) Adsorption

Adsorption was conducted in a 100 mL polyethylene vessel containing a 50 mL 2 mg/L Sb(III) solution. Limonite was added to make a mineral concentration of 0.6 g/L. The initial pH values of the solutions were set to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0.

2.2.4. Effects of Ionic Strength and Coexisting Anions on Sb(III) Adsorption

An ionic strength experiment was conducted in a 100 mL polyethylene vessel with Sb and limonite concentrations identical to Section 2.2.3. A sodium chloride solution was added to adjust the ionic strength to 0.001, 0.01, and 0.1 M. The effects of coexisting NO₃⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻, SiO₄⁴⁻, and humic acid (HA) on Sb(III) adsorption were studied. Initial Sb and limonite concentrations were identical to Section 2.2.3. Three concentration levels (0.001, 0.01, and 0.1 M) were conducted for each anion by adding the corresponding sodium salt solution.

2.3. XPS Characterization

Limonites before and after experiments were analyzed to obtain XPS spectra using an ESCALAB™ 250Xi (Thermo Scientific™, Waltham, MA, USA) XPS spectrometer equipped with a 150 W monochromated Al Ka X-ray source (1486.6 eV). All the binding energies were calibrated during analyses with carbon 1 s peak at a binding energy of 284.8 eV. XPS data were processed using the software XPSPEAK 4.1.

3. Results and Discussion

3.1. Adsorption Kinetics

Two-staged Sb adsorption at pH 3.0 is observed in Figure 3. In the rapid first stage, X1, X2, Y1, and Y2 achieve respective Sb adsorption capacities of 91.6%, 85.1%, 91.3%, and 97.1% within 1 h. In the slow second stage, it takes at least 8 h for all the adsorptions to reach a removal ratio of 98%. Thereafter, adsorption hardly increases, and reaction equilibrium is achieved after 24 h. Antimony adsorption abilities under a low Sb condition...
(2 mg/L) are $Y_1 \approx Y_2 > X_2 > X_1$. This two-staged reaction characteristic is an important time-setting guidance for subsequent adsorption experiments.

![Figure 3. Adsorption of Sb on limonites as a function of reaction time.](image)

The adsorption data are fitted with pseudo-first-order and pseudo-second-order adsorption kinetic models (Appendix A). The fitted curves are shown in Figure 3, and the corresponding kinetic parameters are listed in Table 2. For $X_1$ and $X_2$, correlation coefficients ($R^2$) indicate that the pseudo-second-order kinetic model is more suitable for describing the adsorption processes, while for $Y_1$ and $Y_2$ both models are suitable. Previous studies focusing on Sb(III) adsorption have shown that the adsorption kinetics depend highly on the properties of iron oxides [24,38–43]. As the main difference between Xinqiao and Yeshan limonites is surface area (13.8 and 12.7 m$^2$/g for Xinqiao limonites, and 124.8 and 171.7 m$^2$/g for Yeshan limonites) (Table 1), it is induced that the low surface area of Xinqiao limonites makes the adsorption rates to be constrained both by Sb concentration and the number of surface adsorption sites.

**Table 2. Kinetic parameters for Sb adsorption on limonites.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo-First-Order</th>
<th>Pseudo-Second-Order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>$k_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td>X1</td>
<td>1.475</td>
<td>0.223</td>
</tr>
<tr>
<td>X2</td>
<td>2.008</td>
<td>0.117</td>
</tr>
<tr>
<td>Y1</td>
<td>3.162</td>
<td>0.106</td>
</tr>
<tr>
<td>Y2</td>
<td>3.134</td>
<td>0.557</td>
</tr>
</tbody>
</table>

3.2. Adsorption Isotherms and Thermodynamics

Adsorption isotherms (Figure 4) show that Yeshan limonites have much higher Sb(III) adsorption ability under the same conditions than Xinqiao limonites. This is likely derived from the surface area, where Yeshan limonites have a much higher surface area than Xinqiao limonites (Table 1). SEM (Figure 1) and TEM observations also show that most of the Fe and Mn minerals in Yeshan limonites are nano-sized, implying excellent adsorption potential [36,44]. In Figure 4, it is also observed that at the same temperature (25, 35, and 45 °C), the general Sb adsorption pattern is $X_2 > X_1$, indicating obvious adsorption enhancement by Mn oxides. As to Yeshan limonites, both surface area and Mn oxides could have contributed to Sb adsorption. Previous studies have demonstrated that due to much higher redox potential [45], Mn oxides, just as those in $X_2$ and $Y_2$, have a much stronger ability than iron oxides to oxidize Sb(III) to Sb(V) [28–31]. Sb(V) is usually presented as...
and thus is easily chemically adsorbed by iron oxides, which have a positive surface charge under low pH conditions [1,13]. Furthermore, temperature is an important parameter of Sb adsorption. The adsorption capacities increase with temperature.

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Currently, studies focusing on Sb adsorption by iron oxides consider it to be a chemical process that can be described by Langmuir, Freundlich, and/or Sips isothermal adsorption models [24,39–42,46–50]. Langmuir and Freundlich’s isothermal equations (Appendix B) are used to fit the experimental results shown in Figure 4. The corresponding fitting parameters are listed in Table 3. The fitting correlation coefficients ($R^2$) show that the Freundlich equation is suitable for describing all results except X1, for which the Langmuir equation is better. Theoretically, the ideal Langmuir model is suitable for monolayer adsorption where active sites (in this study, lattice sites in Fe oxides could be the main active sites) are energetically homogeneous, and the interactions between adsorbed molecules are ignored [51]; thus, the adsorption capacity of a material is determined by the total active sites on the surface. The Freundlich model is suitable for adsorption where the active sites are energetically heterogeneous, and adsorption is constrained by previously adsorbed molecules [52]. In contrast to other limonites, X1 shows homogeneous Sb adsorption. Possible reasons are that X1 has low Mn content and surface area.
Table 3. Parameters for two thermodynamic adsorption equations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>T</th>
<th>K_F</th>
<th>n</th>
<th>R²</th>
<th>K_L</th>
<th>Q_max</th>
<th>R²</th>
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</thead>
<tbody>
<tr>
<td>X1</td>
<td>298.15</td>
<td>1.424</td>
<td>2.47</td>
<td>0.957</td>
<td>0.030</td>
<td>12.995</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>1.822</td>
<td>2.50</td>
<td>0.953</td>
<td>0.033</td>
<td>15.839</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>2.393</td>
<td>2.61</td>
<td>0.928</td>
<td>0.041</td>
<td>18.344</td>
<td>0.991</td>
</tr>
<tr>
<td>X2</td>
<td>298.15</td>
<td>2.816</td>
<td>3.38</td>
<td>0.980</td>
<td>0.086</td>
<td>12.442</td>
<td>0.940</td>
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<tr>
<td></td>
<td>308.15</td>
<td>2.158</td>
<td>2.34</td>
<td>0.973</td>
<td>0.046</td>
<td>18.758</td>
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<td>3.432</td>
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<td>0.058</td>
<td>27.727</td>
<td>0.960</td>
</tr>
<tr>
<td>Y1</td>
<td>298.15</td>
<td>5.381</td>
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<td>0.076</td>
<td>26.187</td>
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<td>4.901</td>
<td>2.65</td>
<td>0.980</td>
<td>0.049</td>
<td>34.335</td>
<td>0.950</td>
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<td></td>
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<td>7.566</td>
<td>2.55</td>
<td>0.975</td>
<td>0.043</td>
<td>58.008</td>
<td>0.967</td>
</tr>
<tr>
<td>Y2</td>
<td>298.15</td>
<td>8.609</td>
<td>2.11</td>
<td>0.988</td>
<td>0.024</td>
<td>110.970</td>
<td>0.978</td>
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<tr>
<td></td>
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<td>8.362</td>
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<td>0.020</td>
<td>136.451</td>
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<tr>
<td></td>
<td>318.15</td>
<td>10.297</td>
<td>1.94</td>
<td>0.978</td>
<td>0.021</td>
<td>165.500</td>
<td>0.984</td>
</tr>
</tbody>
</table>

In an adsorption reaction, the Gibbs free energy change ($\Delta G$) is calculated as:

$$\Delta G = -RT\ln K_0$$

(1)

where $R$ is the universal gas constant (8.314 J/(K·mol)) and $T$ is the absolute temperature (K). $K_0$ is an adsorption equilibrium constant obtained by fitting the relationship between $\ln Q_e/C_e$ and $C_e$ and extrapolating the curve to $Q_e = 0$, where the intercept is $\ln K_0$. When $K_0$ values ($K_1$ and $K_2$) at two temperatures ($T_1$ and $T_2$) are obtained, the average standard enthalpy change ($\Delta H$) is calculated using the Van’t Hoof equation:

$$\ln K_2(T_2) - \ln K_1(T_1) = \frac{-\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

(2)

and the entropy change ($\Delta S$) can also be calculated using the equation:

$$\Delta S = \frac{\Delta G - \Delta H}{T}$$

(3)

Thermodynamic parameters in Table 4 indicate that Sb adsorption is a spontaneous endothermic reaction for X1, X2, and Y2 because $\Delta G$ is negative and $\Delta H$ is positive. The negative values of $\Delta G$ and $\Delta H$ for Y1 indicate that adsorption is a spontaneous exothermic reaction in accordance with Sb(III) adsorption on goethite [40]. The values of $\Delta G$ for Y1 and Y2 are much more negative than those for X1 and X2, which probably indicates that the active adsorption sites on Yeshan limonites are energetically higher than those on Xinqiao limonites. This is reasonable because Y1 and Y2 have a much higher surface area than X1 and X2 and thus have much more high-energy active sites. Adsorption of Sb(III) on these high-energy active sites can lead to much more energy release. It is noteworthy that the discussion about energy change is based on the hypothesis of pure adsorption. In fact, Sb(III) oxidation may also lead to energy change. The differences of $\Delta G$ between X1 and X2 and Y1 and Y2 are probably derived from the oxidation of Sb(III) to Sb(V) in experiments X2 and Y2.
3.3. Effect of Initial Solution pH

Adsorption of Sb(III) by limonites X1 and Y1 is independent of pH (Figure 5), in agreement with previous studies of Sb(III) adsorption by iron oxides [24,49,50,53]. For limonites X2 and Y2, adsorption decreases obviously with increasing pH; from pH 3 to 9, the respective decrease ratios are 50% and 30%, respectively. This pattern is similar to the adsorption of Sb(V) by iron oxides [24,41,49,53]. Thus, it is suggested that in X2 and Y2, Mn oxides are key factors that lead adsorption to be pH-dependent; under low pH conditions, Sb(V) presents in the form of Sb(OH)\textsuperscript{6} and is more easily adsorbed by more positively charged iron oxides [1,13]. The pH\textsubscript{pzc} of limonite is probably another constraint that exacerbates the decrease in Sb adsorption with an increasing pH in X2 and Y2. Mn-containing samples have low pH\textsubscript{pzc} values (4.0 for X2 and 4.1 for Y2) relative to the Mn-free counterparts (6.9 for X1 and 7.1 for Y1) (Table 1). X2 and Y2 have wider pH ranges where the surface of limonites is negative, and Sb(V) with the form of Sb(OH)\textsuperscript{6} cannot be adsorbed through electrostatic interaction [24].

![Figure 5. Effect of initial solution pH on Sb adsorption by limonites.](image)

### Table 4. Thermodynamic parameters of Sb adsorption on limonites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>T (K)</th>
<th>K\textsubscript{0} (L/g)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/(mol·K))</th>
<th>ΔG (kJ/mol)</th>
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<tbody>
<tr>
<td>X1</td>
<td>298</td>
<td>1.17</td>
<td>11.58</td>
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<tr>
<td></td>
<td>308</td>
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<td>11.58</td>
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<td>−0.85</td>
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<tr>
<td></td>
<td>318</td>
<td>1.57</td>
<td>11.58</td>
<td>40.16</td>
<td>−1.19</td>
</tr>
<tr>
<td>X2</td>
<td>298</td>
<td>4.95</td>
<td>21.67</td>
<td>80.01</td>
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<tr>
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3.4. Effect of Ionic Strength and Coexisting Anions

In natural and artificial environments, ionic strength is an important variable in Sb adsorption, which can mediate the surficial charge of the adsorbent and the state of Sb in a solution [53]. Figure 6 shows inconsistent effects of ionic strength to adsorption. A positive effect is observed in X1 and X2, where Na\textsuperscript{+} exerts a stable increase in Sb adsorption...
to X1 in the whole pH range and a pH-dependent increase in Sb adsorption to X2 under neutral to alkaline conditions. The effect of ionic strength on Y1 is not obvious, but it is obviously positive for Y2 at a solution pH > 5. Theoretically, cations such as Na\(^+\) and K\(^+\) can adsorb onto the surface of the adsorbent and decrease the negative charge of the surface, thus increasing the electrostatic interactions between adsorbent and anions [54]. The positive effect of ionic strength on Sb adsorption probably indicates an electrostatic-related outer-sphere surface complexation between limonites and Sb in X1, X2, and Y2. However, the relatively low increases in adsorption capacity by Na\(^+\) suggests that an inner-sphere complexation, which is not affected by Na\(^+\), as is found in Sb–Fe oxides complexation by other studies, is also present [2,3,15,41,49,53,55]. In X2 and Y2, Mn minerals could have played key roles in ionic strength-dependent Sb adsorption under neutral to alkaline conditions [30]. Firstly, Sb(III) is adsorbed and oxidized to Sb(V) by Mn minerals. Secondly, outer-sphere complexed Sb(V) is partly released from Mn minerals because Sb(V) in the form of Sb(OH)\(_6\)\(^{3-}\) is repelled from the negatively charged surface of Mn minerals. Thirdly, Na\(^+\) balances the charge of the mineral surface and changes Sb(OH)\(_6\)\(^{3-}\) to NaSb(OH)\(_6\)\(^0\) [53], which thus decreases the repulsion between Sb and adsorbent and the release of outer-sphere complexed Sb(V) [35,46].

Anions such as Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(_2\)\(^-\), CO\(_3\)\(_2\)\(^-\), SiO\(_4\)\(_4\)\(^-\), PO\(_4\)\(_3\)\(^-\), and organic ligands are popular in Sb-contaminated waters. They can play competitive roles with Sb [40], thus decreasing the adsorption efficiency of adsorbents. Results in Figure 7 show a general tendency for the coexisting inorganic anions to exert a negative but limited effect on the adsorption of Sb. Specifically, NO\(_3\)\(^-\) and SO\(_4\)\(_2\)\(^-\) have a lower effect on Sb adsorption than that of CO\(_3\)\(_2\)\(^-\), SiO\(_4\)\(_4\)\(^-\), and PO\(_4\)\(_3\)\(^-\), in agreement with other studies [27,40]. This phenomenon could be explained by the difference in adsorption mechanisms, where NO\(_3\)\(^-\) and SO\(_4\)\(_2\)\(^-\) are adsorbed by Fe oxides mainly through outer-sphere complexation [56,57], while CO\(_3\)\(_2\)\(^-\), SiO\(_4\)\(_4\)\(^-\), and PO\(_4\)\(_3\)\(^-\) are adsorbed by Fe oxides mainly through inner-sphere complexation [56,58,59]. As for limonites, Sb adsorption by X1 is less affected by coexisting
anions than the other three limonites. The effect of HA on Sb adsorption is complex. Antimony adsorption is increased, decreased, and unaffected by HA in X1, X2, Y2, and Y1 experiments. The inhibitions of Sb uptake by HA in X2 and Y2 experiments probably indicate that HA plays a competitive relationship with Sb(V), which is oxidized from Sb(III) by Mn minerals. This part of the experiments indicates that although ionic strength and coexisting anions are effective in Sb adsorption by limonites, they are not the dominant constraints to Sb removal. The effect of anions such as SiO$_4^{2−}$ and PO$_4^{3−}$ on Sb removal could be partly offset by adding Ca$^{2+}$ salts.

![Figure 7](image_url) Effects of coexisting anions on Sb adsorption.

Since Na salts were used in anion experiments, Na$^+$ can also partly offset the effects of anions on Sb adsorption. This offset effect happens mainly in NO$_3^{−}$ and SO$_4^{2−}$ experiments, as Na$^+$, NO$_3^{−}$, and SO$_4^{2−}$ are adsorbed by limonites through outer-sphere complexation. A typical example is experiment X1, in which outer-sphere complexation is the main process (Figure 6), and Na$^+$ totally offsets the effects of NO$_3^{−}$ and SO$_4^{2−}$ (Figure 7).

3.5. XPS Results

It is observed in Figure 8 that limonites X2, Y1, and Y2 after adsorption show obvious 3d$_{3/2}$ XPS spectra of Sb [60], indicating efficient Sb adsorption. Shifts in binding energy (BE) to higher values are also observed after adsorption. For electrons of a specific element, their BEs are usually positively correlated to elemental valence. This rule is also applicable for Sb [60], where the BEs of Sb(III) 3d$_{3/2}$ and Sb(V) 3d$_{3/2}$ are usually 538.8−539.6 eV, and 539.8−541.7 eV, respectively [61]. Thus, such shifts possibly indicate partial or total oxidation of Sb(III) to Sb(V) by minerals in limonites. The shift extents of BE are Y2 > Y1 > X2, which may indicate that Mn content controls the oxidation of Sb. For Mn-free Y1, the XPS result-implicated oxidation of Sb(III) to Sb(V) could be due to Fe oxides [39,40,53]. The 2p XPS peaks of Mn are shown in Figure 9. It is observed that the peak intensity of Y2 is much higher than that of X2, consisting of the difference in Mn content (Table 1). For peak position, decreases in BE both for 2p$_{1/2}$ and 2p$_{3/2}$ peaks are observed after adsorption, indicating the reduction in Mn [62]. Specifically, for X2, such a decrease is obvious only to peak 2p$_{1/2}$, which may indicate that Mn reduction in X2 is weaker than that in Y2.
indicating the reduction in Mn [62]. Specifically, for X2, such a decrease is obvious only to peak 2p1/2, which may indicate that Mn reduction in X2 is weaker than that in Y2.

Figure 8. XPS spectra of Sb 3d3/2 after adsorption experiments.

Figure 9. XPS spectra of Mn 2p before and after Sb adsorption.

3.6. Limonite as a Potential Adsorbent and Oxidant for Sb Removal

Thermodynamic experiments show that under acid conditions (pH = 3.0), Yeshan, rather than Xinqiao limonites, are much better for Sb removal (Figure 4). Experiments of the effect of pH on Sb adsorption also show better Sb removal ability for Yeshan limonites in the pH range of 3–9 (Figure 5). This source-related adsorption difference is derived from the surface area, where Yeshan limonites have a much higher surface area than Xinqiao limonites (Table 1).
The performance of limonites in Sb treatment is also Mn-dependent. Manganese oxides can oxidize Sb(III) to Sb(V), significantly decreasing its biological toxicity in all situations. As for Sb removal, thermodynamic experiments indicate that Mn-containing limonites are better than their Mn-free counterparts under high Sb and low-solution pH conditions (Figure 4). This is due mainly to (1) the relatively higher surface area of Mn-containing limonites (Y1 and Y2) and (2) the oxidation of Sb(III) to Sb(V) by Mn oxides, where Sb(V) is adsorbed more easily by iron oxides than Sb(III) under a low-pH condition [53]. However, the effect of Mn oxides on Sb removal could change depending on the solution’s pH and ion strength. Antimony removal by Mn-containing limonites decreases with an increasing solution pH, as more Sb(V), which is oxidized by Mn oxides, is present as dissolved NaSb(OH)$_6$ and the surface of minerals in limonite becomes more negative [53]. Such a pH effect is offset by cations, which can partially neutralize the negative surface charge of minerals. Thus, promoting ion strength could be considered in the Sb—limonite system under circumneutral conditions. Limonites Y1, Y2, and their mixtures are all excellent Sb(III) removal agents; which one should be used depends on the goals and characteristics (e.g., pH) of the Sb-containing water.

Limonite is widely distributed throughout the world. In China, its reserve is about 1.23 billion tons [63,64], accounting for 2.3% of the total iron ore source [63]. However, as a typical refractory iron ore, limonite is rarely employed in iron and steel production. This study finds a new way of using Mn-contained limonite for Sb(III) removal from wastewater. There is no doubt that, in contrast to the metallurgical industry, the application of limonite in wastewater treatment engineering is much more economical.

4. Conclusions

In this study, the kinetics, thermodynamics, and effects of pH, ion strength, and anions on the adsorption of Sb(III) by natural limonites were investigated for the first time. It is shown that both pseudo-first- and pseudo-second-order models are suitable for describing the adsorption processes for Yeshan limonites, while the pseudo-second-order model can be used to describe the adsorption processes for Xinqiao limonites. The Freundlich model is available for all adsorption experiments except X1 (Langmuir). All adsorption experiments are spontaneous reactions ($\Delta G < 0$). All adsorption experiments except Y1 ($\Delta H < 0$, exothermic reaction) are endothermic reactions ($\Delta H > 0$). For Mn-free (X1 and Y1) and Mn-containing (X2 and Y2) limonites, Sb adsorption is independent of pH and decreases with increasing pH, respectively. Generally, ion strength has a weak positive effect on Sb adsorption. The effects of anions on Sb adsorption are grouped into three types: weak negative (NO$_3^-$ and SO$_4^{2-}$), negative (CO$_3^{2-}$, SiO$_4^{4-}$, and PO$_4^{3-}$), and indefinite (HA). It is shown that due to the much higher surface area, Yeshan, rather than Xinqiao limonites, is a better material for Sb(III) removal in an aqueous solution. Additionally, Mn is another important constraint on Sb removal. Manganese oxides in limonites can decrease the toxicity of Sb by oxidizing Sb(III) to Sb(V) and promote the adsorption of Sb by changing the chemical states of Sb and the surface property of the adsorbent. Temperature, pH, ion strength, and Mn content are also important factors for the better use of limonite as an Sb treatment material.

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in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Appendix A

The kinetic fitting equations are as follows: \( \frac{dq}{dt} = k_1(q_e - q_t) \) Pseudo-first-order (1), \( \frac{dq}{dt} = k_2(q_e - q_t)^2 \) Pseudo-second-order (2), where \( q_e \) and \( q_t \) (mg/g) are adsorption capacities at equilibrium state and time \( t \), respectively, and \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (L/(mg-min)) are pseudo-first-order and pseudo-second-order adsorption rate constants, respectively.

Appendix B

The classical thermodynamic equations are shown as \( Q_e = Q_{\text{max}} \frac{k_1 C_e}{1 + k_1 C_e} \) Langmuir (3), \( Q_e = K_f C_e^{1/n} \) Freundlich (4), where \( Q_e \) (mg/g) is the adsorption capacity at equilibrium, \( C_e \) (mg/L) is the equilibrium concentration of Sb, \( Q_{\text{max}} \) (mg/g) is the maximum adsorption capacity, \( K_f \) (L/mg) is Langmuir adsorption equilibrium constant, \( K_f \) is Freundlich adsorption equilibrium constant, which can be regarded as the adsorption capacity of per concentration unit, and \( n \) is the Freundlich equilibrium parameter, which is related to the adsorption strength.

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