Study and analysis of arsenic adsorption during sludge incineration

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Abstract. This paper studies the mechanism of arsenic adsorption by different adsorbents during sludge incineration. The mechanism of arsenic adsorption in the sludge incineration process was studied in a vertical furnace. The arsenic adsorption performance of CaCO₃ and Fe₂O₃ at different temperatures was studied. When the temperature is 900 ℃, the overall adsorption performance is the best. Therefore, the arsenic adsorption performance of Al₂O₃, molecular sieve and its metal load at 900 ℃ is further studied for comparison. The research results show that: the optimal adsorption temperature of CaCO₃ is 900 ℃, the optimal adsorption temperature of Fe₂O₃ is 800 ℃, and the adsorption performance of CaCO₃ is better than Fe₂O₃. Ca²⁺: Al³⁺=0.5 and Fe³⁺: Al³⁺=0.4 are close to the adsorption saturation state when Al₂O₃ adsorbs arsenic at 900 ℃. When the molecular sieve adsorbs arsenic at 900 ℃, the adsorption effect is best when the molecular sieve is 10X, Ca²⁺: Al³⁺=0.8 and Fe³⁺: Al³⁺=0.6 are close to the adsorption saturation state.

1. Introduction
For a long time, the harmless treatment of harmful substances has attracted the attention of the public, especially scholars in various fields. Among them, the treatment of arsenic has received particular attention in recent years. Long-term exposure to arsenic will cause great harm to human health [1]. Arsenic is a kind of metalloid, which exists widely in nature, and also has a high content in nature and human body [2]. Arsenic is extremely harmful to the human body, so it is also listed as the first category of carcinogens by the International Agency for Research on Cancer (IARC) [3]. Arsenic mainly exists in nature in the form of organic arsenic and inorganic arsenic, and both of them have certain toxicity. Generally speaking, the toxicity of inorganic arsenic is stronger than that of organic arsenic [4], and the toxicity of trivalent arsenic As(III) is 50-100 times that of pentavalent arsenic As(V) [5]. If the human body is exposed to inorganic arsenic for a long time, many diseases will occur, such as cancer [6-7], cardiovascular disease [8-9], black foot disease (BFD) [10].

Municipal sewage sludge (MSS) contains hazardous substance arsenic, and there are many ways to solve sludge. Among them, sludge incineration technology is a common method, but certain harmful fumes will also be generated during the incineration process. Among them, the arsenic contained in the sludge will be gasified and concentrated in the fly ash [11]. When the incineration temperature exceeds 900K, the arsenic in the fly ash mainly exists in the form of As₂O₃ [12]. When the incineration temperature is lower than 800 ℃, a certain amount of dioxins will be produced during the incineration of sludge[13], and dioxins are extremely harmful to the human body[14], so the experimental temperature is 800 ℃, 900 ℃ and 1000 ℃. The study found that calcium-based and iron-based substances have a good adsorption effect on As₂O₃, so this paper chooses CaCO₃ and Fe₂O₃.
as adsorbents to study their adsorption effect on arsenic. For further research, Al₂O₃ and molecular sieves were selected for physical adsorption of arsenic, and Al₂O₃ and molecular sieves were loaded with Ca²⁺ and Fe³⁺ to study the arsenic adsorption performance of metal loading.

2. Experimental equipment and methods

2.1. Experimental samples
The sludge required for the experiment was taken from a sewage treatment plant. Because of its high initial water content, it needs to be dehydrated first, and the dehydrated sludge into an electric heating constant temperature blast drying box and dry it at 120°C for 24 hours. The dried sludge is ground and sieved to 45-105µm, and put into a sealed bag for sealing. Industrial analysis and elemental analysis of the sludge required for the experiment were carried out. The analysis results are shown in Table 1.

| Proximate analysis/%(mass, ad) | Ultimate analysis/%(mass, ad) | As (mg/kg) |
|--------------------------------|-------------------------------|------------|
| M 3.97                        | V 37.5                        | A 55.18    |
| FC 3.35                       | C 17.78                       | H 1.91     |
| O* 17.58                      | N 2.05                        | S 1.53     |
| S 25.78                       |                               |            |

2.2. Experimental device

2.2.1. Vertical furnace
Figure 1 shows a schematic diagram of a vertical furnace. The vertical furnace is used for the experimental study of the arsenic adsorption mechanism. From the industrial analysis and elemental analysis of sludge, the proportions of N₂, CO₂, O₂ and SO₂ in the mixed gas are 78.50%, 16.83%, 4.13%, and 0.54% respectively, and the total flow of the mixed gas is 2L/min.

2.2.2. Wet digestion
Take 0.1g of the sample obtained from the experiment, place it in the digestion tank, and add 5ml of hydrochloric acid solution to it, then dissolving it on a thermostat heater at 180°C for 20min. If the digestion is still not complete, you can add 10ml nitric acid solution to the digestion tank and digested at 160°C for 30 min. Pour the digestion solution into a plastic centrifuge tube, and add deionized water.
to the digestion tank to make the volume to 50ml, dilute the solution after constant volume by 100 times, and add thiourea and HCl to make the content of 1% and 3% respectively.

2.2.3. Atomic Fluorescence Analyzer
This article uses the hydride AFS method to analyze and test the arsenic in the sample. The instrument used in the experiment is AFS-930 atomic fluorescence spectrometer. The reaction equation is:

$$\text{K}_a \text{BH}_4 + 3 \text{H}_2 \text{O} + \text{HCl} = \text{H}_3 \text{BO}_3 + \text{KaCl} + 8 \text{H}^+ + \text{E}^{m+} = \text{EH}_n + \text{H}_2(g)$$

In the formula, $\text{E}^{m+}$ represents the element to be tested, and $\text{EH}_n$ is gaseous hydride.

3. Experimental results and analysis

3.1. Arsenic adsorption performance of CaCO$_3$ and Fe$_2$O$_3$
Figure 2 shows the arsenic adsorption capacity of CaCO$_3$ and Fe$_2$O$_3$ at different temperatures. The arsenic adsorption performance of CaCO$_3$ is obviously better than that of Fe$_2$O$_3$. The optimal adsorption temperature of CaCO$_3$ is 900°C, and that of Fe$_2$O$_3$ is 800°C.

CaCO$_3$ will decompose slowly in the temperature range of 550-650°C [15], and the temperature at which CaCO$_3$ can be completely decomposed is 842°C [16]. Figure 3 shows the decomposition rate of CaCO$_3$ at different temperatures in the experiment. Therefore CaCO$_3$ decomposes into CaO in a small amount at 800°C, and at 900°C, it will decompose a lot and form a lot of pore structure, and its specific surface area will increase. At this time, the adsorption performance of CaCO$_3$ is obviously enhanced. When the temperature rises to 1000°C, the decomposition rate of CaCO$_3$ does not increase significantly, but sintering occurs [17], destroying its surface structure, so the best adsorption temperature of CaCO$_3$ is 900°C. For Fe$_2$O$_3$, when the temperature exceeds a certain value, Fe$_2$O$_3$ will deteriorate due to high temperature sintering, and with the increase of temperature, the sintering situation becomes more serious, which leads to the decrease of active sites and porosity on the adsorbent [18]. The study found that the adsorption performance of Fe$_2$O$_3$ is the best when the temperature is 645°C [19], therefore, the optimal adsorption temperature of Fe$_2$O$_3$ is 800°C.

![Figure 2. The arsenic adsorption of CaCO$_3$ and Fe$_2$O$_3$](image)

![Figure 3. Decomposition rate of CaCO$_3$](image)

3.2. Arsenic adsorption performance of Al$_2$O$_3$ and molecular sieves
It can be seen from the above that the optimal adsorption temperature of CaCO$_3$ is 900°C, and the optimal adsorption temperature of Fe$_2$O$_3$ is 800°C. Therefore, we choose 900°C as the comprehensive optimum temperature, and study the arsenic adsorption performance of Al$_2$O$_3$ and molecular sieve at 900°C.

3.2.1. Arsenic adsorption performance of Al$_2$O$_3$
The adsorption of arsenic on Al$_2$O$_3$ is mainly physical adsorption [20], the adsorption capacity is small, and metal loading can enhance the adsorption performance [21], so the Al$_2$O$_3$ is loaded with Ca$^{2+}$ and Fe$^{3+}$ metals, and the result is shown in Figure 4. As the concentration of metal ions increases, the
amount of arsenic adsorption supported by Al2O3 metal gradually increases. It can be seen from Figure 2 that the arsenic adsorption performance of CaCO3 is stronger than that of Fe2O3, so the adsorption performance of Al2O3 loaded with Ca2+ is better. With the increase of metal ion concentration and Al3+ molar ratio, the arsenic adsorption capacity of Al2O3 gradually increases. When Ca2+:Al3+=0.5 and Fe3+:Al3+=0.4, the Al2O3 metal loading is close to the adsorption saturation, when the molar ratio continues to increase, the arsenic adsorption amount remains basically unchanged.

3.2.2. Arsenic adsorption performance of molecular sieve
Molecular sieve has a better pore structure and specific surface area than Al2O3, so we further study the arsenic adsorption performance of molecular sieve, and selected five molecular sieves: 3A, 4A, 5A, 10X, 13X, and the apertures of the five molecular sieves increased in turn. Figure 5 shows the arsenic adsorption capacity of different molecular sieves. As the pore size increases, the adsorption performance of the molecular sieve first increases and then decreases. This is because as the pore size increases, the pore structure of the molecular sieve becomes better and the specific surface area increases, making it easier to adsorb arsenic. However, when the pore size is much larger than the particle size of As2O3, the adsorption of As2O3 by the molecular sieve tends to be planar, which loses the significance of the molecular sieve porous structure adsorption. Figure 1 shows the adsorption performance of molecular sieve metal loaded arsenic, and its adsorption performance is similar to that of Al2O3 metal loaded. However, it can be seen that the adsorption performance of molecular sieve is much stronger than that of Al2O3, and When Ca2+: Al3+=0.8 and Fe3+: Al3+=0.6, the metal loading of the molecular sieve is close to the adsorption saturation, when the molar ratio continues to increase, the arsenic adsorption capacity is basically unchanged.
4. Conclusion
(1) The arsenic adsorption performance of CaCO₃ is obviously better than that of Fe₂O₃. The best adsorption temperature of CaCO₃ is 900°C, and the best adsorption temperature of Fe₂O₃ is 800°C.
(2) With the increase of ion concentration, the adsorption performance of Al₂O₃ metal loading arsenic gradually increases. When Ca²⁺: Al³⁺=0.5 and Fe³⁺: Al³⁺=0.4, Al₂O₃ metal loading is close to adsorption saturation.
(3) When the molecular sieve is 10X, the adsorption effect is the best. As the ion concentration increases, the metal-loaded arsenic adsorption performance of the molecular sieve gradually increases. When Ca²⁺: Al³⁺=0.8 and Fe³⁺: Al³⁺=0.6, the molecular sieve metal load is close to adsorption saturation.

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