Arsenic removal from water using a novel amorphous adsorbent developed from coal fly ash
Kaihua Zhang, Dongxue Zhang and Kai Zhang

ABSTRACT

A novel effective adsorbent of alumina/silica oxide hydrate (ASOH) for arsenic removal was developed through simple chemical reactions using coal fly ash. The iron-modified ASOH with enhancing adsorption activity was further developed from raw fly ash based on the in situ technique. The adsorbents were characterized by X-ray diffraction, Fourier transform infrared spectrometry, scanning electron micrograph, laser particle size and Brunauer-Emmet-Teller surface area. The results show that the adsorbents are in amorphous and porous structure, the surface areas of which are 8–12 times that of the raw ash. The acidic hydrothermal treatment acts an important role in the formation of the amorphous structure of ASOH rather than zeolite crystal. A series of adsorption experiments for arsenic on them were studied. ASOH can achieve a high removal efficiency for arsenic of 96.4% from water, which is more than 2.5 times that of the raw ash. Iron-modified ASOH can enhance the removal efficiency to reach 99.8% due to the in situ loading of iron (Fe). The condition of synthesis pH = 2–4 is better for iron-modified ASOH to adsorb arsenic from water.

Key words | alumina/silica oxide hydrate, amorphous adsorbent, arsenic, coal fly ash, modification

INTRODUCTION

Arsenic is a highly toxic pollutant affecting millions of people globally. Its threat to human and animal health is aggravated by the long-term persistence in the environment and the strong accumulation in animals and humans via the food chain (Hughes 2002; Sharma & Sohn 2009). In recent years, arsenic pollution in the water system becomes particularly serious, because of increasingly intensive human activities, e.g. agricultural application of pesticides, herbicides and fertilizers, and industrial wastewater discharges from mining, metallurgy, coal-fired power generation, petroleum refining, ceramic industries, electronics, pharmaceuticals and dye manufacturing (Kim et al. 2002; Smedley & Kinniburgh 2002), etc. The removal of arsenic from aqueous solution has become increasingly important. Many treatment methods for arsenic removal have been developed, such as adsorption, chemical coagulation-precipitation, electrodialysis, reverse osmosis, ion exchange, membrane separation and biological treatment (Han et al. 2002; Baciocchi et al. 2005; Fan et al. 2008; Li et al. 2009; Wang et al. 2014). Among them, adsorption technology is regarded as one of the most promising techniques because it is simple to operate, environmentally benign, efficient, and cost-effective (Zhang & Itoh 2005; Fan et al. 2008; Li et al. 2009, 2012). Different adsorbents have been reported to be effective for arsenic removal, including hydrotalcite (Turk et al. 2009), quartz sand (Guo et al. 2007), activated carbon (Chen et al. 2007), and more. Nevertheless, these adsorbents have a high cost, and many of them are difficult to be separated entirely from the treated solution after adsorption because of the fine powders. Developing low-cost materials with high adsorption capability is a great challenge for the future.

Coal fly ash (CFA) is a waste by product of thermal power plants which may cause serious environmental problems. Recently, it has attracted more and more attention because of its lower price as well as unique adsorption activity for removal of both gaseous and water pollutants, such as purification treatments of volatile organic compounds (Zhang et al. 2012; Zhou et al. 2014), SO2 (Srinivasan & Grutzeck 1999) and trace heavy metals from flue gas (Xu et al. 2013; Zhang et al. 2013), reducing contents of heavy metal cations (Hsu et al. 2008; Nascimento et al. 2009; Balsamo et al. 2010), phosphate (Guan et al. 2009) and dye (Atun et al. 2011) from wastewater, etc. However, one of the major weak points of CFA is the relatively
lower specific surface areas (generally not more than 20 m²/g), which make it not comparable to adsorbents that possess a well-developed pore structure, for example, activated carbon (its specific surface areas generally can be as high as 1,000–3,000 m²/g). Another major weak point is the chemically inert surface structure which is unfavorable for adsorption. The two shortcomings have severely restricted its large-scale application as a high-efficiency adsorbent.

In order to overcome the two defects to enhance the adsorption capability of CFA, researchers have actively explored various methods including surfactant modification (Li et al. 2009; Nascimento et al. 2009; Balsamo et al. 2010; Xie et al. 2013; Zhang et al. 2013), heat and acid treatment (Nascimento et al. 2009; Atun et al. 2011) and zeolitization under alkaline hydrothermal conditions (Tanaka et al. 2008; Zhang et al. 2012; Zhou et al. 2014). Li et al. (2009) synthesized an amorphous FeOOH-loaded adsorbent by dissolution and precipitation processes using the high iron-containing fly ash for arsenic removal. Nascimento et al. (2009) reported a synthetic zeolite by hydrothermal method using Brazilian CFA for removal of heavy metal cations from aqueous solutions. Qiu & Zheng (2007) synthesized a cancrinite-type zeolite from fly ash and found it showed a higher adsorption capacity than active carbon, silica gel, etc., then further modified the zeolite by loading with alumina via a wet-impregnation method and found its adsorption capacity was significantly improved.

Nevertheless, to the best of our knowledge, almost all studies were conducted by zeolitization and further modification with iron, alumina and so on to enhance specific surface area and adsorption activity, moreover, the combined use of these two respects was always attained by at least a two-step synthesis, i.e. initially preparing zeolite from CFA and further modifying zeolite with chemical agents, which increased the complexity of the process system as well as the production cost, thus breached the original intention of CFA utilization with low cost. A novel adsorbent of alumina/silica oxide hydrate (ASOH), with amorphous structure and high surface area, was synthesized by simple chemical reactions. Its adsorption characteristic for arsenic from water and the influencing factors were further evaluated.

**EXPERIMENTAL**

**Materials**

The CFA used in this study was sampled from a coal-fired power station located in Shanxi province, China; it was collected by the electrostatic precipitators after the bituminous coal burnt in the circulating fluidized bed boiler. The samples were naturally air dried at room temperature for about 30 days, and then were sieved to obtain particles with a size less than 200 mesh. Typical chemical composition of the ash is listed in Table 1.

Standard solution containing 1,000 ± 4 mg/L of arsenic (V) was purchased from Inorganic Ventures (USA); its starting material is As₂O₅ and H₂O. Working solutions with different arsenic contents (0.1, 0.5, 1.0, 10 and 50 mg/L) were directly prepared by diluting the standard solution with distilled water in volumetric flasks, and were ready for the experiment of arsenic removal. HCl (10 wt.%, 20 wt.%) and NaOH (10 wt.%, 20 wt.%) solutions were prepared for pH adjustment. FeCl₃·6H₂O was obtained from Tianjin Guangfu Fine Chemical Research Institute and in analytical reagent grade.

**Adsorbent synthesis**

**Synthesis of ASOH**

ASOH was prepared according to the following procedure: first, a weight ratio of 1:1 of CFA and NaOH powders were mixed well by grinding for about 10 min in the carnelian mortar, and then treated at 700 °C for 2 h, thus the alkali fusion CFA (AF-CFA) was obtained. Secondly, 10 g of AF-CFA was added to six times the weight of 10 wt.% HCl solution, and the mixture was heated to 80 °C in a water bath for 3 h with stirring and then placed steadily at 70 °C for 6 h. Thirdly, the mixture was dewatered by centrifugation

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**Table 1** | Chemical composition of the CFA used in this study

<table>
<thead>
<tr>
<th>Element as oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>MnO</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (mass, %)</td>
<td>41.65</td>
<td>29.06</td>
<td>8.17</td>
<td>9.50</td>
<td>0.57</td>
<td>1.55</td>
<td>0.33</td>
<td>1.08</td>
<td>1.30</td>
<td>0.08</td>
<td>0.04</td>
</tr>
</tbody>
</table>
and continuously rinsed several times with distilled water until the pH of the leachate remained constant in three consecutive rinses, then dried at 105 °C for 12 h. The composite solid obtained was broken to separate the powders in the carnelian mortar, and afterwards stored in the capped polyethylene bottle for use.

**In situ synthesis of iron-modified alumina/silica oxide hydrate (Fe/ASOH)**

The only difference between synthesis of Fe/ASOH and ASOH is the *in situ* incorporation of iron component at the second stage. The details are described as follows:

10 g of AF-CFA was added to six times the weight of 10 wt.% HCl solution, and 0.74 g of FeCl₃·6H₂O was introduced in it simultaneously. The pH of the obtained mixture was measured to be 2.3. The mixture was heated to 80 °C in a water bath for 3 h with stirring and then placed steadily at 70 °C for 6 h. The color of the solution gradually changed to yellow. The mixture was then dewatered, rinsed, dried and ground, which is the same as the third stage of ASOH synthesis procedure, thus Fe/ASOH was obtained.

By adjusting pH of the mixture of AF-CFA, 10 wt.% HCl and FeCl₃·6H₂O, a series of Fe/ASOH in different pH conditions (pH = 1, 4, 6, 9) was subsequently obtained for investigating the effect of synthesis pH on arsenic removal. During the heating process in the water bath, the color of the mixtures presented different variation trends with the changing pH conditions. At pH = 1, it changed to brick-red gel; at pH = 2.3 (no pH adjustment in synthesis), it changed to yellow; when pH ≥ 4, the supernatant almost turned to colorless. This may be due to the precipitation of Fe³⁺ in solution. With synthesis pH increasing, more Fe ions were precipitated from the solution and the supernatant becomes colorless.

**Analytical methods**

The X-ray diffraction (XRD) patterns of CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3, 4, 9) were obtained using X-ray diffractometer (Rigaku Ultima III, Japan). The operating conditions were 40 kV and 40 mA, using Cu Kα radioactive source. Their functional groups were tested by the technology of Fourier transform infrared spectrometry (FT-IR) (Bruker Vertex 70 V, USA) in the wavenumbers of 4,000–400 cm⁻¹. The surface morphology of CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3) were obtained using scanning electron micrograph (SEM) (Carl Zeiss Supra 55, German). The technology of laser particle size (LPS) was used to analyze the particle size distribution of these samples by the laser particle sizer (Mastersizer 2000, UK). The Brunauer–Emmet–Teller (BET) specific surface area was determined by fitting the linear portion of the BET plot to BET equation, pore size distribution and pore volume were calculated based on the desorption plot of N₂ adsorption–desorption isotherm using the Barrett–Joyner–Halenda method (Micrometritics ASAP 2460, USA).

After the adsorption reaction, the supernatant was sampled and the arsenic concentration was determined by atomic fluorescence spectroscopy (AFS-9800, Beijing Haiguang Instruments Co., Ltd).

**Arsenic sorption experiments**

The adsorption of arsenic on ASOH and Fe/ASOH (pH = 1, 2.3, 4, 6, 9) was studied through batch experiments. In contrast, the adsorption of arsenic on CFA and AF-CFA was also investigated. In order to determine arsenic removal conditions, the contact time and arsenic initial concentration were comprehensively tested. Specifically, a series of 50 mL capped polyethylene bottle were shaken in a shaker at room temperature (nearly 25 °C) and 60 rpm. In each test, 35 mL of arsenic solution was loaded in the bottle and the adsorbent dosage was 5 g/L. Arsenic initial concentrations were in the range of 0.1 to 50 mg/L. During the adsorption process, the test bottles were shaken for a fixed time (from 0.5 to 24 h), and then the suspensions were immediately centrifuged to separate the solid adsorbent from the solution. The supernatant was sampled and then analyzed for the equilibrium arsenic concentration. Arsenic removal was calculated by the difference between the concentrations of arsenic before and after adsorption. Several repeated runs were conducted to ensure the reproducibility of each run. The results indicated that the relative deviation of each run was generally within ±6.0%. All results within this deviation are regarded as unchanged.

**RESULTS AND DISCUSSION**

**Characteristics of the adsorbents**

The XRD patterns of CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3, 4, 9) are shown in Figure 1. The main diffraction peaks of CFA are assigned to quartz (SiO₂) and mullite (3Al₂O₃·2SiO₂). A wide diffraction peak is simultaneously detected at 15° < 2θ < 35°, which reveals great amounts of
amorphous glassy phase exit in CFA. In the XRD pattern of AF-CFA, quartz and mullite peaks disappear almost completely with the wide peak of glassy phase, new peaks of magnetite (Fe₃O₄), lime (CaO), nepheline (NaAlSi₄) and soda feldspar (NaAlSi₃O₈) are prominent. This suggests that during the alkali fusion process using NaOH, the firm crystal structure of quartz and mullite entirely breaks down at high temperature, the glassy phase with a higher degree of polymerization also decomposes, and the new crystal phases such as nepheline and soda feldspar are formed. Compared with AF-CFA, almost none of the diffraction peaks appears in the XRD patterns of ASOH and Fe/ASOH (pH = 2.3, 4, 9); only small amounts of the halite crystal phase are observed in the XRD pattern of Fe/ASOH (pH = 4). This shows that during AF-CFA acidification by hydrochloric acid, the nepheline and soda feldspar crystals react with hydrochloric acid to get a new substance, and the new substance is noncrystalline, while the lime and magnetite are dissolved and leach into the HCl solution. The halite crystals existed in Fe/ASOH (pH = 4) and seem to be an impurity which has been left during the rinse process.

Figure 2 illustrates the FT-IR transmittance spectra of CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3, 4, 9). In the spectra of CFA, the bands at 3,436 and 1,640 cm⁻¹ are assigned to O-H stretching vibration and deformation vibration separately, implying the presence of surface silanol (Si-OH) and physically adsorbed water. These two bands vanish in the spectra of AF-CFA, indicating that the surface hydroxyl group and free water are removed at high temperature due to instability; then they become more prominent in that of ASOH and Fe/ASOH, especially in Fe/ASOH (pH = 9), which shows the Si-OH, perhaps including Fe-OH, is reformed. Bands at 1,090 cm⁻¹ and 785 cm⁻¹ are attributed to the asymmetric and symmetric stretching vibration of Si-O-Si, respectively, and the band at 670 cm⁻¹ could be assigned to Si-O deformation mode (Li et al. 2015; Zhang et al. 2015). These bands faint dramatically in the spectra of AF-CFA, showing the Si-O-Si structure almost entirely collapsed by alkali fusion. The big adsorption at 1,090 cm⁻¹ is observed again in ASOH and Fe/ASOH, implying the Si-O-Si structure is regenerated during acidification; nevertheless, it shows an obvious red shift due to Fe incorporation, and the symmetric vibration at 785 cm⁻¹ disappears, maybe for the same reason. Bands at 670 cm⁻¹ and 580 cm⁻¹ could be ascribed to Al-O and Fe-O stretching vibrations, respectively. The two peaks become more obvious with synthesis pH increasing in the spectra of Fe/ASOH, implying more Al and Fe ions are precipitated from the solution to get an oxygen-bridged structure or hydroxyl compound. Adsorption at 1,460 cm⁻¹ in the spectra of AF-CFA is attributed to the typical band of NaOH.

The morphology changes of CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3, 4) are shown in Figure 3. ASOH and Fe/ASOH (pH = 2.3, 4) exhibit irregular and amorphous shape, the surface gets into a loose porous network structure, and the size of granule also increases sharply, which
is drastically different from the rough crystal formation of the original ash. The uniform distribution of Fe compound and its good adhesion to substrate were observed on the surface of Fe/ASOH (pH = 2.3, 4), which is exactly due to the advantage of in situ synthesis. LPS analysis shows that the mean particle size of CFA, ASOH and Fe/ASOH (pH = 2.3, 4) are 3.78 μm, 13.59 μm, 10.70 μm and 15.623 μm, respectively. The modified products are about 3–4 times as large as CFA, which can efficiently accelerate the separation effect after adsorptive treatment.

The nitrogen adsorption–desorption isotherm of CFA, ASOH and Fe/ASOH (pH = 2.3, 4) is shown in Figure 4. The Type IV adsorption isotherm of ASOH and Fe/ASOH (pH = 2.3, 4) and their hysteresis loop imply the mesoporous structure of material. N2 volume adsorbed has increased remarkably more than CFA, indicating the specific surface area of ASOH and Fe/ASOH goes up greatly. Table 2 further lists their specific surface area and pore structure, ASOH and Fe/ASOH (pH = 2.3, 4) are in porous structure with specific surface areas of 120.05 m²/g, 106.78 m²/g and 162.38 m²/g, respectively, which is 8–12 times that of CFA. They also have a much larger pore volume than that of CFA. The pore size of Fe/ASOH (pH = 2.3, 4) displays a little smaller than that of ASOH possibly because iron occupy bits of pores. All the results show that a large number of new pores are generated after alkali fusion and acidification treatment.

Modification mechanisms

Based on the analysis of XRD, FT-IR and SEM, a possible mechanism for modification of CFA could be proposed as follows: first, CFA undergoes alkali fusion by NaOH at the high temperature of 700 °C, which results in the breakdown of Si-O-Si and Si-O-Al bonds excited in quartz, mullite and glassy phase of CFA, and leads to the formation of aluminosilicate crystals with greater hydration activity. Secondly, aluminosilicate solid crystals react with HCl under hydrothermal and appropriate pH conditions to get a sol-gel system. This is because aluminosilicate radical ions and iron ions precipitate from the solution and generate the primary particles of SiO2·H2O, Al(OH)3 and Fe(OH)3, which can easily gather into small aggregates and reform the loose oxygen-bridged structures including Si-O-Si, Si-O-Al, Si-O-Fe, Si-O-H and so on, thus getting the amorphous ASOH or Fe/ASOH. Most other impurity metals, such as Na, Ca and a part of Fe and Al, can dissolve and leach into the acid solution.

It is particularly noteworthy that the acidic hydrothermal treatment, together with alkali fusion, is probably the most significant reason for generating the amorphous structure of ASOH rather than zeolite, because it can make a major portion of Na ions leach into the solution through a quick acid-base reaction, but not incorporate into the framework of Si-O-Si or Si-O-Al bonds to get zeolite. And to the best of our knowledge, zeolitization from CFA in the previous literature is mostly in alkaline hydrothermal condition (Qiu & Zheng 2007; Tanaka et al. 2008; Guan et al. 2009; Atun et al. 2011; Zhang et al. 2012; Zhou et al. 2014) and the required alkalinity of hydrothermal condition is very high (Zhang et al. 2012; Zhou et al. 2014). So this study successfully developed a novel effective adsorbent of ASOH from CFA in acidic hydrothermal condition, which has not been reported so far.
Adsorption behavior

For comparing the removal of arsenic (V) by CFA, AF-CFA, ASOH and Fe/ASOH (pH = 2.3), test was conducted under the same conditions. As shown in Figure 5, the absorption capacities of CFA, AF-CFA, ASOH and Fe/ASOH are 0.077 g/kg, 0.016 g/kg, 0.193 g/kg and 0.200 g/kg, respectively, achieving removal efficiency of 38.4%, 8.0%, 96.4% and 99.8% separately. The removal capabilities of ASOH and Fe/ASOH are more than 2.5 times that of CFA in this condition, which indicates that ASOH and Fe/ASOH are much more effective than CFA. This phenomenon could mainly attribute to the porous and amorphous structure of ASOH and Fe/ASOH and, hereby, the high surface area, which is 8–12 times that of the raw ash, and thus present much higher removal capabilities for arsenic than CFA at same conditions in wastewater. Previous literature showed that loading of Fe compound on the surface of adsorbents had good affinities and a high removal efficiency for arsenic (Li et al. 2009); the higher removal efficiency of Fe/ASOH than ASOH in this paper affirms this statement. The semi-finished product of AF-CFA has poor absorption capacities, which is not suitable to be used as adsorbent.

Effect of synthesis pH

In order to investigate the effect of synthesis pH on arsenic removal, adsorption experiments by a series of Fe/ASOH synthesized in different pH conditions (pH = 1, 2.3, 4, 6, 9) were carried out. As shown in Figure 6, Fe/ASOH adsorbent
can always achieve more than 80% removal efficiency when synthesis pH ≤ 6. Especially at pH = 2–4, the absorption efficiency reaches the maximum of more than 99%. But the removal capabilities of Fe/ASOH sharply decrease when synthesis pH > 6. This can be ascribed to the strong influence of synthesis pH on the surface charge property or chemical composition of Fe/ASOH. When pH value was adjusted to 2–4, aluminosilicate radical ions and iron ions could maintain in a perfect equilibrium state of precipitation-solution. But when pH is too low, more Fe(OH)3 and Al(OH)3 gel can dissolve into the solution and lead to the reduction of adsorption active sites for arsenic on Fe/ASOH surface. When pH is too high, although Fe can completely precipitate and the active sites for arsenic do not decrease, the too high alkalinity may result in the polarization of the surface chemical bond of Si-O, Al-O and Fe-O, and thus lead to the change of surface charge distribution (Zhou et al. 2014), which would be unfavorable to adsorb the arsenic in wastewater.

**Batch adsorption results and isotherm model**

To obtain the adsorption equilibrium time, kinetic adsorption experiments were conducted, in which the Fe/ASOH (pH = 2.3) dosage was 5 g/L and the initial arsenic concentration was 1 mg/L. The profile of contact time and the arsenic removal is presented in Figure 7(a); the results showed that arsenic removal increased sharply and achieved 90.1% removal efficiency after the first 0.5 h, while it did not attain 99.8% until after 24 h.

Arsenic solutions at different initial concentration from 0.1 to 50 mg/L were treated with 5 g/L of adsorbent, the experiment results are shown in Figure 7(b). The removal efficiency increases initially, which manifests that low arsenic concentration leads to less contact chance between arsenic and the adsorbent; however, it then decreases as arsenic concentration continues rising, which is due to the
unavailability of binding sites for arsenic. When the initial arsenic concentration is in the low range of 0.1–18 mg/L, Fe/ASOH (pH = 2.3) adsorbent can always achieve above 80% removal efficiency, which suggests that Fe/ASOH is an effective adsorbent for treating wastewater with low arsenic concentration.

The Langmuir and Freundlich isotherm models (Li et al. 2019; Nascimento et al. 2009) were used to analyze the arsenic adsorption onto Fe/ASOH adsorbent. Figure 8 presents the Langmuir isotherm plot and constants $q_{\text{max}}$ and k. The correlated coefficient $R^2$ was near 0.90, so it appears that the adsorption behavior basically fits the Langmuir isotherm. The $R^2$ value obtained from the Freundlich isotherm was less than 0.6, indicating that the adsorption does not follow the Freundlich isotherm.

**CONCLUSIONS**

The study successfully develops a novel effective adsorbent of ASOH for arsenic removal from water by using CFA as raw material; the adsorbent is in an amorphous and porous structure with a specific surface area of 120 m²/g, which is over eight times that of the raw ash; it can achieve a high removal efficiency for arsenic of 96.4% from water, which is more than 2.5 times of the raw ash. By in situ loading of Fe, the removal efficiency can be further improved to 99.8%. Compared with synthesis of the crystal structure of zeolite from CFA in literatures, synthesizing amorphous ASOH does not require complicated procedures of Al/Si control, crystallizing and more that are needed for zeolitization. So synthesizing ASOH from CFA can not only successfully achieve a high removal efficiency for arsenic from water, but can also provide a potential application for CFA as a kind of solid waste from power stations, to be reused with a simple process and at low cost.

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**REFERENCES**


