

# Synergistic Adsorption by Biomass-based Fe-Al (Hydr)oxide Nanocomposite of Fluoride and Arsenic

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**Abstract:** Fe-Al (hydr)oxide nano-/micro-particles were well grown and dispersed on a wheat straw template, which was characterized by a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and a vibrating sample magnetometer (VSM). The adsorption mechanism of the biomass-based Fe-Al (hydr)oxide nanocomposite was studied by the adsorption isotherms, which followed the Langmuir model better than the Freundlich and Temkin models. In particular, a synergistic adsorption by the mixed Fe-Al (hydr)oxide nano-/micro-particles based on the wheat straw was found, with higher maximum adsorption capacity ( $Q_0$ ) than that of the material containing only  $\text{Fe}_3\text{O}_4$  or  $\text{Al}(\text{OH})_3$  nano-/micro-particles, which was most obvious when the mole ratio of Fe to Al was 1:1. The degree of this unusual effect was reasonably determined by the departure between the experimental and calculated maximum adsorption capacity ( $Q_0 - Q_0(\text{cal})$ ), which showed that the synergistic effect was most pronounced when the mole ratio of Fe to Al was approximately 1:1. The good adsorption capacity of the mixed Fe-Al (hydr)oxide nano-/micro-particles and the good dispersity by the wheat straw matrix were combined in the biomass-based Fe-Al (hydr)oxide nanocomposite. The nanocomposite material showed high adsorption capacity for both fluoride ( $\text{F}^-$ ) and arsenic ( $\text{As}(\text{III})$  and  $\text{As}(\text{V})$ ), and had the advantage of magnetic separation by tuning its compositions.

**Keywords:** adsorption; synergistic effect; nanocomposite; biomass; fluoride; arsenic

## 1 Introduction

Anion pollution in water is a worldwide problem harming human health and natural

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ecosystems<sup>[1-6]</sup>. Fluoride is a necessary element for humans; however, the excessive ingestion of fluoride may cause many chronic diseases<sup>[7-8]</sup>. Arsenic, which mainly exists as arsenite and arsenate in nature, can seriously damage human systems and increase cancer risk<sup>[9]</sup>. In many areas, water resources continuously deteriorate and are possibly contaminated by both fluoride and arsenic<sup>[10]</sup>. Therefore, the removal of these harmful anions from water is critical.

Many techniques have been developed for the purification of water, such as precipitation<sup>[11]</sup>, filtration<sup>[12-13]</sup>, membrane separation<sup>[14-15]</sup>, coagulation<sup>[16-17]</sup>, ion exchange<sup>[18-19]</sup>, oxidation<sup>[20-21]</sup>, electrolysis<sup>[22-23]</sup>, and adsorption<sup>[24-26]</sup>. Among them, adsorption is one of the most important methods because of its wide applicability, easy operation, high efficiency, and low cost. Nanoparticles have attracted significant interest for the adsorption and removal of pollutants from water owing to their high efficiency based on large surface areas. Many nanoparticle adsorbents composed of alumina<sup>[27]</sup>, iron oxide<sup>[28]</sup>, magnesium oxide<sup>[29]</sup>, titanium oxide<sup>[30]</sup>, and zinc oxide<sup>[31]</sup> have been applied to water treatment. A general problem of nanoparticle adsorbents is their aggregation, which leads to the decrease in the number of active sites<sup>[6]</sup>. In addition, the residue of nanoparticles in water could cause a secondary pollution.

To avoid the aggregation of nanoparticles, template materials to disperse them, including graphene oxide<sup>[32]</sup>, microspheres<sup>[33-36]</sup>, carbon<sup>[37-39]</sup>, layered double hydroxides<sup>[40]</sup>, and cellulose<sup>[41-42]</sup>, have been extensively studied. Wheat straw is an eco-friendly and low-cost biomass-based material available in large amounts, which is mainly composed of cellulose, hemicelluloses, and lignin with numerous hydroxyl groups. Metal ions could be adsorbed by the hydroxyl groups on the surface of wheat straw and grown to nano-/micro-particles<sup>[43]</sup>. With a vascular bundle structure and hydroxyl groups on its surface<sup>[44-45]</sup>, wheat straw could be a suitable matrix to disperse nanoparticles. A previous study showed that the aggregation of magnetic nano-/micro-particles can be efficiently avoided by

growing and dispersing them onto wheat straw, and the material can be used for adsorption and easily separated from water<sup>[43]</sup>.

In this study, Fe-Al (hydr)oxide nano-/micro-particles were simultaneously grown onto wheat straw through a co-precipitation method. A synergistic adsorption by the mixed Fe-Al (hydr)oxide nano-/micro-particles dispersed onto wheat straw was unexpectedly found with the enhancement of adsorption capacity. The synergistic effect was determined by the departure between the experimental and calculated maximum adsorption capacity fitted from Langmuir adsorption isotherms. The synergistic effect for the adsorption was most pronounced when the Fe and Al mole ratio was approximately 1:1. This material could be used for the removal of fluoride and arsenic and be separated from water under a magnetic field.

## 2 Experimental

### 2.1 Materials

Wheat straw was obtained from the countryside of China. After being cleaned and dried, the wheat straw was mechanically ground into fragments by a miniature plant grinding machine (FZ102, Tianjin City Taisite Instrument Co., Ltd). The specific surface area of the wheat straw fragments is 1.91 m<sup>2</sup>/g. Ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), and ammonia water (NH<sub>3</sub>·H<sub>2</sub>O, 25 wt%) were used for the synthesis of Fe-Al (hydr)oxide nano-/micro-particles. Sodium fluoride (NaF), sodium arsenite (NaAsO<sub>2</sub>), and disodium hydrogen arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) were used for the test solutions. All the chemicals were purchased from Beijing Chemical Works (Beijing, China) with an analytical grade and used without further purification.

### 2.2 Synthesis of biomass-based Fe-Al (hydr)oxide nanocomposite

The biomass-based Fe-Al (hydr)oxide nanocomposite was synthesized through a co-precipitation method. Approximately 0.8 g of wheat straw fragments were

suspended in a 50-mL solution with  $\text{FeCl}_3$ ,  $\text{FeSO}_4$  (the mole ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is 2:1), and  $\text{Al}(\text{NO}_3)_3$ . The total ion concentration of the solution was 0.5 mol/L, with mole ratios of total Fe to Al set as 4:1, 3:2, 1:1, 2:3, and 1:4. Under nitrogen atmosphere, 10 mL of ammonia water (25 wt%) was added dropwise into the solution with vigorous stirring at 70°C for 4 h. The synthesized materials were separated and washed by deionized water several times, and then dried for use. Wheat straw-based nanocomposite loaded only with  $\text{Fe}_3\text{O}_4$  or  $\text{Al}(\text{OH})_3$  was also synthesized for comparison (the products named as  $\text{Fe}_3\text{O}_4$  nanocomposite and  $\text{Al}(\text{OH})_3$  nanocomposite, respectively).

### 2.3 Characterization of biomass-based Fe-Al (hydr)-oxide nanocomposite

The specific surface area of the wheat straw fragments was measured through nitrogen adsorption by the BET method using an automated gas sorption analyzer (Quadrastorb SI-MP). The morphologies of the synthesized biomass-based Fe-Al (hydr)oxide nanocomposites were observed by a scanning electron microscope (SEM) (S-4800, Hitachi) equipped with energy-dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) was studied by using a D8 Focus (Bruker) for crystal characterization. The magnetic properties were characterized using a vibrating sample magnetometer (SQUID-VSM, Quantum Design).

### 2.4 Adsorption experiments

Adsorption experiments were conducted in an aqueous solution with different initial concentrations of ions under stirring at room temperature for 24 h. The adsorbent dose was 1 g/L for all the experiments. The concentrations of fluoride ion were measured by a fluoride analyzer (PXSJ-216, INESA). Arsenic was quantified by an inductive coupled plasma

emission spectrometer (ICP) (710-OES, Varian). The adsorption capacity  $q_e$  (mg/g) was calculated from the following equation (Eq.(1)):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where  $C_0$  (mg/L) and  $C_e$  (mg/L) represent the initial and equilibrium concentration of adsorbate in the solution, respectively.  $V$  (L) is the solution volume, and  $m$  (g) is the adsorbent mass.

## 3 Results and discussion

### 3.1 Characterization of the nanocomposite material

The surface morphologies of wheat straw fragments and the nano-/micro-particle-loaded nanocomposites were studied by SEM, as shown in Fig.1. The surface of the original wheat straw fragments is very smooth (Fig.1(a)). Growth of Fe-Al (hydr)oxides ( $n(\text{Fe}):n(\text{Al})=1:1$ ) results in the flocculent deposition of well dispersed nano-/micro-particles as shown in Fig.1(b), indicating the suitability of wheat straw as a template. Fig.1(c) and Fig.1(d) show that  $\text{Fe}_3\text{O}_4$  nanoparticles are well dispersed by the wheat straw, while the  $\text{Al}(\text{OH})_3$  particles have almost grown to micrometer size and are coarsely distributed.

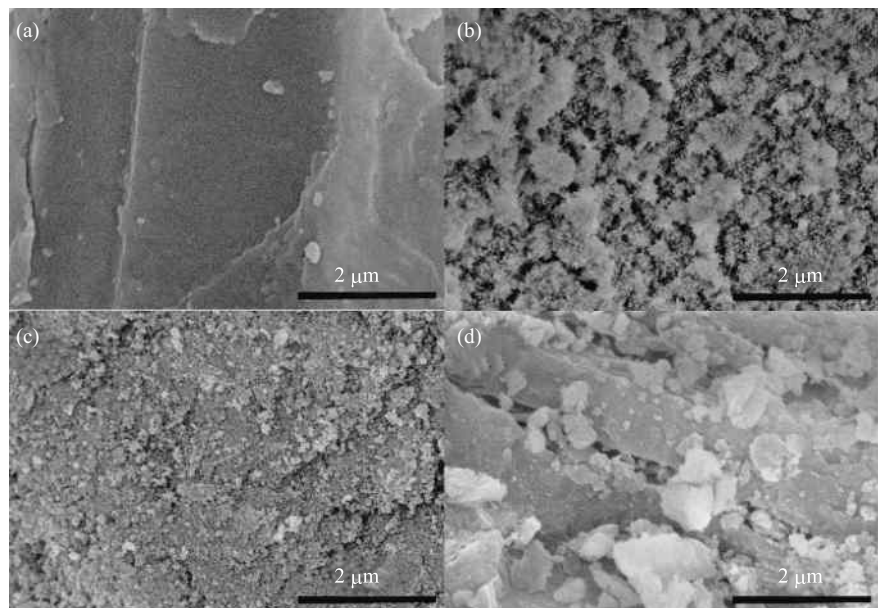


Fig.1 SEM images of (a) original wheat straw fragments, (b) Fe-Al (hydr)-oxide nanocomposite ( $n(\text{Fe}):n(\text{Al})=1:1$ ), (c)  $\text{Fe}_3\text{O}_4$  nanocomposite and (d)  $\text{Al}(\text{OH})_3$  nanocomposite

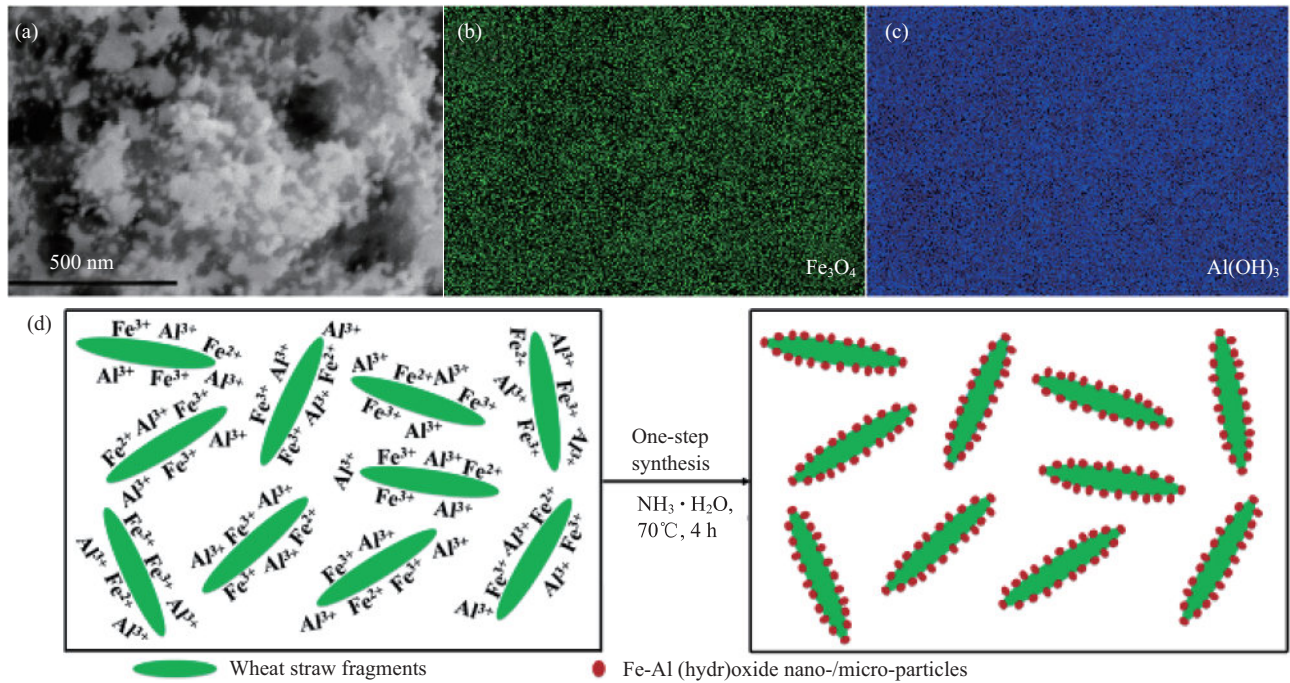


Fig.2 (a) High-magnification SEM image of Fe-Al (hydr)oxide nanocomposite ( $n(\text{Fe}):n(\text{Al})=1:1$ ), and the same area for EDS elemental maps of (b)  $\text{Fe}_3\text{O}_4$  and (c)  $\text{Al}(\text{OH})_3$ . (d) Schematic representation of Fe-Al (hydr)oxide nano-/micro-particles co-precipitating and growing onto wheat straw matrix

As shown in Fig.2(a)~Fig.2(c), the mixed Fe-Al (hydr)oxide nano-/micro-particles ( $n(\text{Fe}):n(\text{Al})=1:1$ ) could well grow to coral-like floccules, and both  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  compositions are uniformly distributed on the surface of the wheat straw matrix investigated by EDS elemental mapping. The co-precipitation formation process of Fe-Al (hydr)oxides onto wheat straw is likely to be effective in avoiding the aggregation of particles, as shown in Fig.2(d).

The XRD patterns of wheat straw fragments, Fe-Al (hydr)oxide nanocomposite ( $n(\text{Fe}):n(\text{Al})=1:1$ ),  $\text{Fe}_3\text{O}_4$  nanocomposite, and  $\text{Al}(\text{OH})_3$  nanocomposite are shown in Fig.3. The diffraction peaks at  $2\theta=16.2^\circ$  and  $22.2^\circ$  are those of native cellulose I (Fig.3(a))<sup>[44]</sup>. Loading with Fe-Al (hydr)oxide nano-/micro-particles causes the appearance of many other diffraction peaks (Fig.3(b)), nearly hiding the cellulose peaks. That is because the full growth of Fe-Al (hydr)oxides coats the surface of the wheat straw. In Fig.3(c) and Fig.3(d), the characteristic diffraction peaks of  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  are found. The  $\text{Fe}_3\text{O}_4$  diffraction peaks are at  $2\theta=30.4^\circ$ ,  $35.6^\circ$ ,  $43.3^\circ$ ,  $57.1^\circ$ ,  $62.8^\circ$ <sup>[46]</sup> and the typical  $\text{Al}(\text{OH})_3$

characteristic diffraction peaks are at  $2\theta=13.8^\circ$ ,  $28.5^\circ$ ,  $38.4^\circ$ ,  $49.1^\circ$ <sup>[47]</sup>. The diffraction peak at  $2\theta=22.2^\circ$  of cellulose is relatively more obvious in  $\text{Al}(\text{OH})_3$  nanocomposite, which is possibly due to the incomplete surface coverage by  $\text{Al}(\text{OH})_3$ . Fig.3(b) shows that in the Fe-Al (hydr)oxide nanocomposite, some of the  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  characteristic diffraction peaks appeared at the same time ( $2\theta=13.8^\circ$ ,  $28.5^\circ$  from  $\text{Al}(\text{OH})_3$  and  $2\theta=35.6^\circ$ ,  $57.1^\circ$ ,  $62.8^\circ$  from  $\text{Fe}_3\text{O}_4$ ). The Fe-Al (hydr)-oxide nano-/micro-particles are completely mixed and

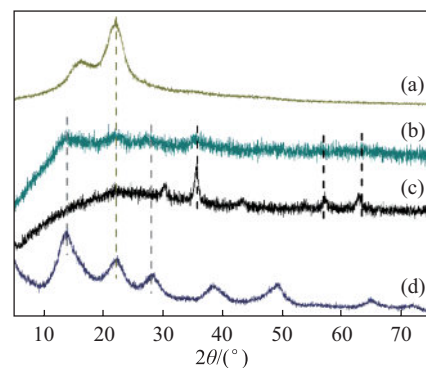
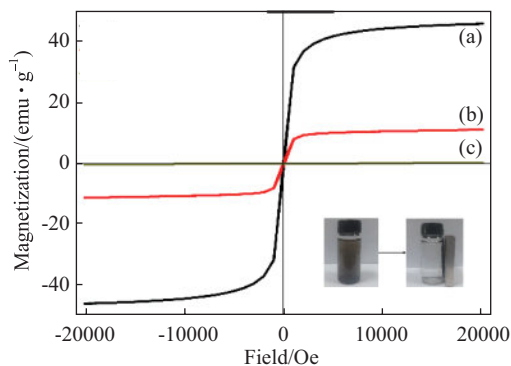


Fig.3 XRD patterns of (a) wheat straw fragments, (b) Fe-Al (hydr)oxide nanocomposite ( $n(\text{Fe}):n(\text{Al})=1:1$ ), (c)  $\text{Fe}_3\text{O}_4$  nanocomposite, and (d)  $\text{Al}(\text{OH})_3$  nanocomposite

grown with each other and well dispersed by the wheat straw template, making a close relative intensity in all the characteristic peaks.

The magnetic hysteresis loops of  $\text{Fe}_3\text{O}_4$  nanocomposite and Fe-Al (hydr)oxide nanocomposites with Fe to Al mole ratios of 4:1 and 1:4 are shown in Fig.4.  $\text{Fe}_3\text{O}_4$  nanocomposite shows a typical superparamagnetic behavior<sup>[48]</sup> with the saturated magnetization of 46.13 emu/g, as shown in Fig.4(a). With the mixing of  $\text{Al}(\text{OH})_3$  particles, the Fe-Al (hydr)-oxide nanocomposite can maintain a certain magnetism when the mole ratio of Fe to Al is 4:1, with the saturated magnetization of 11.24 emu/g as shown in Fig.4(b). When the Al composition is much higher, with an Fe to Al mole ratio of 1:4, the magnetism decreases, with a saturated magnetization of 0.23 emu/g as shown in Fig.4(c). The magnetism of the Fe-Al (hydr)-oxide nanocomposite could be tuned by using different magnetic compositions of  $\text{Fe}_3\text{O}_4$ , and the nanocomposite material could be possibly separated under an external magnetic field as shown in the inset of Fig.4.



\* The inset shows the dispersion and magnetic separation of the nanocomposite material ( $n(\text{Fe}):n(\text{Al})=4:1$ ) in water.

Fig.4 Magnetic hysteresis loops of (a)  $\text{Fe}_3\text{O}_4$  nanocomposite and Fe-Al (hydr)oxide nanocomposite with Fe to Al mole ratios of (b) 4:1 and (c) 1:4 at 298 K

### 3.2 Fluoride adsorption behavior of the nanocomposite material

As shown in Fig.5, the adsorption capacity ( $q_e$ ) increases with the initial fluoride anion concentration ( $C_0$ ) in all Fe-Al (hydr)oxide nanocomposites with different mole ratios of Fe to Al. The  $\text{Fe}_3\text{O}_4$  nanocomposite has no effect on  $\text{F}^-$  adsorption, while

the Fe-Al (hydr)oxide nanocomposite with an Fe to Al mole ratio of 4:1 has an obvious adsorption capacity of the fluoride anion, indicating that growing the mixed Fe-Al (hydr)oxides onto wheat straw with only a small amount of Al composition can add the advantage of fluoride adsorption.

The fluoride adsorption capacity  $q_e$  increases as the Fe to Al mole ratio changes from 4:1 to 1:1, which is reasonably due to the good  $\text{F}^-$  adsorption capacity of  $\text{Al}(\text{OH})_3$ . With further increase of Al composition in Fe-Al (hydr)oxides (Fe to Al mole ratio changes from 1:1 to 1:4), the adsorption capacity  $q_e$  of fluoride anion decreases, which is possibly due to the aggregation of the particles and the decrease of dispersing and loading effects through the wheat straw. As shown in Fig.5, it seems that the adsorption capacity of  $\text{F}^-$  is most obvious when the mole ratio of Fe to Al is approximately 1:1 in the Fe-Al (hydr)oxide nanocomposite, and it is even higher than that of  $\text{Al}(\text{OH})_3$  nanocomposite.

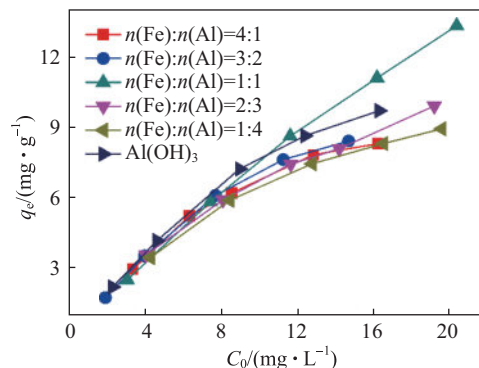


Fig.5 Effect of initial fluoride anion concentration and mole ratio of Fe to Al in Fe-Al (hydr)oxide nanocomposite on adsorption capacity  $q_e$  of fluoride anion

To understand the adsorption mechanism of the Fe-Al (hydr)oxide nanocomposite, we study the adsorption isotherms. In this study, the equilibrium condition was kept at room temperature. There are three main models of adsorption isotherms, which are the Langmuir model (monolayer adsorption, adsorption energy on the surface is uniform) expressed as Eq.(2), Freundlich model (multilayer adsorption, adsorption energy decreases with surface coverage) expressed as Eq.(3), and Temkin model (multilayer adsorption, the decrease of adsorption energy with surface coverage is linear

rather than logarithmic) expressed as Eq.(4).

$$\frac{C_e}{Q_0} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (2)$$

In Eq.(2),  $C_e$  (mg/L) is the equilibrium concentration and  $q_e$  (mg/g) is the adsorption capacity.  $Q_0$  (mg/g) and  $b$  (L/mg) are the maximum adsorption capacity and adsorption energy related to Langmuir constants, respectively.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

In Eq.(3),  $K_f$  (mg/g) and  $n$  are the adsorption capacity and adsorption intensity of Freundlich constants, respectively.

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (4)$$

In Eq.(4),  $R$  is the gas constant 8.314 J/(mol • K) and  $T$  is the absolute temperature 298.15 K.  $A_T$  (L/mg) and  $b_T$  (J/mol) are the constants of the Temkin model.

The adsorption isotherms are studied by the three models, and all the fitted parameters are listed in Table 1. The fitted adsorption isotherms follow the Langmuir model better than the other two models, with a higher value of fitting correlation coefficient  $r^2$ . It indicates that the process performed by nanocomposite material is much more like a monolayer adsorption. As shown in Fig.6, the adsorption isotherms of the Fe-Al (hydr)-oxide nanocomposite with different Fe to Al mole ratios for  $F^-$  adsorption are well fitted by the Langmuir model.

The constant  $Q_0$  of the Langmuir model represents the maximum adsorption capacity of the adsorbent. As presented in Fig.7 and Table 1, with the increase of Al composition, the value of  $Q_0$  increases first and reaches a maximum when the mole ratio of Fe to Al is approximately 1:1, and then decreases with further increase of Al composition. Generally, it is expected that the adsorption capacity of binary matrix composites would be between the two neat compositions. For Fe-Al (hydr)oxide nanocomposite, because  $Fe_3O_4$  has no adsorption effect on fluoride anion, it is expected that with the increase of Fe composition in Fe-Al (hydr)-oxides, the value of  $Q_0$  would monotonically decrease. However, the results indicate that the adsorption

Table 1 Langmuir, Freundlich and Temkin parameters of Fe-Al (hydr)oxide nanocomposite with different Fe to Al mole ratios for  $F^-$  adsorption

| Nanocomposite     | Langmuir parameters     |                           |         |
|-------------------|-------------------------|---------------------------|---------|
|                   | $Q_0/(mg \cdot g^{-1})$ | $b/(L \cdot mg^{-1})$     | $r^2$   |
| $n(Fe):n(Al)=4:1$ | 9.21                    | 1.11                      | 0.99764 |
| $n(Fe):n(Al)=3:2$ | 9.35                    | 1.33                      | 0.99879 |
| $n(Fe):n(Al)=1:1$ | 20.62                   | 0.25                      | 0.99284 |
| $n(Fe):n(Al)=2:3$ | 11.01                   | 0.62                      | 0.96321 |
| $n(Fe):n(Al)=1:4$ | 10.27                   | 0.56                      | 0.99656 |
| $Al(OH)_3$        | 10.36                   | 1.73                      | 0.99297 |
| Nanocomposite     | Freundlich parameters   |                           |         |
|                   | $K_f/(mg \cdot g^{-1})$ | $n$                       | $r^2$   |
| $n(Fe):n(Al)=4:1$ | 4.51                    | 2.99                      | 0.93701 |
| $n(Fe):n(Al)=3:2$ | 4.40                    | 2.37                      | 0.94586 |
| $n(Fe):n(Al)=1:1$ | 3.97                    | 1.54                      | 0.98535 |
| $n(Fe):n(Al)=2:3$ | 4.58                    | 2.99                      | 0.99553 |
| $n(Fe):n(Al)=1:4$ | 3.92                    | 2.74                      | 0.97863 |
| $Al(OH)_3$        | 5.44                    | 2.87                      | 0.98520 |
| Nanocomposite     | Temkin parameters       |                           |         |
|                   | $A_T/(L \cdot mg^{-1})$ | $b_T/(kJ \cdot mol^{-1})$ | $r^2$   |
| $n(Fe):n(Al)=4:1$ | 15.28                   | 1401.96                   | 0.98820 |
| $n(Fe):n(Al)=3:2$ | 16.42                   | 1345.47                   | 0.99824 |
| $n(Fe):n(Al)=1:1$ | 2.95                    | 594.49                    | 0.97518 |
| $n(Fe):n(Al)=2:3$ | 10.90                   | 1236.83                   | 0.94895 |
| $n(Fe):n(Al)=1:4$ | 6.48                    | 1177.91                   | 0.99975 |
| $Al(OH)_3$        | 33.98                   | 1401.70                   | 0.98247 |

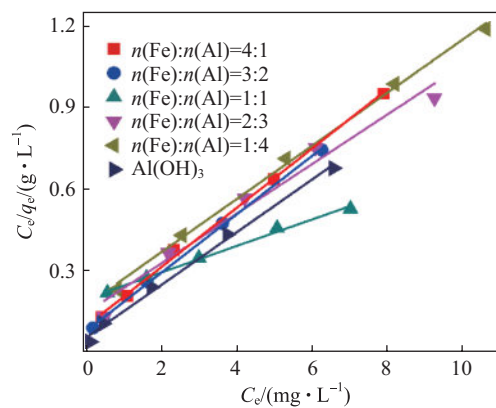


Fig.6 Adsorption isotherms of Fe-Al (hydr)oxide nanocomposite with different Fe to Al mole ratios for  $F^-$  adsorption fitted by Langmuir model

capacity is unexpectedly higher with the intermediate Fe to Al mole ratios. In particular, the value of  $Q_0$  is obviously higher when the mole ratio of Fe to Al is 1:1, as shown in Fig.7. Such a synergistic adsorption of  $F^-$  is found with the mixed Fe-Al (hydr)oxide

nanocomposite, which has a higher value of  $Q_0$  than both  $\text{Fe}_3\text{O}_4$  nanocomposite and  $\text{Al}(\text{OH})_3$  nanocomposite. This could lead to the enhancement of adsorption capacity particularly when the Fe to Al mole ratio is 1:1.

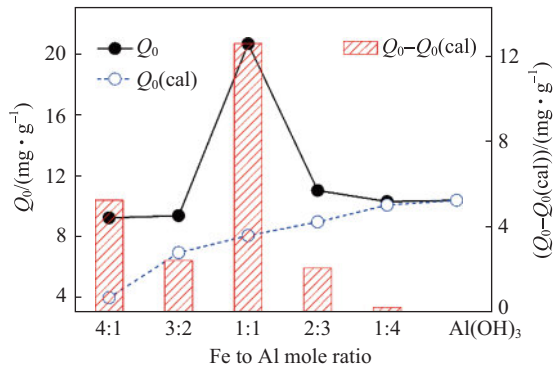


Fig.7 Maximum adsorption capacity  $Q_0$  from the Langmuir model of Fe-Al (hydr)oxide nanocomposites with different Fe to Al mole ratios for experimental  $\text{F}^-$  adsorption.  $Q_0(\text{cal})$  is calculated from the adsorption of  $\text{Al}(\text{OH})_3$  nanocomposite and the mole number of  $\text{Al}(\text{OH})_3$  in different samples. The histogram shows the departure between experimental and calculated maximum adsorption capacity ( $Q_0 - Q_0(\text{cal})$ )

To further determine the degree of the synergistic effect, we investigate the departure between the experimental and calculated values of ( $Q_0 - Q_0(\text{cal})$ ). In Fe-Al (hydr)oxide nanocomposite, the adsorption mechanism is monolayer adsorption and  $\text{Al}(\text{OH})_3$  is the only effective composition for  $\text{F}^-$  adsorption. If the number of active sites for adsorption is proportional to the number of adsorbent molecules, under the same adsorption condition, the value of ( $C_0 - C_e$ ) could be proportional to the mole number of the adsorbent. From this ideal condition, we can calculate  $C_e$  and  $q_e$  from the adsorption results of  $\text{Al}(\text{OH})_3$  nanocomposite and the mole number of  $\text{Al}(\text{OH})_3$  in different samples. Then, we can obtain  $Q_0(\text{cal})$  from the fitting of the Langmuir model, and the value of  $Q_0(\text{cal})$  monotonically decreases with the decrease of Al composition in the material, as shown in Fig.7.

The value of ( $Q_0 - Q_0(\text{cal})$ ) could reflect the difference between the maximum adsorption capacity in the experimental condition and that in the ideal calculation condition without considering other special effects. In Fig.7, the values of  $Q_0$  are higher than the

corresponding  $Q_0(\text{cal})$  across all the materials with different Fe to Al mole ratios, which clearly indicates that there is a synergistic effect for  $\text{F}^-$  adsorption by the Fe-Al (hydr) oxide nanocomposite. Moreover, the departure of ( $Q_0 - Q_0(\text{cal})$ ) reaches a maximum near a 1:1 mole ratio of Fe to Al. Therefore, it is concluded that the maximum adsorption capacity of the nanocomposite material is enhanced by the synergistic effect with the different Fe to Al mole ratios, and with an approximately 1:1 mole ratio of Fe to Al, the degree of this unusual effect is most significant, which is possibly due to the good adsorption of fluoride by the mixed nano-/micro-particles well dispersed through the wheat straw.

### 3.3 Arsenic adsorption behavior of the nanocomposite material

The effect of the initial concentration and mole ratio of Fe to Al in Fe-Al (hydr)oxide nanocomposite on the adsorption capacity  $q_e$  of arsenic ( $\text{As}(\text{III})$  and  $\text{As}(\text{V})$ ) is shown in Fig.8. Both  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  nano-/micro-particles in Fe-Al (hydr)oxide nanocomposites have adsorption effect on arsenic. With different Fe to Al mole ratios of the Fe-Al (hydr)oxide nanocomposite, generally the adsorption capacity  $q_e$  of both  $\text{As}(\text{III})$  and  $\text{As}(\text{V})$  increases from  $\text{Fe}_3\text{O}_4$  nanocomposite and  $\text{Al}(\text{OH})_3$  nanocomposite to the materials with mixed Fe and Al compositions. Then, the adsorption capacity further increases when the Fe and Al mole ratio is close to 1:1, as shown in Fig.8(a) and Fig.8(b). From the adsorption of both  $\text{As}(\text{III})$  and  $\text{As}(\text{V})$ , it is found that in many cases the adsorption capacity of the materials with the mixed Fe-Al (hydr)oxides is higher than that with either  $\text{Al}(\text{OH})_3$  nanocomposite or  $\text{Fe}_3\text{O}_4$  nanocomposite.

The adsorption isotherms for  $\text{As}(\text{III})$  and  $\text{As}(\text{V})$  are fitted by the Langmuir model, Freundlich model, and Temkin model using Eq.(2), Eq.(3), and Eq.(4), and the obtained parameters are listed in Table 2 and Table 3. The results show that both  $\text{As}(\text{III})$  and  $\text{As}(\text{V})$  adsorption isotherms are well fitted by the Langmuir model with a higher fitting correlation coefficient ( $r^2$ )

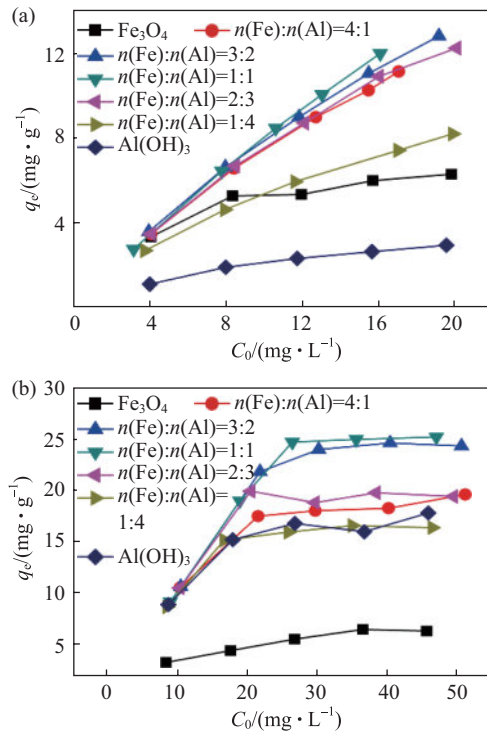


Fig.8 Adsorption capacity  $q_e$  of Fe-Al (hydr)oxide nanocomposites for (a) As(III) and (b) As(V) with different initial concentrations and Fe to Al mole ratios

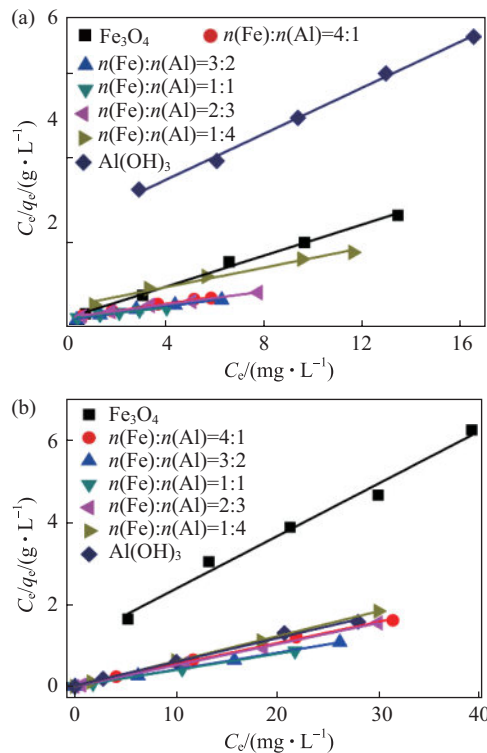


Fig.9 Adsorption isotherms by the fitting of the Langmuir model for (a) As(III) and (b) As(V) adsorption through Fe-Al (hydr)oxide nanocomposites with different Fe to Al mole ratios

Table 2 Langmuir, Freundlich and Temkin parameters of Fe-Al (hydr)oxide nanocomposite with different Fe to Al mole ratios for As(III) adsorption

| Nanocomposite                   | Langmuir parameters                   |                                         |         |
|---------------------------------|---------------------------------------|-----------------------------------------|---------|
|                                 | $Q_0/(\text{mg} \cdot \text{g}^{-1})$ | $b/(\text{L} \cdot \text{mg}^{-1})$     | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 6.61                                  | 1.07                                    | 0.99308 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 14.80                                 | 0.46                                    | 0.98858 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 15.66                                 | 0.60                                    | 0.97381 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 19.11                                 | 0.40                                    | 0.98831 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 15.88                                 | 0.42                                    | 0.99033 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 10.54                                 | 0.26                                    | 0.97810 |
| $\text{Al}(\text{OH})_3$        | 4.46                                  | 0.12                                    | 0.99600 |
| Nanocomposite                   | Freundlich parameters                 |                                         |         |
|                                 | $K_f/(\text{mg} \cdot \text{g}^{-1})$ | $n$                                     | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 3.74                                  | 4.75                                    | 0.91389 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 4.61                                  | 1.98                                    | 0.99332 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 5.67                                  | 2.21                                    | 0.99851 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 5.11                                  | 1.56                                    | 0.99357 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 4.71                                  | 2.01                                    | 0.98493 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 2.64                                  | 2.16                                    | 0.99941 |
| $\text{Al}(\text{OH})_3$        | 0.64                                  | 1.79                                    | 0.97191 |
| Nanocomposite                   | Temkin parameters                     |                                         |         |
|                                 | $A_T/(\text{L} \cdot \text{mg}^{-1})$ | $b_T/(\text{kJ} \cdot \text{mol}^{-1})$ | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 48.74                                 | 2545.96                                 | 0.93528 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 4.44                                  | 750.68                                  | 0.98739 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 7.00                                  | 768.62                                  | 0.96756 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 4.54                                  | 632.77                                  | 0.97335 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 4.22                                  | 715.23                                  | 0.98550 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 2.73                                  | 1089.29                                 | 0.97231 |
| $\text{Al}(\text{OH})_3$        | 0.99                                  | 2366.60                                 | 0.99887 |

than that of the other models, as shown in Fig.9(a) and Fig.9(b). This indicates that the adsorption process prefers the monolayer adsorption by Fe-Al (hydr)oxide nanocomposite.

The maximum adsorption capacity  $Q_0$  from the fitting of the Langmuir model for arsenic (As(III) and As(V)) adsorption is shown in Fig.10. Regarding the effective compositions of  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  for arsenic adsorption,  $\text{Fe}_3\text{O}_4$  nanocomposite has a relatively higher value of  $Q_0$  for As(III), while  $\text{Al}(\text{OH})_3$  nanocomposite has a higher value of  $Q_0$  for As(V). The value of the maximum adsorption capacity ( $Q_0$ ) for both As(III) and As(V) increases first and reaches a maximum when the Fe to Al mole ratio is 1:1, and then decreases with a further increase of Al composition,

Table 3 Langmuir, Freundlich and Temkin parameters of Fe-Al (hydr)oxide nanocomposite with different Fe to Al mole ratios for As(V) adsorption

| Nanocomposite                   | Langmuir parameters                   |                                     |         |
|---------------------------------|---------------------------------------|-------------------------------------|---------|
|                                 | $Q_0/(\text{mg} \cdot \text{g}^{-1})$ | $b/(\text{L} \cdot \text{mg}^{-1})$ | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 7.81                                  | 0.12                                | 0.98055 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 19.39                                 | 1.95                                | 0.99642 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 24.35                                 | 32.59                               | 0.99990 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 25.17                                 | 19.19                               | 0.99998 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 19.44                                 | 17.44                               | 0.99953 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 16.43                                 | 8.43                                | 0.99976 |
| $\text{Al}(\text{OH})_3$        | 17.34                                 | 2.52                                | 0.99211 |

| Nanocomposite                   | Freundlich parameters                 |       |         |
|---------------------------------|---------------------------------------|-------|---------|
|                                 | $K_f/(\text{mg} \cdot \text{g}^{-1})$ | $n$   | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 1.77                                  | 2.76  | 0.96351 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 14.52                                 | 11.50 | 0.97082 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 19.18                                 | 10.37 | 0.52211 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 19.21                                 | 8.01  | 0.58496 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 15.78                                 | 12.15 | 0.59531 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 12.58                                 | 10.24 | 0.88588 |
| $\text{Al}(\text{OH})_3$        | 12.72                                 | 9.91  | 0.94152 |

| Nanocomposite                   | Temkin parameters                     |                                         |         |
|---------------------------------|---------------------------------------|-----------------------------------------|---------|
|                                 | $A_T/(\text{L} \cdot \text{mg}^{-1})$ | $b_T/(\text{kJ} \cdot \text{mol}^{-1})$ | $r^2$   |
| $\text{Fe}_3\text{O}_4$         | 1.20                                  | 1471.12                                 | 0.94449 |
| $n(\text{Fe}):n(\text{Al})=4:1$ | 189749.27                             | 2003.46                                 | 0.97606 |
| $n(\text{Fe}):n(\text{Al})=3:2$ | 220430.60                             | 1508.88                                 | 0.58787 |
| $n(\text{Fe}):n(\text{Al})=1:1$ | 17787.35                              | 1183.90                                 | 0.69599 |
| $n(\text{Fe}):n(\text{Al})=2:3$ | 1048115.81                            | 2092.11                                 | 0.57644 |
| $n(\text{Fe}):n(\text{Al})=1:4$ | 64720.41                              | 2094.80                                 | 0.91063 |
| $\text{Al}(\text{OH})_3$        | 37646.49                              | 1967.47                                 | 0.94245 |

as shown in Fig.10(a) and Fig.10(b) (listed in Table 2 and Table 3). Most values of  $Q_0$  for the materials with intermediate Fe to Al mole ratios of Fe-Al (hydr)oxides are unexpectedly higher than that for the material only loaded with  $\text{Fe}_3\text{O}_4$  or  $\text{Al}(\text{OH})_3$ . Once again, the synergistic adsorption is clearly found from the adsorption of both As(III) and As(V), with an obvious enhancement of adsorption capacity. This unusual behavior is most obvious with an Fe to Al mole ratio of 1:1, which results in a higher value of  $Q_0$  than that of all other nanocomposites.

To further study this synergistic effect for arsenic adsorption, we calculate the value of  $Q_0(\text{cal})$  based on the adsorption results of  $\text{Fe}_3\text{O}_4$  nanocomposite and  $\text{Al}(\text{OH})_3$  nanocomposite, with the ideal addition for

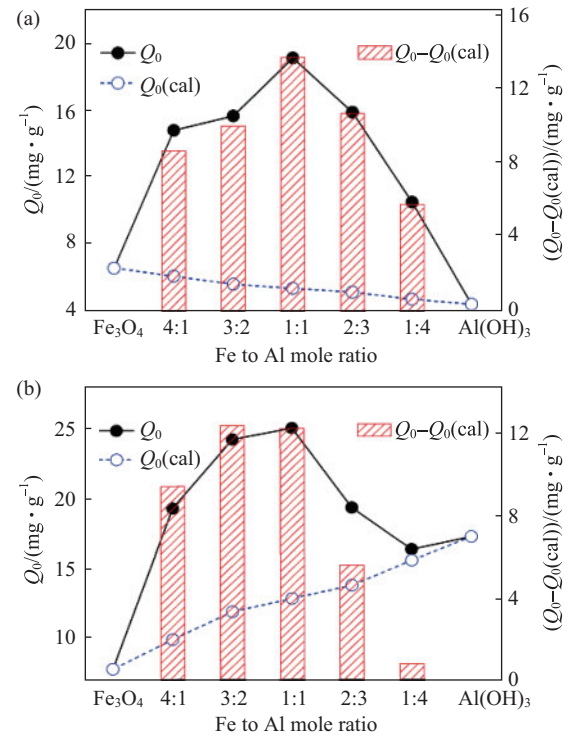


Fig.10 Maximum adsorption capacity  $Q_0$  from the Langmuir model of experimental (a) As(III) and (b) As(V) adsorption by Fe-Al (hydr)oxide nanocomposites with different Fe to Al mole ratios.  $Q_0(\text{cal})$  is calculated from the adsorption of  $\text{Fe}_3\text{O}_4$  nanocomposite and  $\text{Al}(\text{OH})_3$  nanocomposite and  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  mole numbers in different samples. The histogram shows the departure of  $Q_0$  and  $Q_0(\text{cal})$  ( $Q_0 - Q_0(\text{cal})$ )

the adsorption capacity, and the mole number of  $\text{Fe}_3\text{O}_4$  and  $\text{Al}(\text{OH})_3$  in different samples, which is obtained from the fitting of the Langmuir model. The degree of this synergistic effect for arsenic adsorption could be determined by  $(Q_0 - Q_0(\text{cal}))$ . As shown in Fig.10, all the values of the departure of  $(Q_0 - Q_0(\text{cal}))$  are positive for both the adsorption of As(III) and As(V), and the value becomes a maximum when the Fe and Al mole ratio is approximately 1:1. The synergistic effect of Fe-Al (hydr)oxide nanocomposite for arsenic adsorption is obtained through all different Fe to Al mole ratios, and this unusual effect is most obvious when the Fe to Al mole ratio is approximately 1:1. This is possibly due to the good adsorption of arsenic by the mixed Fe and Al compositions and the good dispersity of nano-/micro-particles through the wheat straw.

Meanwhile, the maximum adsorption capacity ( $Q_0$ ) of the Fe-Al (hydr)oxide nanocomposite ( $n(\text{Fe}):n(\text{Al})=1:1$ )

for fluoride and arsenic adsorption was compared with many similar studies, as listed in Table 4. Enhanced by the synergistic effect, both fluoride ( $F^-$ ) and arsenic (As(III) and As(V)) can be efficiently adsorbed by Fe-Al (hydr)oxide nanocomposite with competitive adsorption capacities. Moreover, the material could also maintain the advantage of magnetic separation. Besides, Fe-Al (hydr)oxide nanocomposite is easily obtained by a one-step synthesis with low-cost compounds and materials.

Table 4 Comparison of the Langmuir capacity of different materials for fluoride and arsenic adsorption

| Material                                                                 | $Q_0/(\text{mg} \cdot \text{g}^{-1})$ |         |       | Reference  |
|--------------------------------------------------------------------------|---------------------------------------|---------|-------|------------|
|                                                                          | $F^-$                                 | As(III) | As(V) |            |
| Modified native cellulose fibers                                         | 8.59                                  | 8.96    | 27.93 | [5]        |
| Ti/La oxides on activated carbon                                         | 27.80                                 | —       | 30.30 | [10]       |
| Cellulose@iron oxide nanoparticles                                       | —                                     | 23.16   | 32.11 | [26]       |
| Magnetite-reduced graphene oxide                                         | —                                     | 13.10   | 5.83  | [32]       |
| Magnetic wheat straw                                                     | —                                     | 3.90    | 8.06  | [43]       |
| Fe-Al (hydr)oxide nanocomposite<br>( $n(\text{Fe}):n(\text{Al}) = 1:1$ ) | 20.62                                 | 19.11   | 25.17 | This study |

#### 4 Conclusions

A biomass-based (wheat straw) Fe-Al (hydr)oxide nano-/micro-particle nanocomposite was obtained by a convenient, one-step synthesis. Favoring a monolayer adsorption process, the adsorption isotherms of the Fe-Al (hydr)oxide nanocomposite were well fitted by the Langmuir model. A synergistic adsorption was clearly found from both the adsorption of fluoride and arsenic with the enhancement of adsorption capacity, particularly when the Fe to Al mole ratio was 1:1. The synergistic effect determined by the departure of the experimental ( $Q_0$ ) and calculated ( $Q_0(\text{cal})$ ) showed that this unusual effect was most pronounced with a 1:1 mole ratio of Fe and Al, which was possibly caused by the good adsorption of the mixed Fe-Al (hydr) oxides and the good dispersity of nano-/micro-particles by the wheat straw template. This Fe-Al (hydr)oxide

nanocomposite could be a high-efficiency, low-cost adsorbent for the removal of fluoride ( $F^-$ ) and arsenic (As(III) and As(V)) from water with a magnetic separation.

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