Utilization of annealed aluminum hydroxide waste with incorporated fluoride for adsorptive removal of heavy metals

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HIGHLIGHTS

- $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ can effectively adsorb As(III), As(V), and Cd(II).
- More significant decrease of S_{BET} and pH_{iep} is observed at higher AT.
- Incorporated-F inhibit the removal of Cd and As as compared to pristine $\text{Al}(\text{OH})_3$.
- Elevated AT benefit Cd adsorption whereas inhibit the removal of As(III) and As(V).
- Annealing these aluminas at elevated AT may control fluoride leaching control.

GRAPHICAL ABSTRACT

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ABSTRACT

The removal of fluoride by Al hydroxide [$\text{Al}(\text{OH})_3$] adsorption and aluminum (Al) coagulation produces spent wastes of $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. This study prepared the annealed $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and pristine $\text{Al}(\text{OH})_3$ at annealing temperature (AT) of 200 °C, 600 °C, and 900 °C, and compared their removal behaviors towards cadmium [Cd(II)], arsenite [As(III)], and arsenate [As(V)]. Annealing treatment decreased their BET surface area (S_{BET}) and isoelectric point (pH_{iep}), and a more significant extent of decrease was observed at elevated AT. The incorporation of fluoride lowered their efficiency towards the removal of Cd(II), As(III), and As(V) as compared to $\text{Al}(\text{OH})_3$. The elevated AT benefited Cd(II) adsorption whereas it inhibited the removal of As(III) and As(V) by any of the obtained aluminas, owing to the shift of pH_{iep} to lower pH ranges at elevated AT. The adsorption of Cd(II) increased whereas that of As(III) and As(V) decreased with elevated pH, with electrostatic interactions playing a determining role. The release of fluoride from $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ did occur, and it could be controlled by annealing them at elevated AT. The annealed aluminas showed good affinity towards different heavy metals and may be reclaimed for the treatment of industrial wastewater.

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1. Introduction

The discharge of toxic heavy metals such as cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), and mercury (Hg) has caused

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serious pollution in rivers, soils, and underground waters in the past several decades in China. Long-term exposure to heavy metals can result in chronic damage to blood composition, lungs, brains, kidneys, liver, and other vital organs, and their mixtures show more significant toxicity than that they were separately existed [1]. Heavy metals also have acute toxicity, and high levels of inorganic arsenic at concentrations of above 60 mg/L in water can even be fatal. Industrial wastewaters are important heavy metal sources, and the control of point sources is easier and more cost-effective compared to the remediation of 'non-point' polluted water environments. However, the intentional or unexpected discharge of wastewater with high levels of heavy metals sometimes occurs in developing countries such as China. To avoid this as much as possible, stringent regulation of pollutant-producing factories is crucially important. On the other hand, the development of low-cost and easy-to-operate technologies also plays an important role.

In the past several decades, various methods such as flocculation [2], adsorption [3–5], ion exchange [6], reverse osmosis [7], electro dialysis [8], and precipitation [9] have been developed for the removal of heavy metals. However, the widespread application of some technologies has been restricted by high costs, the production of excessive amounts of concentrated solutions, and the disposal of secondary sludge and so on. To enable long-term stable operation of treatment facilities, it is important to decrease the treatment costs as much as possible. On the other hand, some industries produce a great deal of solid wastes [10–12], and their safe disposal has received great concern. However, if these spent wastes can be reused for the treatment of wastewater, it not only achieves the reclamation of spent wastes but also reduces the cost of heavy metal removal. This concept would be extremely attractive and cost-effective from an engineering point-of-view, and the utilization of industrial wastes for the adsorption of heavy metals has been widely investigated in the past decade [10–12].

The wide occurrence of fluorosis creates the need for the removal of fluoride from drinking water. Aluminum (Al) based coagulants and adsorbents have been widely used for defluoridation [13,14], inevitably producing a great deal of discharged sludge and spent adsorbents globally. These inorganic solid wastes with high levels of Al and fluoride should be disposed of properly to avoid secondary pollution in soils and underground water and so on. The traditional disposal methods for sewage sludge include farmland application, landfilling, and incineration, whereas for these inorganic sludges and adsorbents, strategies such as landfilling, stabilization, pond disposal, and soil disposal are feasible [15]. In our previous study, *in situ* prepared AlOxHy , which can be freshly coated onto porous carriers to achieve adsorbent granulation, has been developed and its fluoride removal efficiency has been well evaluated [16]. Once eventually exhausted, the spent AlOxHy with adsorbed fluoride as expressed by $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ may be safely disposed of by cheap and convenient means such as solidification in roadbeds or encapsulation in cement–lime mixtures. Coagulation is also a cost-effective defluoridation method, and Al–F complex formation is involved in fluoride removal [13]. The wide application of coagulation for defluoridation is restricted by the large-scale production of spent sludge as expressed by $\text{Al(OH)}_3\text{-F}_{\text{coag}}$. The reclamation of these two solid wastes not only minimizes their discharge into water environments but also is economically valuable. Our previous study indicated that freeze-dried $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ are potentially attractive for the removal of heavy metals such as arsenic [17]. However, the experimental freeze-drying procedure is not practically feasible from an engineering point-of-view. Generally, most discharged sludge is dewatered by filter pressing, and the ratios of moisture content can be as high as 70% or more. As for the long-distance transportation of the spent sludge with high moisture content, the cost is much too high and restricts its large-scale reclamation in areas distant from landfills.

To promote their reclamation, these spent sludge may be used as raw materials to prepare commercial adsorbents after being annealed. This economically valuable strategy reduces the moisture content, decreases the transportation cost and expands their application range as much as possible. However, the adsorption efficiency of this spent sludge after thermal pretreatment should be well evaluated.

Based on these considerations, we first prepared two solid wastes obtained from the defluoridation processes of adsorption and coagulation, which were respectively expressed as $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, and pristine Al(OH)_3 was also prepared for comparison. The materials were annealed at different temperatures, and were then characterized by XPS, FTIR, and XRD to illustrate the effects of thermal treatment on their characteristics. Finally, the adsorptive behaviors of Cd(II), As(III), and As(V) on these solid wastes were evaluated in terms of adsorption kinetics and the effect of pH, and the mechanisms involved were proposed accordingly.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical-reagent grade and were directly used unless otherwise noted. The stock solutions of fluoride, Al, Cd(II), As(III), and As(V) salts were prepared by dissolving sodium fluoride (NaF), aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), cadmium nitrate [$\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$], sodium arsenite (NaAsO_2), and sodium arsenate (Na_3AsO_4) in deionized water, respectively.

2.2. Preparation of $\text{Al(OH)}_3\text{-F}$ solid wastes

The adsorbents $\text{Al(OH)}_3\text{-F}_{\text{ads}}$, $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, and pristine Al(OH)_3 were prepared according to the methods described in our previous study [17]. Briefly, the pristine Al(OH)_3 was prepared by the stoichiometric reaction between AlCl_3 and NaOH. To prepare the $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, NaF solution was added into the AlCl_3 solution prior to dosing the NaOH solution whereas NaF solution was introduced after the hydrolysis of Al^{3+} ions to produce $\text{Al(OH)}_3\text{-F}_{\text{ads}}$. To obtain their powders, the suspensions were filtered by 0.45- μm membranes, washed with distilled water, and then freeze-dried.

2.3. Annealing treatment

The $\text{Al(OH)}_3\text{-F}_{\text{ads}}$, $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, and Al(OH)_3 powders were respectively annealed in an oven using a heating rate of 8 °C/min up to 200 °C, 600 °C, or 900 °C, and then the annealing temperature (AT) was kept constant for 2 h. The obtained samples were stored in a desiccator before use.

2.4. Batch adsorption experiments

The initial concentrations of Cd(II), As(III), or As(V) were adjusted to 70 mg/L by diluting their stock solutions, and the pH was adjusted thereafter. The species distribution of Cd(II), As(III), and As(V) over wide pH ranges from 3 to 8, as calculated by the Visual MINTEQ software, is illustrated in Fig. S1. NaNO_3 solution was added to provide a background ionic strength of 0.01 M. Batch adsorption kinetic experiments were conducted in beakers with magnetic stirring (350 rev min^{−1}) at pH 7.0 ± 0.2 after dosing 200 mg adsorbent into 1000-mL solution (25 ± 1 °C). pH was adjusted during adsorption using 0.1 M NaOH and 0.1 M HNO_3 to minimize pH variation. Sampling was carried out at intervals during adsorption and the obtained samples were filtered through 0.45- μm filter membranes and kept at 4 °C for further analysis.

Table 1The S_{BET} and pH_{iep} of the adsorbents before thermal treatment and those being annealed at 200 °C, 600 °C, and 900 °C.

Annealing Temperature (°C)	Parameter	Al(OH) ₃ -F _{ads}	Al(OH) ₃ -F _{coag}	Al(OH) ₃
before thermal treatment	S_{BET} (m ² /g)	150.2	123.7	195.6
	Pore size (nm)	16.56	16.62	17.96
	Pore volume (mL/g)	0.25	0.26	0.28
	pH_{iep}	7.35	7.95	8.00
	$R_{\text{F:Al}}$	2.16	0.84	/
200	S_{BET} (m ² /g)	152.3	124.5	193.4
	Pore size (nm)	10.26	12.31	11.34
	Pore volume (mL/g)	0.23	0.24	0.25
	pH_{iep}	7.15	7.10	7.45
	$R_{\text{F:Al}}$	0.22	0.75	/
600	S_{BET} (m ² /g)	121.4	95.6	140.4
	Pore size (nm)	6.46	9.92	8.73
	Pore volume (mL/g)	0.20	0.22	0.23
	pH_{iep}	6.75	6.66	6.55
	$R_{\text{F:Al}}$	0.21	0.12	/
900	S_{BET} (m ² /g)	112.5	70.4	130.4
	Pore size (nm)	5.36	6.29	5.93
	Pore volume (mL/g)	0.21	0.22	0.21
	pH_{iep}	6.45	6.25	6.20
	$R_{\text{F:Al}}$	0.22	0.11	/

To study the effect of pH on the uptake of Cd(II), As(III), or As(V), their initial concentrations were 70 mg/L and the adsorbent doses were 0.02 g/L. Prior to the addition of the adsorbents, the pH was adjusted by NaOH and HNO₃ solutions over the range from 3 to 8, and pH adjustment was made as needed during adsorption to avoid significant pH deviation.

2.5. Analysis and characterization

The concentrations of Al, Cd and As were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, OPTIMA 2000DA, PerkinElmer, USA). The detection limit was 0.3 µg/L, and duplicate analyses indicated the error was within 5%. The concentrations of fluoride were analyzed by a fluoride ion selective electrode (PF-1, Kangyi Instrument Ltd., China). BET Surface area (S_{BET}) was measured by low-temperature nitrogen adsorption, and the data were interpreted using the BET equation. The nitrogen adsorption tests were carried out in a Micromeritics Surface Area Analyzer (ASAP2000, Micromeritics, USA). The ζ -potential of samples was measured by a ζ -potential analyzer (Zetasizer 2000, Malvern, UK). Fourier transform infrared spectrometry (Perkin-Elmer, 1600 series) was used to analyze the functional groups on the adsorbents' surfaces. The XRD patterns of samples were obtained on a Rigaku GeigerFlex diffractometer with Cu K α radiation, using a scanning rate of 2° 2 θ min⁻¹. X-ray photoelectron spectroscopy (XPS) results were acquired by an ESCA-lab-220i-XL spectrometer (Shimadzu, Japan) with monochromatic Al K α radiation (225W, 15 mA, 15 kV).

2.6. Adsorption models

The pseudo-first-order and pseudo-second-order kinetic models, as described in Eqs. (1) and (2) [18–20], were tested to simulate the experimental data in kinetic adsorption experiments.

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e and q are the amount of Cd or As adsorbed (mg/g) at equilibrium and at time t , respectively; k_1 and k_2 are the pseudo-first-order and pseudo-second-order kinetic rate constants.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. S_{BET} and pH_{iep}

Table 1 illustrates the S_{BET} and pH_{iep} of Al(OH)₃, Al(OH)₃-F_{ads}, and Al(OH)₃-F_{coag} after being annealed at 200 °C, 600 °C, and 900 °C. The annealing temperature was observed to affect the characteristics of these adsorbents. Before thermal treatment, the S_{BET} of Al(OH)₃, Al(OH)₃-F_{ads}, and Al(OH)₃-F_{coag} were determined to be 195.6, 150.2, and 123.7 m²/g, and their corresponding pH_{iep} values were observed to be 8.00, 7.35, and 7.95. The annealing at 200 °C showed little effect on their S_{BET} values but greatly decreased the pH_{iep} to 7.45, 7.15, and 7.10, respectively. At elevated AT of 600 °C and 900 °C, the S_{BET} and pH_{iep} decreased, and more significant decrease was observed at elevated AT. The extent of S_{BET} decrease with elevated AT followed the order Al(OH)₃-F_{coag} > Al(OH)₃ > Al(OH)₃-F_{ads} whereas that of pH_{iep} decrease was Al(OH)₃-F_{ads} > Al(OH)₃-F_{coag} > Al(OH)₃. Annealing treatment contributes to the dehydration of adsorbents, destroying their pore structure and decreasing the S_{BET} . On the other hand, the loss of the bound water molecules and the disappearance of surface hydroxyl groups on adsorbents' surfaces contributed to the decrease of pH_{iep} .

3.1.2. XRD spectra

Fig. 1 compares the XRD spectra of Al(OH)₃, Al(OH)₃-F_{ads}, and Al(OH)₃-F_{coag} before and after annealing treatment at 200 °C, 600 °C, and 900 °C. Prior to thermal treatment, these adsorbents showed broad diffraction peaks mainly related to β -Al(OH)₃ and α -AlOOH. The presence of these peaks indicates the relatively low crystallinity of these adsorbents. After being annealed at 200 °C, increased diffraction intensity of the peaks at 2 θ of 18, 37, and 49° was observed. This corresponded to the improved crystallinity with the appearance of new crystalline phases such as γ -Al₂O₃. In comparison, the peaks of α -AlOOH as observed at 2 θ of 18, 64 and 84° weakened greatly. At increased AT of 600 °C, Al(OH)₃, Al(OH)₃-F_{ads}, and Al(OH)₃-F_{coag} showed some differences in their XRD patterns; however the extent was relatively low. The peaks of γ -Al₂O₃ at 2 θ of 32 and 27° and weak peaks of α -Al₂O₃ at 2 θ of 57 and 76° appeared, whereas the peaks of β -Al(OH)₃ and α -AlOOH could hardly be observed.

After the further elevated AT of 900 °C, Al(OH)₃, Al(OH)₃-F_{ads}, and Al(OH)₃-F_{coag} showed remarkable differences in their XRD pat-

Fig. 1. XRD spectra of the adsorbents before thermal treatment and those being annealed at 200 °C, 600 °C, and 900 °C. (1- $\text{Al}(\text{OH})_3$; 2- $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$; 3- $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$).

terns. In detail, $\text{Al}(\text{OH})_3$ showed strong peaks of $\alpha\text{-Al}_2\text{O}_3$ at 2θ of 35, 57, and 76°. As for $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ with incorporated fluoride, new peaks at 2θ of 45 and 52° appeared besides those due to $\alpha\text{-Al}_2\text{O}_3$, and these peaks were attributed to $\alpha\text{-AlF}_3$ [6]. Fluoride ion has a similar ionic radius and charge as hydroxyl ion, and this enables the transformation of Al-F hydroxides into AlF_3 and Al_2O_3 with various crystalline phases at high AT. In addition, fluoride tends to replace the surface hydroxyls on adsorbent surfaces, and this changes the critical AT for the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ [21,22]. The thermal treatment of $\text{Al}(\text{OH})_3$ at different AT contributed to the formation of alumina with different structural transitions [23–25]. Thermal treatment of Boehmite in the temperature ranges 400–700 °C, 700–1050 °C, 1050 °C, and 1100 °C tends to produce alumina in the different crystal phases $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$, respectively. By comparison, Bayerite transforms to $\eta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$ in the temperature ranges 300–600 °C, 800–1000 °C, and above 1000 °C [26].

3.1.3. FTIR spectra

Fig. 2 illustrates the FTIR spectra of $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ after annealing treatments at 200 °C, 600 °C, and 900 °C. The bands at 3450 cm^{-1} and 1650 cm^{-1} correspond to the adsorbed water and the O–H stretching of hydroxyl groups and are indicative of the adsorption of water molecules [27]. These two bands weakened after annealing treatment, and their intensity decreased more significantly at elevated AT. This indicated the dehydration and disappearance of the adsorbed water molecules. These three adsorbents all showed two new bands at 1130 cm^{-1} and 450 cm^{-1} after being annealed at 600 °C and 900 °C, which were attributed to the formation of Al–OH and Al_2O_3 , respectively [28].

Comparatively, the hydroxyl groups on the $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ surface showed a lower extent of decrease than those on the surfaces of $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ after annealing. The formation of Al–OH on the $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ surface was observed to be less than on

the surfaces of $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. These results indicate the involvement of fluoride in the crystallization of Al hydroxide, and the different ways of combining fluoride and alumina affect the formation of crystallized products greatly.

3.1.4. XPS spectra

Fig. 3 illustrates the XPS spectra of F 1s on $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ before thermal treatment and after being annealed at 200 °C, 600 °C, and 900 °C. The thermal treatment contributed to the increased binding energy of F 1s for both $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. Quantitatively, the binding energy of F 1s shifted more significantly for $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, from 684.8 to 685.5 eV, than for $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$. The elevated binding energy is attributed to the loss of outer electron density, and this might be attributed to the formation of AlF_3 , as observed in Fig. 1. Thermal treatment also contributed to elevated molar ratios of fluoride to Al ($R_{\text{F:Al}}$) on both $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ surfaces. With elevated AT from 200 °C to 600 °C, the $R_{\text{F:Al}}$ of $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ increased significantly from 0.16: 1–0.53: 1, whereas that of $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ increased more slightly from 0.09: 1–0.15: 1. Fluoride mainly existed on the surface of $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, and the dehydration improved the exposure of fluoride. By comparison, Al–F complexes were involved in the formation of $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ and fluoride was solidified therein, and a lower extent of $R_{\text{F:Al}}$ increase was observed accordingly.

3.2. Adsorption kinetics of Cd(II), As(III), and As(V) onto these adsorbents

3.2.1. Adsorption kinetics of Cd(II)

Fig. 4 illustrates the adsorption kinetics of Cd(II) onto $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and $\text{Al}(\text{OH})_3$ after being annealed at 200 °C, 600 °C, and 900 °C. Cd(II) adsorbed rapidly onto these adsorbents in the initial 120 min, and subsequently the adsorption velocity slowed down greatly. In the initial adsorption stage, Cd(II) mainly reacted with macro pore and particle exterior sites, whereas in the

Fig. 2. FTIR spectra of $\text{Al(OH)}_3\text{-F}_{\text{ads}}$, $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, and Al(OH)_3 after being annealed at 200 °C, 600 °C, and 900 °C.

later slow adsorption stage, the micropores within these adsorbents may involve in Cd(II) adsorption. Comparatively, the alumina obtained by annealing Al(OH)_3 showed higher adsorption density of Cd(II) ($Q_{\text{Cd(II)}}$) and required less time to achieve equilibrium adsorption than the materials obtained by annealing $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$. Alumina obtained from Al(OH)_3 exhibits high

Fig. 3. XPS spectra of F 1 s on $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ before thermal treatment and those after being annealed at 200 °C, 600 °C, and 900 °C.

S_{BET} , and the adsorption of Cd(II) may be mainly controlled by pore diffusion and surface diffusion [29]. Comparatively, the presence of fluoride in $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ lowered the S_{BET} and the pore volume compared to Al(OH)_3 , and relatively lower adsorption velocity was observed accordingly.

To quantitatively compare the adsorption kinetics, pseudo-first-order and pseudo-second-order kinetic models were used to fit the obtained experimental data, and Table 2 summarizes the values of q_e , k_1 , k_2 , and the correlation coefficient (R^2). The pseudo-second-order model was better than the pseudo-first-order model at fitting the experimental data, as indicated by the higher R^2 values.

Additionally, the aluminas obtained at elevated AT showed higher adsorption rate, as expressed by k_1 and k_2 , and more significant adsorption density (Q) towards Cd(II) for these three adsorbents. Quantitatively, after annealing Al(OH)_3 at 200 °C, 600 °C, and 900 °C, the obtained aluminas showed the maximal $Q_{\text{Cd(II)}}$ of 20.2, 30.5, and 34.4 mg/g accordingly. It was noted that thermal treatment decreased S_{BET} , and this effect adversely affected Cd(II) adsorption. The improved Cd(II) adsorption at elevated AT was mainly attributed to the lowered pH_{iep} . At AT of 600 °C and 900 °C, the pH_{iep} of the obtained alumina decreased to below 7, and this effect benefited the adsorption of positively charged Cd(II) . This result indicates that electrostatic attraction plays a more important role in the adsorption of Cd(II) onto these aluminas as compared to the amount of surface sites.

Fig. 4. Adsorption kinetics of Cd(II) onto the alumina obtained from $\text{Al(OH)}_3\text{-F}_{\text{ads}}$, $\text{Al(OH)}_3\text{-F}_{\text{coag}}$, and Al(OH)_3 after being annealed at 200 °C, 600 °C, and 900 °C. (Experimental conditions: $[\text{Cd(II)}]_0 = [\text{As(III)}]_0 = [\text{As(V)}]_0 = 70 \text{ mg/L}$, contact time = 24 h, $\text{pH} = 7$, ionic strength = 0.01 M NaNO_3 , adsorbent doses = 0.02 g/L).

Table 2
Kinetics parameters of pseudo-first-order and pseudo-second-order models involve in the adsorption of Cd(II) onto the adsorbents after being annealed at 200 °C, 600 °C, and 900 °C.

Adsorbents	Annealing Temperature (°C)	Kinetic models					
		Pseudo-first-order			Pseudo-second-order		
		k_1 (*10) (1/min)	Q (mg/g)	R^2	k_2 (*10 ²) (g/(mg min))	Q (mg/g)	R^2
Al(OH) ₃ -F _{ads}	200	0.07	14.1	0.95	0.10	18.2	0.99
	600	0.14	18.8	0.94	0.16	20.5	0.98
	900	0.28	26.0	0.92	0.22	29.2	0.98
Al(OH) ₃ -F _{coag}	200	0.12	16.2	0.95	0.15	18.7	0.98
	600	0.24	20.6	0.94	0.27	23.2	0.98
	900	0.30	25.4	0.93	0.31	27.8	0.99
Al(OH) ₃	200	0.13	20.0	0.96	4.12	20.2	0.99
	600	0.27	29.5	0.96	5.02	30.5	0.99
	900	0.46	33.4	0.97	6.11	34.4	0.99

3.2.2. Adsorption kinetics of As(III)

Fig. 5 illustrates the adsorption kinetics of As(III) onto Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ after annealing at 200 °C, 600 °C, and 900 °C, and the fitted parameters are illustrated in Table 3. Alumina obtained from Al(OH)₃ showed the highest adsorption density for As(III) ($Q_{As(III)}$). Additionally, the alumina obtained from Al(OH)₃-F_{ads} with adsorbed fluoride showed higher $Q_{As(III)}$ than that obtained from Al(OH)₃-F_{coag} with complexed fluoride. Fluoride was incorporated into the Al hydroxide in different ways for these two materials, and different adsorption behaviors towards As(III) were observed thereafter. Elevated AT inhibited rather than improved the adsorption of As(III) onto these adsorbents, contrary to the results observed in Cd(II) adsorption, and decreased $Q_{As(III)}$ and slowed adsorption density was observed. The extent of $Q_{As(III)}$ decrease with elevated AT followed the same trend as that of S_{BET} decrease, i.e., Al(OH)₃-F_{coag} > Al(OH)₃ > Al(OH)₃-F_{ads}. Both pseudo-first-order and pseudo-second-order models were able to adequately describe the adsorption of As(III) onto these adsorbents, and the fitted R^2 values showed insignificant difference between these two models. It was inferred that physical adsorption dominated in the adsorption of As(III) onto the three adsorbents.

3.2.3. Adsorption kinetics of As(V)

Fig. 6 illustrates the adsorption kinetics of As(V) onto the different aluminas obtained after annealing Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ at different AT of 200 °C, 600 °C, and 900 °C, and Table 4 illustrates the fitting of the data by pseudo-first-order and pseudo-second-order models. Elevated AT also inhibited the adsorption of As(V) onto these aluminas, as observed for As(III). Prior to thermal treatment, Al(OH)₃-F_{ads} showed the maximum As(V) adsorption density ($Q_{As(V)}$) of 78.6 mg/g. After being annealed at 200 °C, 600 °C, and 900 °C, $Q_{As(V)}$ decreased to 74.2, 58.3, and 32.9 mg/g, accordingly. The aluminas obtained from Al(OH)₃-F_{coag} and Al(OH)₃ also showed lowered $Q_{As(V)}$ at elevated AT, and Al(OH)₃ showed the highest extent of $Q_{As(V)}$ decrease among these three adsorbents. The lowered $Q_{As(V)}$ was attributed to the combined effects of thermal treatment on S_{BET} and pH_{iep} . First, the annealing treatment decreased the S_{BET} and reduced the specific surface energy, and inhibited adsorption of $H_2AsO_4^-$ and $HAsO_4^{2-}$ was observed accordingly. Moreover, thermal treatment lowered pH_{iep} , and these aluminas showed more significantly negative surfaces. This effect adversely affected the adsorption of negatively charged As(V) accordingly. Additionally, thermal treatment also slowed down the adsorption of As(V) onto these aluminas, as indicated from the lowering of k_1 and k_2 values with elevated AT. The lowered S_{BET} and pH_{iep} increased the repulsive forces between As(V) and adsorbent surfaces and inhibited the transfer of As(V) within liquid films.

The calculated R^2 values indicated that the pseudo-second-order model was better than the pseudo-first-order model to describe the adsorption of As(V). This may indicate the presence of multiple adsorption sites on the surfaces of these aluminas. Comparatively, the alumina obtained from Al(OH)₃-F_{ads} showed the lowest k_1 and k_2 values among these adsorbents, and this indicated the inhibitive effect of adsorbed fluoride on the adsorption of As(V). The different types of incorporated fluoride resulted in different surface characteristics for the adsorbents and affected the adsorption of As(V) thereafter.

Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} showed little difference in adsorption density towards Cd(II), but more significant difference is observed while removing As(III) and As(V). This may be attributed to the different mechanisms involved in their adsorption. Fluoride incorporated into Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} via different mechanisms, and affected their interfacial characteristics accordingly [17]. The adsorption of positive Cd(II) is achieved by forming surface complexes with surface hydroxyl groups, and fluoride showed little effects therein. Comparatively, the precipitation of Al-F complexes involves in the formation of Al(OH)₃-F_{coag}, and this effect consumes much more sites available for arsenic adsorption as compared to the adsorbed fluoride on Al(OH)₃-F_{ads} surfaces.

3.3. Effect of pH on the adsorption of Cd(II), As(III), and As(V)

Fig. 7 illustrates the effects of pH on the adsorption of Cd(II), As(III), and As(V) onto alumina obtained from Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃, respectively. Thermal treatment benefited the adsorption of Cd(II), and elevated AT and pH was correlated to higher adsorption density ($Q_{Cd(II)}$) over a wide pH range from 4 to 8. After being annealed at 200 °C, all aluminas showed relatively low $Q_{Cd(II)}$ below 15 mg/g at pH < 7. At pH 8, however, $Q_{Cd(II)}$ increased remarkably to as high as 48.4, 51.3, and 69.2 mg/g for alumina obtained from Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃, respectively. At the elevated AT of 600 °C, a more significant affinity towards Cd(II) was observed for these aluminas. Quantitatively, the alumina obtained from Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ showed $Q_{Cd(II)}$ of 29.3, 28.5, and 40.3 mg/g at pH 7 and of 51.4, 58.8, and 70.4 mg/g at pH 8, respectively. Generally, AT had less effect on $Q_{Cd(II)}$ in the lower pH range from 4 to 6 than that at pH 7–8 as for a given alumina.

The interactions between Cd(II) and adsorbent surfaces play an important role in Cd(II) adsorption. At lowered pH below 6, the increased concentration of H^+ showed more significant competition towards adsorption sites and inhibited Cd(II) adsorption. After being annealed at 200 °C, the pH_{iep} of these aluminas were in the range from 7 to 8, and their positively charged surfaces inhibited the adsorption of positive Cd(II). After being annealed at 600 °C and 900 °C, the pH_{iep} shifted to lower pH, below 7. These aluminas

Fig. 5. Adsorption kinetics of As(III) onto the alumina obtained from $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and $\text{Al}(\text{OH})_3$ after being annealed at 200 °C, 600 °C, and 900 °C. (Experimental conditions: $[\text{Cd}(\text{II})]_0 = [\text{As}(\text{III})]_0 = [\text{As}(\text{V})]_0 = 70 \text{ mg/L}$, contact time = 24 h, pH = 7, ionic strength = 0.01 M NaNO_3 , adsorbent doses = 0.02 g/L).

Table 3

Kinetics parameters of pseudo-first-order and pseudo-second-order models involve in the adsorption of As(III) onto the adsorbents after being annealed at 200 °C, 600 °C, and 900 °C.

Adsorbent	Annealing Temperature (°C)	Kinetic models					
		Pseudo-first-order			Pseudo-second-order		
		k_1 (*10) (1/min)	Q (mg/g)	R^2	k_2 (*10 ²) (g/(mg min))	Q (mg/g)	R^2
$\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$	200	0.078	28.6	0.99	0.23	34.2	0.97
	600	0.05	19.9	0.99	0.15	25.4	0.98
	900	0.036	17.3	0.99	0.12	23.4	0.99
$\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$	200	0.14	14.1	0.98	0.31	16.1	0.98
	600	0.08	10.7	0.98	0.22	13.0	0.98
	900	0.039	7.1	0.98	0.13	9.7	0.99
$\text{Al}(\text{OH})_3$	200	0.49	36.8	0.96	0.94	39.6	0.99
	600	0.36	31.5	0.96	0.72	34.5	0.99
	900	0.03	19.5	0.99	0.05	25.7	0.97

Fig. 6. Adsorption kinetics of As(V) onto the alumina obtained from $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and $\text{Al}(\text{OH})_3$ after being annealed at 200 °C, 600 °C, and 900 °C. (Experimental conditions: $[\text{Cd}(\text{II})]_0 = [\text{As}(\text{III})]_0 = [\text{As}(\text{V})]_0 = 70 \text{ mg/L}$, contact time = 24 h, pH = 7, ionic strength = 0.01 M NaNO_3 , adsorbent doses = 0.02 g/L).

showed negatively charged surfaces at pH 7, and the adsorption of Cd(II) was benefited accordingly. After being annealed at 600 °C and 900 °C, alumina obtained from $\text{Al}(\text{OH})_3$ showed the highest S_{BET} and lowest pH_{iep} among these aluminas, and the highest affinity towards Cd(II) was observed as a result. Generally, the aluminas obtained from $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ showed higher $Q_{\text{Cd(II)}}$ than those from $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, especially at the high AT of 900 °C.

Elevated AT generally showed inhibitive rather than positive effects on the adsorption of As(III) and As(V) onto these aluminas. In addition, pH also showed inhibiting effects on the adsorption

of both arsenic species, and $Q_{\text{As(III)}}$ and $Q_{\text{As(V)}}$ decreased with elevated pH as for a given alumina. These trends were attributed to the shift of pH_{iep} to the lower pH range after annealing at elevated AT. Electrostatic interactions were inferred to play a more important role in the adsorption of As(III) onto these aluminas than S_{BET} . At pH < 6, the obtained aluminas showed positively charged surfaces, and this effect benefited the removal of negatively charged As(V), i.e., H_2AsO_4^- and HAsO_4^{2-} . At pH above 7.5, these alumina showed negatively charged surfaces and inhibited the adsorption of As(V). The stronger competition effect of OH^- at higher pH also

Table 4
Kinetics parameters of pseudo-first-order and pseudo-second-order models involve in the adsorption of As(V) onto the adsorbents after being annealed at 200 °C, 600 °C, and 900 °C.

Adsorbents	Annealing Temperature (°C)	Kinetic models					
		Pseudo-first-order			Pseudo-second-order		
		k_1 (*10) (1/min)	Q (mg/g)	R^2	k_2 (*10 ²) (g/(mg min))	Q (mg/g)	R^2
Al(OH) ₃ -F _{ads}	200	0.36	69.81	0.94	0.21	76.08	0.99
	600	0.24	54.36	0.95	0.15	60.51	0.98
	900	0.10	31.47	0.94	0.12	36.39	0.99
Al(OH) ₃ -F _{coag}	200	0.5	53.66	0.96	0.25	57.92	0.98
	600	0.3	42.10	0.96	0.18	46.38	0.98
	900	0.16	26.64	0.97	0.13	30.28	0.99
Al(OH) ₃	200	1.8	113.66	0.97	3.03	97.24	0.99
	600	2.68	78.48	0.97	2.52	80.32	0.99
	900	3.7	52.42	0.97	2.09	54.38	0.99

Fig. 7. Effects of pH on the adsorption of Cd(II), As(III), and As(V) onto the alumina obtained from Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ after being annealed at 200 °C, 600 °C, and 900 °C. (Experimental conditions: [Cd(II)]₀ = [As(III)]₀ = [As(V)]₀ = 70 mg/L, contact time = 24 h, pH = 7, ionic strength = 0.01 M NaNO₃, adsorbent doses = 0.02 g/L).

had an adverse effect. Comparatively, Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} with incorporated fluoride showed lower $Q_{As(III)}$ than Al(OH)₃ did, owing to their lower S_{BET} and higher pH_{iep} .

3.4. Evaluation of fluoride leaching

Fluoride leaching is also an important issue to be carefully evaluated. Fig. 8 illustrates the concentrations of leached fluoride ($F_{leaching}$) with prolonged time in the adsorption of Cd(II), As(III), and As(V) by Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag}. The leaching of fluoride did occur and $F_{leaching}$ increased rapidly in the initial 150 min whereas in the second stage from 150 min to 24 h $F_{leaching}$ increased slightly. The adsorption of Cd(II) increased whereas $F_{leaching}$ decreased with elevated AT for both Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag}. Comparatively, the adsorption of arsenic showed similar trends to $F_{leaching}$ in regarding to the effect of elevated AT. The different mechanisms involve in their adsorption may play an important role. Surface complexation dominates in Cd(II) adsorp-

tion whereas the adsorption of As(III) and As(V) is attributed to ion exchange. For a given alumina, the extent of fluoride leaching was more significant during the adsorption of As(V) than that observed in adsorbing As(III), and this indicated the partial replacement of interlayer fluoride by negatively-charged As(V) (Fig. S1). Additionally, the annealing treatment at elevated AT immobilized fluoride and decreased its leaching into solution. Elevated AT contributed to a higher degree of crystallinity (Fig. 1), and the stronger incorporation of fluoride inhibited its release thereafter.

In China the discharge of fluoride is regulated by the Chinese Industrial Wastewater Discharge Standard, and its concentration in wastewater should be below 10 mg/L for the Class-I Standard. Table 5 illustrates the maximum $F_{leaching}$ involved in the adsorption of Cd(II), As(III), and As(V) onto different aluminas. It was observed that the release of fluoride from Al(OH)₃-F_{ads} was more significant than that from Al(OH)₃-F_{coag}, and fluoride leaching could be inhibited by annealing at elevated AT. As for the Al(OH)₃-F_{ads} with more fluoride on the surface, the AT of above 600 °C is preferred to

Fig. 8. The concentrations of leached fluoride in the adsorption of Cd(II), As(III), and As(V) onto the alumina obtained from $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ after being annealed at 200 °C, 600 °C, and 900 °C. (Experimental conditions: $[\text{Cd}(\text{II})]_0 = [\text{As}(\text{III})]_0 = [\text{As}(\text{V})]_0 = 70 \text{ mg/L}$, contact time = 24 h, pH = 7, ionic strength = 0.01 M NaNO_3 , adsorbent doses = 0.02 g/L).

Table 5

The maximum concentrations of leached fluoride after the adsorption of Cd(II), As(III), and As(V) onto the $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ after being annealed at 200 °C, 600 °C, and 900 °C.

Adsorbents	Annealing Temperature (°C)	Adsorbed pollutants		
		Cd(II)	As(III)	As(V)
$\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$	200	10.3	11.0	13.8
	600	8.9	10.2	11.1
	900	6.8	6.8	6.8
$\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$	200	9.6	8.7	10.6
	600	8.4	7.9	9.1
	900	6.5	5.4	5.8

achieve the Class-I Standard, whereas the AT of 200 °C is sufficient to control fluoride release from $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. The leaching of fluoride may also be controlled by optimizing the adsorbents doses and pH in engineering point-of-view.

4. Conclusions

The spent wastes of $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ may be reutilized as adsorbents for the removal of heavy metals such as Cd(II), As(III), and As(V) after being annealed, and the adsorption density onto these aluminas follows the trend $\text{As(V)} > \text{Cd(II)} \approx \text{As(III)}$. The annealing temperature greatly affected the surface characteristics of the obtained aluminas, and S_{BET} and pH_{iep} decreased with elevated AT for $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and $\text{Al}(\text{OH})_3$. The incorporation of fluoride into $\text{Al}(\text{OH})_3$ adversely inhibits adsorption of these pollutants compared to $\text{Al}(\text{OH})_3$, and Cd(II) adsorption is least affected by the incorporated fluoride. $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ with complexed fluoride shows less adsorption efficiency than $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ with adsorbed fluoride, and the state of incorporated fluoride affects their adsorptive behaviors greatly. The leaching of fluoride does occur, and fluoride leaching may be inhibited

by annealing at elevated AT and by optimizing adsorbents doses and pH. The low-cost $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ have practical value as raw materials to produce adsorbents with high efficiency towards different heavy metals in wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2016.05.052>.

References

- [1] S.J. Cobbina, Y. Chen, Z. Zhou, X. Wu, T. Zhao, Z. Zhang, W. Feng, W. Wang, Q. Li, X. Wu, L. Yang, Toxicity assessment due to sub-chronic exposure to individual and mixtures of four toxic heavy metals, *J. Hazard. Mater.* 294 (2015) 109–120.
- [2] M.A. Alam, C. Wan, X.Q. Zhao, L.J. Chen, J.S. Chang, F.W. Bai, Enhanced removal of Zn^{2+} or Cd^{2+} by the flocculating *Chlorella vulgaris* JSC-7, *J. Hazard. Mater.* 289 (2015) 38–45.
- [3] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: a review, *J. Hazard. Mater.* 211 (2012) 317–331.
- [4] G. Zhao, J. Li, X. Ren, C. Chen, X. Wang, Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management, *Environ. Sci. Technol.* 45 (2011) 10454–10462.
- [5] C.J. Madadrang, H.Y. Kim, G. Gao, N. Wang, J. Zhu, H. Feng, M. Gorrang, M.L. Kasner, S. Hou, Adsorption behavior of EDTA-graphene oxide for Pb (II) removal, *ACS Appl. Mater. Interfaces* 4 (2012) 1186–1193.

- [6] M. Naushad, A. Mittal, M. Rathore, Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II) and Pb(II) metal ions over a composite cation exchanger, *Desalin. Water Treat.* 54 (2015) 2883–2890.
- [7] S. Chung, S. Kim, J.O. Kim, J. Chung, Feasibility of combining reverse osmosis–ferrite process for reclamation of metal plating wastewater and recovery of heavy metals, *Ind. Eng. Chem. Res.* 53 (2014) 15192–15199.
- [8] A. Mahmoud, A.F. Hoadley, An evaluation of a hybrid ion exchange electrodialysis process in the recovery of heavy metals from simulated dilute industrial wastewater, *Water Res.* 46 (2012) 3364–3376.
- [9] F. Fu, L. Xie, B. Tang, Q. Wang, S. Jiang, Application of a novel strategy—advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater, *Chem. Eng. J.* 189 (2012) 283–287.
- [10] I. Pulford, J. Hargreaves, J. Ďurišová, B. Kramulova, C. Girard, M. Balakrishnan, V. Batra, J. Rico, Carbonised red mud—A new water treatment product made from a waste material, *J. Environ. Manage.* 100 (2012) 59–64.
- [11] I. Smičiklas, S. Smiljanić, A. Perić-Grujić, M. Šljivić-Ivanović, M. Mitrić, D. Antonović, Effect of acid treatment on red mud properties with implications on Ni(II) sorption and stability, *Chem. Eng. J.* 242 (2014) 27–35.
- [12] M. Dinesh, U.P. Charles, Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142 (2007) 1–53.
- [13] W.X. Gong, J.H. Qu, R.P. Liu, H.C. Lan, Effect of aluminum fluoride complexation of fluoride removal by coagulation, *Colloid. Surf. A* 39 (2012) 88–93.
- [14] W.X. Gong, J.H. Qu, R.P. Liu, H.C. Lan, Adsorption of fluoride onto different types of aluminas, *Chem. Eng. J.* 54 (2012) 126–133.
- [15] S.H. Joo, M.F. Dello, E. Antmann, Sustainable approaches for minimizing biosolids production and maximizing reuse options in sludge management: a review, *J. Environ. Manage.* 158 (2015) 133–145.
- [16] R.P. Liu, W.X. Gong, H.C. Lan, Y.P. Gao, H.J. Liu, J.H. Qu, Defluoridation by freshly-prepared aluminum hydroxides, *Chem. Eng. J.* 175 (2011) 144–149.
- [17] J.W. Ju, Z. He, R.P. Liu, H.J. Liu, X.W. Zhang, J.H. Qu, Reusability of Al-F hydroxide precipitates generated in adsorption and coagulation treatment of fluoride for adsorptive removal of arsenic, *Environ. Eng. Sci.* 32 (2015) 613–621.
- [18] H. Yuh-Shan, Citation review of Lagergren kinetic rate equation on adsorption reactions, *Scientometrics* 59 (2004) 171–177.
- [19] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [20] S. Azizian, Kinetic models of sorption: a theoretical analysis, *J. Colloid Interface Sci.* 276 (1) (2004) 47–52.
- [21] C.-C. Leng, N. Pinto, Effects of surface properties of activated carbons on adsorption behavior of selected aromatics, *Carbon* 35 (1997) 1375–1385.
- [22] A.E. Yilmaz, R. Boncukcuoğlu, M. Kocakerim, İ.H. Karakaş, Waste utilization: the removal of textile dye (Bomplex Red CR-L) from aqueous solution on sludge waste from electrocoagulation as adsorbent, *Desalination* 277 (2011) 156–163.
- [23] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Le Cloirec, Structure characterization and adsorption properties of pyrolyzed sewage sludge, *Environ. Sci. Technol.* 39 (2005) 4249–4257.
- [24] A.O. Babatunde, J.L. Kumar, Y. Zhao, Constructed wetlands using aluminium-based drinking water treatment sludge as P-removing substrate: should aluminium release be a concern, *J. Environ. Monit.* 13 (2011) 1775–1783.
- [25] H.C. Chu, L.H. Lin, H.J. Liu, K.M. Chen, Utilization of dried activated sludge for the removal of basic dye from aqueous solution, *Desalin. Water Treat.* 51 (2013) 7074–7080.
- [26] D.S. Tong, M. Liu, L. Li, C.X. Lin, W.H. Yu, Z.P. Xu, C.H. Zhou, Transformation of alunite residuals into layered double hydroxides and oxides for adsorption of acid red G dye, *Appl. Clay Sci.* 70 (2012) 1–7.
- [27] M. Karthikeyan, K.S. Kumar, K. Elango, Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution, *J. Fluorine Chem.* 130 (2009) 894–901.
- [28] R. Ianoş, I. Lazău, C. Păcurariu, The influence of combustion synthesis conditions on the α -Al₂O₃ powder preparation, *J. Mater. Sci.* 44 (2009) 1016–1023.
- [29] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, *J. Colloid. Interface Sci.* 333 (2009) 14–26.