Synthesis of Ce(III)-doped Fe_3O_4 magnetic particles for efficient removal of antimony from aqueous solution

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HIGHLIGHTS

- Doping of Ce into Fe_3O_4 was achieved based on a facile solvothermal method.
- After doping, the removal capacity was increased by 5 times for “Sb(V)” and 2 times for “Sb(III)”.
- Decreasing pH improved adsorption of Sb(V) but decreased adsorption of Sb(III).
- Antimony sorption mechanisms on Ce-doped Fe_3O_4 were illustrated.

GRAPHICAL ABSTRACT

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ABSTRACT

Aqueous antimony (Sb) pollution from human activity is of great concern in drinking water due to its adverse health effect. Magnetic Fe_3O_4 particles, with high separation ability from solution, have been considered as a low-cost Sb adsorbent for contaminants. However, the limited adsorption capacity has restricted its practical application. In this study, a solvothermal approach was developed for doping Ce(III) into Fe_3O_4 , thereby increasing the adsorption efficacy for both Sb(III) and Sb(V). In contrast to un-doped Fe_3O_4 , the adsorption capacity towards Sb(III) and Sb(V) in Ce-doped materials increased from 111.4 to 224.2 mg/g and from 37.2 to 188.1 mg/g at neutral pH, respectively. Based on the combined results of XPS, XRD, and FTIR, it confirmed that Ce atom successfully doped into the Fe_3O_4 structure, resulting in the decreased particle size, increased the surface area, and isoelectric point. Furthermore, the vibrating sample magnetometer (VSM) results showed that the Ce doping process had some side effects on the primitive magnetic property, but remaining the high separation potential during water treatment. According to the high removal efficiency and magnetic property, the Ce-doped Fe_3O_4 of great simplicity should be a promising adsorbent for aqueous Sb removal.

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1. Introduction

Antimony (Sb) which is a well-known highly toxic element but also important raw material for flame retardant, polyethylene terephthalate (PET)-production, additive in glassware and ceramic [1]. In uncontaminated natural water samples, the antimony exists mainly in the pentavalent [Sb(V)] and trivalent [Sb(III)] oxidation states, in a low concentration range (<0.1 ppb) [2]. However, elevated concentrations of Sb (even ppm level) could be found in some aquatic systems because of anthropogenic influences such as untreated wastewater from antimony mines and smelting plants [3], leaching of municipal waste [4], and so on. Severe health implications including direct lung damage and induced cancer have been found to be associated with the excessive long-term intake of antimony [5]. To protect public health, antimony and its compounds have been listed as priority pollutants by U.S. Environmental Protection Agency (USEPA) and the World Health Organization (WHO) guidelines for drinking water quality imposes a maximum allowable concentration of $6 \mu\text{g/L}$ for antimony. Anthropogenic antimony emissions have been reported, posed a serious threat to environment and human health. For instance, the higher concentrations of Sb in wastewater and surface water near the Xikuangshan mines, in China, were reported to be $1.33\text{--}21.8 \text{ mg/L}$ and $0.1\text{--}7.0 \text{ mg/L}$, respectively [6]. The concentrations of Sb in several household wells of Slovakia were exceeded the Sb containing drinking water limit as much as 25 times higher than WHO guideline [7]. Therefore, purification of water contaminated by antimony is an urgent issue need to resolve in some areas.

Removal of antimony from water has been highly observed in recent years and many techniques have been explored for this purpose, mainly based on adsorption [8], bioremediation [9], coagulation/flocculation [10], ultrafiltration [11], and ion exchange [12]. Among these techniques, the adsorption is considered as an attractive technique with some significant advantages such as simplicity, low-cost, and eco-friendly [13]. Recently, varieties of adsorbents have been developed for the removal of antimony from aqueous solution [8,14–16]. Nevertheless, the disadvantages of these conventional adsorbents should be addressed, such as greater difficulty of adsorbing Sb(V), which is the principal form of antimony in the aqueous environments, as compared to Sb(III) [17] and difficult to separate from the aquatic system when they are saturated. As an alternative mode, magnetic adsorbents (e.g., $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , nZVI, etc.) exhibited combine adsorption properties with the magnetic properties, which make the adsorbents separated from liquid phase using an external magnetic field easily, and could be re-applied several times after desorbing the adsorbed contaminants [18–20]. Magnetic separation of magnetic adsorbents is a more efficient approach to solid-water separation than conventional methods (e.g., centrifugation, sedimentation, filtration) [21]. Moreover, this approach is particularly adapted when separation is complex, i.e., when polluted water contains solid residues not magnetic and the magnetic separation makes it easy to separate only adsorbents from the mixture [22].

Magnetite, the iron oxide Fe_3O_4 , which has been extensively studied as an excellent magnetic material. However, it suffers from an inherent limitation as lower sorption capability, which constrains its applications as an effective adsorbent [23,24]. Doping of various transition metals into the magnetite spinel structure would have significant effects such as increased amount of surface defects, increased hydroxyl amount, tunable surface charge, and electronic properties, which can greatly enhance materials adsorption performance [25–27]. Therefore, the question is which metal to be used and what method would work best for addition into the magnetite structure. Cerium (Ce) has been considered as a good doping component owing to its ferric oxide usually has high affinity surface hydroxyl groups and showed promising adsorption capacity

[28,29]. To meet the requirement of suitable size distribution, fabricating doped Fe_3O_4 by solvothermal process should be a good choice which allows for the precise control over the size, shape distribution, and crystallinity of metal oxide micro- and nano-particles [30]. On the other hands, solvothermal method can avoid conventional co-precipitation technologies' ultrafine-size defect which can cause the inefficient magnetic separation from treated water due to the randomly directed forces of Brownian motion, which are stronger than the magnetic forces [(Eq. S1)] [31]. In addition, the concentration and ratio of precursors seem to be a key-role to control the shape of crystallites resulting of a solvothermal process [30].

In this work, a series of magnetic cerous ferrite (Ce^{III} -doped Fe_3O_4) particles were synthesized by solvothermal process under various Fe: Ce ratio of precursors conditions and evaluated their aqueous Sb(III) and Sb(V) sorption capacity, and the effects of solution pH and coexisting anions (i.e. Cl^- , SO_4^{2-} , and PO_4^{3-}) on adsorption were also investigated. Moreover, we characterized the properties of the Ce^{III} -doped Fe_3O_4 system in detail. Based on these results, possible mechanisms for the adsorption of Sb(III) and Sb(V) on the Ce-doped Fe_3O_4 adsorbent had been proposed. Consecutive cyclic experiments were conducted to evaluate the regeneration and reusability of the adsorbent. To our best knowledge, no report was available in literature on the superior antimony removal performance and mechanism study of the magnetic cerous ferrite adsorbent. With further development, this study may offer a low-cost and easy-handle treatment option to remove antimony contamination from water.

2. Materials and methods

2.1. Materials and chemicals

All chemicals used in this study were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd, China. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) were selected as the synthetic raw material. Ethylene glycol [$(\text{CH}_2\text{OH})_2$] was used as reductant and surfactant. Sodium acetate (CH_3COONa , or NaAc) and poly-ethylene glycol [$\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$, avg mol wt = 6 000] were used as the assisted-precipitate reagent. The stock solutions of Sb(III) and Sb(V) at 100 mg/L as Sb were prepared by dissolving potassium antimony L (+)-tartrate hemihydrate ($\text{C}_4\text{H}_4\text{KO}_7\text{Sb} \cdot 0.5\text{H}_2\text{O}$) and potassium hexahydroxoantimonate (V) ($\text{KSb}(\text{OH})_6$) in ultrapure water, respectively. The stock solutions were prepared weekly and stored at 4°C . In this study, the concentrations of antimony species were measured as elemental concentration. The Sb(III) and Sb(V) working solutions were freshly prepared by diluting stock solutions with ultrapure water. Potassium nitrate (KNO_3 , 0.1 M) was used as background electrolyte in the batch adsorption study.

2.2. Adsorbents preparation and characterization

The Ce^{III} -doped Fe_3O_4 particles were fabricated by solvothermally synthesis of Fe^{III} and Ce^{III} , according to the modified version of the procedure of Deng et al. [32]. As a typical synthesis process, 5.0 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and predetermined amounts (0.0 , 1.25 , 2.14 , 3.33 , and 5.0 mmol) of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were dissolved and combined in 80 mL of ethylene glycol solvent, followed by addition of 7.2 g of sodium acetate and 2.0 g of polyethylene glycol. The mixture was stirred at 70°C in a water bath for 1.0 h , further it was sealed in a 100 mL Teflon-lined stainless steel autoclave and then heated to and maintained at 200°C for 12.0 h . After cooling to room temperature naturally, it was formed in a black (or gray) precipitate, which

was collected by magnetic separation and purified by washing with ethanol and oxygen-free water. After being dried at 60 °C under vacuum overnight, the collected powder was finely ground and stored under the protection of nitrogen for further experiments. The final products were represented as Ce-doped_(x) Fe₃O₄ (x = 0.0, 0.2, 0.3, 0.4, and 0.5) according to the various Ce/Ce + Fe molar ratio (x value) in the precursor solution.

In the synthesis process (Fig. 1), Fe(III) and Ce(III) ions were used as the precursor. Precipitation of their hydroxide in the form of colloidal solution proceeds as follows:

In the presence of a mild reducing agent (e.g., ethylene glycol), Fe(II) may appear in the system. Ethylene glycol can undergo dehydration and the so-formed acetaldehyde reduces Fe(III) to Fe(II) and gives ferrous hydroxide [33]:

Both Ce^{III} and Fe^{II}/Fe^{III} co-exist in the reaction mixture thus enabling magnetite-like formation:

Additionally, controlling the temperature of solvothermal synthetic process ensured a controlled rate of nucleation and growth from the supersaturated solution, which could affect the size of products.

The Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of the adsorbents were obtained from nitrogen adsorption/desorption isotherms using an ASAP 2010 analyzer (Micromeritics, US). The X-ray powder diffraction (XRD) patterns from Ce-doped Fe₃O₄ samples were recorded using an X'Pert PRO MPD diffractometer (PANalytical, the Netherlands). The identification of the crystalline was obtained using the X'Pert High Score Plus software with PDF-4+ and ICDD databases. The Fourier transform infrared (FTIR) spectrum of samples were taken at 400–4000 cm^{−1} wavenumber range conducted on a Bruker Tensor 27 spectrometer (Bruker, Germany). For surface investigation, X-ray photoelectron spectroscopy (XPS) was performed by an Axis Ultramaging photoelectron spectrometer (Kratos, U.K) using a monochromatic Al K α (1486.6 eV) X-ray source. All binding energy (B.E.) values were referenced to the carbon peak C1s at 284.80 eV and the analytical results were done using XPS peak fitting program (XPS Peak). The relative atomic concentration of elements (surface composition of sample) were calculated from peak area ratios normalized by the corresponding atomic sensitivity factors [34]. The TEM images were captured on a Hitachi H-7500 transmission electron microscopy (Hitachi, Japan). The zeta potential of Ce-doped Fe₃O₄ samples were measured by a Malvern Zetasizer 2000 (Malvern, U.K.). The prepared samples were subjected to magnetic characterization using the VSM (vibrating sample magnetometer) in PPMS (Physical Property Measurement System, Quantum, US) at a temperature of 300 K. The changes in physical properties of adsorbents were studied by the TGA (Thermogravimetric analysis, Mettler-Toledo, Switzerland). The temperature rising procedure is as follows: (1) 30–120 °C using a heating rate of 10 °C/min, (2) kept at 120 °C for 10 min, and (3) further heated from 120 to 800 °C at a heating rate of 20 °C/min. To avoid the influence of oxidation, all the samples were kept under argon protection during the entire heating process.

2.3. Adsorption and desorption experiments

Adsorption kinetics, isotherm, and the effects of solution pH, and coexisting anions (Cl[−], SO₄^{2−}, and PO₄^{3−}) were determined in batch adsorption experiments. Desorption experiments were conducted to investigate the reusability and regeneration potential of the sorbent.

For adsorption kinetics, 0.18 g Ce-doped Fe₃O₄ were added into 900 mL solution with an initial Sb(III) or Sb(V) concentration of 50 mg/L, and KNO₃ at 0.1 M was used to maintain background ionic strength (IS). Solution pH was adjusted at different time intervals by 0.1 M HNO₃ and 0.1 M NaOH in the range of 7.0 ± 0.2. The mixtures were stirred at 150 rpm using an electromotive stirrer (MY3000-6, MEIYUYIQI CO, China) to disperse the adsorbent, and then approximately 4 mL aliquots were taken from the suspension at preselected time (*t*) for determination of the remaining antimony. All the adsorption experiments were carried out at 25 °C. The adsorption capacity of Sb ions at preselected time (*t*) was calculated by Eq. (7).

$$q_t = (C_0 - C_t)V/W \quad (7)$$

Where, q_t represents the adsorption capacity (mg Sb/g sorbent), C_0 and C_t are the concentrations of antimony (mg/L) in initial and at preselected time (*t*), respectively. *V* is the volume of the solution (L), and *W* is the mass of adsorbent used (g). For further elucidation of the adsorption mechanism, the pseudo-first-order, pseudo-second-order, and Elovich kinetic models [Eqs. (S2)–(S4)] was fitted to the experimental data.

In adsorption isotherms experiments, 10 mg Ce-doped Fe₃O₄ was added in the polypropylene centrifuge tube and then 50 mL Sb-containing solutions (with Sb concentrations from 10 to 100 mg/L). Solution pH 7.0 ± 0.2 and the ionic strength was maintained as 0.1 M KNO₃. The tubes were shaken on an end-over-end tumbler at 40 rpm for 12.0 h at 25 °C. Then, all the samples were filtered by 0.45 μm membrane and analyzed for residual aqueous antimony. Two adsorption isotherm models, Langmuir and Freundlich [Eqs. (S5)–(S6)], were used to describe the Sb(III)/Sb(V) adsorption behavior.

It was also evaluated the effects of solution pH on antimony adsorption. A given volume of Sb(III)/Sb(V) stock solution was added to conical flask, and the volume was increased to 100 mL with ultrapure water to obtained initial Sb concentration of 50 mg/L. After pH adjustment to predetermined value [3.0–7.0 for Sb(III) and 3.0–10.0 for Sb(V)], 20 mg of adsorbents were added in the flask and shaken at 150 rpm for 12.0 h using a constant temperature shaker (HZQ-F160, HDL, China). It is noted that Sb(III) tends to precipitate in the form of Sb₂O₃ under alkaline condition [35,36], therefore the pH of Sb(III) adsorption experiment only ranged from 3.0 to 7.0. The pH of the solutions was adjusted every 4.0 h with 0.1 M HNO₃ or/and 0.1 M NaOH solution to designated values during sorption process. The concentration of Sb after equilibrium adsorption was measured.

To investigate the influence of commonly coexisting anions (chloride, sulfate, and phosphate) on the removal of Sb, the potassium salts (0.1 M KCl, 0.05 M K₂SO₄ and 0.03 M KH₂PO₄) were introduced into the 50 mg Sb/L solution. Moreover, the blank sample was prepared in similar process without adding coexisting anion. All the solution pH was adjusted to 7.0 by 0.1 M HNO₃ and 0.1 M NaOH. A defined amount (200 mg/L) of Ce-doped Fe₃O₄ was then added and the mixtures were agitated for 12.0 h at 25 °C. After filtration by 0.45 μm membrane, the concentration of residual antimony was analyzed.

The regeneration of adsorbents is an important aspect in sorption research. Thus three cycles of adsorption/desorption of Sb(III) process were carried out to evaluate the reusability of the as-prepared adsorbents. The reusability of the adsorbents was

Fig. 1. Schematic representation of the synthetic process of the Ce-doped Fe₃O₄ adsorbent.

conducted after washing the used adsorbents with 0.5 M NaOH for 12.0 h under stirring followed by vacuum filtration and freeze drying. The regenerated adsorbent was again applied to evaluate recycle ability [37].

2.4. Analytical methods

The bulk composition of Ce-doped Fe₃O₄ was determined using acid-digestion method. It was achieved by treating the samples in conc. HCl (100 mg sample in 20 mL of 10 M HCl) at 70 °C overnight and the dilution of dissolved metals (Fe and Ce) were measured by inductive coupled plasma-optic emission spectrometry (ICP-OES 710 Agilent Technology, US) analysis [38].

Total Sb concentration in the adsorption and desorption experiments was determined by ICP-OES. Prior to analysis, samples were acidified with 1% HNO₃ and all ICP-OES samples were analyzed within 48.0 h.

3. Results and discussion

3.1. Adsorbent characterization

The Ce and Fe contents in the Ce-doped Fe₃O₄ samples were determined by acid-digestion method (bulk composition) and XPS technique (surface composition), both of which were ideal for quantification of elements. The chemical compositions of the samples are summarized in Table 1. The result showed that cerium in samples was increased with increasing the Ce/Ce + Fe ratio of precursor solution. However, the reported chemical compositions of the as-prepared samples were not exactly the same as those of the initial mixed solutions. The maximum Ce/(Fe + Ce) molar ratio of

Ce-doped Fe₃O₄ was about 0.23 for Ce-doped_(0.5) Fe₃O₄, a similar result can be found from co-precipitation samples synthesized by Zhang et al. [39]. To compare with other trivalent ions, the maximum doping ratio of Fe-oxide for Al^{III}, Cr^{III}, Mn^{III}, V^{III}, and Co^{III} is in the range from 0.06 to 0.47 [40]. We attempted to increase the precursor's Ce/Ce + Fe ratio more than 0.5, but it was difficult to get the precipitate. This could be because of the higher concentration of doping element hampered the nucleation process of resulting particles. The maximum doping ratio may also related to doping ion radius, valence states of elements, and vacancy of Fe-oxide structure.

The specific surface areas (*S*_{BET}) of Ce-doped Fe₃O₄ systems were determined by nitrogen adsorption-desorption measurements (Fig. S1 and Table 1). According to the IUPAC classification, all the samples exhibited type-IV isotherms with a very narrow hysteresis loop in the relative pressure (*P*/*P*₀) range of 0.4–1.0, which exhibited typical of less-pore structure [41]. As shown in Table 1, the *S*_{BET} of samples increased with the increasing initial Ce: Fe ratio. A maximum *S*_{BET} was found to be 152.2 m²/g for Ce-doped_(0.5) Fe₃O₄, it was about 4 times higher than the value of the Ce-doped_(0.0) Fe₃O₄ sample (28.2 m²/g), and the higher specific surface areas could provide more surface active sites for diffusion and sorption of adsorbate.

The FTIR spectrum for the Ce-doped Fe₃O₄ systems of different initial Ce:Fe ratio exhibited in Fig. 2a. Two strong absorption peaks at 1572 and 1410 cm^{−1}, we assigned to the C=O stretching vibration of the aldehyde group (−COH) or ketone group (−COR') [42], which was in agreement with Formula (3) and (4). Two bands were observed and assigned to the asymmetric (2929 cm^{−1}) and symmetric (2856 cm^{−1}) stretching vibration of −CH₂−, and the band around 3403 cm^{−1} was ascribed to the stretching of O−H in ethylene glycol [43], which confirmed the trace amount of residual

Table 1

Comparison of structural characteristics of the adsorbents prepared with different Ce:Fe ratio.

Adsorbents	Ce/(Fe + Ce) mol/mol			BET area (m ² /g)	(311) Peak position(°)	FWHM (°)	Average lattice constants	Lattice cell ^c (nm)	Mean particle size (nm)	M _s (emu/g)
	Precursor solution	Prepared sample								
		Bulk ^a	Surface ^b							
Ce-doped _(0.0) Fe ₃ O ₄	0.0	0.000	0.000	28.2	35.422	0.332	7.892	13.8	528.9	66.19
Ce-doped _(0.2) Fe ₃ O ₄	0.2	0.071	0.126	40.6	35.217	0.434	8.465	13.0	106.9	34.81
Ce-doped _(0.3) Fe ₃ O ₄	0.3	0.163	0.171	43.1	35.214	0.537	8.520	12.6	83.4	22.63
Ce-doped _(0.4) Fe ₃ O ₄	0.4	0.175	0.182	63.4	35.239	0.818	9.047	8.1	80.9	11.30
Ce-doped _(0.5) Fe ₃ O ₄	0.5	0.232	0.254	152.2	35.448	0.767	8.933	8.2	–	7.71

^a Determined by acid digestion method.^b Determined by XPS surface analysis.^c Calculated from (220), (311), (400), (511), and (440) peaks by Scherrer equation. **Fig. 2.** (a) FT-IR spectra and (b) XRD patterns of Ce-doped Fe₃O₄ systems, and XPS spectra of (c) Fe 2p and (d) Ce 3d.

ethylene glycol on the surface. The typical low frequency band at around 578 cm⁻¹ referred to Fe^{III}–O vibration in octahedral and tetrahedral sites and that 438 cm⁻¹ were ascribed to Fe^{II}–O vibration in octahedral sites [44,45]. With the amount of doped Ce increased, the Fe–O band of samples was shifted from 600 cm⁻¹ to 584 cm⁻¹. This red shift (decrease in wave number) and peak broadening could be due to the increment of cation vacancy in lattice [46,47], indicating that dopant ions (Ce^{III}) were occupied in the sites, which belonged previously to the iron ions and created new bond with the surrounding atoms. Moreover, a very weak absorption band near 2348 cm⁻¹ was attributed to the attached CO₂ peak and the bands of 1572 cm⁻¹, 1410 cm⁻¹, and 1075 cm⁻¹ were associated to residual NaAc [48].

The as-prepared Ce-doped Fe₃O₄ were characterized using XRD to identify the phases present (Fig. 2b). From the diffraction pattern, it was suggested that all the space group could be indexed in

the cubic Fd $\bar{3}$ m comparing data with PDF-4+ database. The peaks were observed at 2θ = 30.27°, 35.74°, 43.47°, 57.19°, and 62.73°, which represented the Bragg reflections from the (220), (311), (400), (511), and (440) planes, respectively. Apparently, the doping Ce^{III} does not modify the original spinel structure of Fe₃O₄, but can affect the size of the unit cell [40]. The average crystallite diameter of the samples were calculated from the strongest peaks based on the Debye-Scherrer formula [Eq. (S7)]. Another evidence of whether doping has occurred could be obtained from changes in the unit cell dimensions (shown by XRD peaks shifts). Interestingly, a larger cation (Ce^{III}, 115.0 pm) was replaced with a smaller one (Fe^{III}, 78.5 pm or Fe^{II}, 92.0 pm), led to condensed the lattice and broaden full width at half maximum (FWHM). Liu et al. observed similar results in doping Zn^{II} (74 pm) into Fe₃O₄, further confirmed that the doping process leads to Fe³⁺ ions movement from A-sites to B-sites by Mössbauer spectrum [49]. Moreover, as shown in Fig.

Fig. 3. TGA curves of Ce-doped Fe_3O_4 system (Temperature rising procedure: (1) 30–120 °C at 10 °C/min, (2) keep 120 °C for 10 min, and (3) 120–800 °C at 20 °C/min).

S2, the diffraction peak (46.2°) indexed to cubic hexagonal phase of Ce_2O_3 (Reference code: 23-1048) was only appeared in the Ce-doped $_{(0.5)}$ Fe_3O_4 sample.

Although the XRD data of the samples clearly showed the spinel structure, it is difficult to differentiate the $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , due to the similarity of their XRD patterns [50,51]. XPS patterns could be applied to verify the sample because of its sensitivity to $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions. Fig. 2c shows the Fe 2p narrow-scan spectra for the Ce-doped Fe_3O_4 samples. The Ce-doped $_{(0.0)}$ Fe_3O_4 doublet consisted of two wide peaks of Fe $2p_{3/2}$ (710.97 eV) and Fe $2p_{1/2}$ (724.63 eV), which were mainly ascribed to Fe–O bonds and the values are very close to those of magnetite (Fe_3O_4) reported in literatures [50,52]. The Fe

2p peaks of Ce-doped sample shifted to low binding energy could be due to the Fe^{III} was substituted by Ce^{III} , which changed the $\text{Fe}^{\text{III}}:\text{Fe}^{\text{II}}$ ratio in samples. In addition, the XPS spectra of Ce 3d shown in Fig. 2d, the binding energy of Ce $3d_{5/2}$ (885.26 eV) indicated that the dominating chemical state of Ce in Ce-doped Fe_3O_4 was Ce(III), because of the peak at 916.8 eV ($\text{Ce}^{\text{IV}} 3d_{3/2}$) wasn't found. Due to the reducing environment during our synthesis process, oxidized “Ce(IV)-doped” did not exist even when using the Ce^{IV} salt as starting material [28]. In agreement with the result of XRD, the XPS analysis also provided the evidence that the existence of the $\text{Ce}^{\text{III}}_2\text{O}_3$ in the Ce-doped $_{(0.5)}$ Fe_3O_4 formation process. As the content of Ce increased, excessive Ce was readily to be bonded on the surface of the Fe-containing materials, the Ce-based oxides were thereafter formed in the high temperature condition.

In contrast, other lanthanides (Sm, Eu, Gd) also seem to be present in their +3 oxidation states in the doped Fe_3O_4 samples [53]. Based on the combined results of XPS, XRD, and FTIR, it was confirmed that Ce atom successfully doped into the Fe_3O_4 structure.

The thermal stability and percentage of functional groups on Ce-doped Fe_3O_4 were determined by TGA analyses from 30 °C to 800 °C under argon atmosphere (Fig. 3). The initial weight loss at a temperature of 30–120 °C could be attributed to the water desorption from the surface and the adsorbed water was considered to be completely removed after 10 min at 120 °C. The –OH groups on the particle surface could be estimated from the weight loss from 120 to 800 °C [54]. From the TGA results, the weight losses from 120 to 800 °C for Ce-doped Fe_3O_4 particles were calculated from 8.8% to 19.9%. This showed that the surface amount of –OH groups on Ce-doped $_{(0.5)}$ Fe_3O_4 particles was about 2.5 times that of un-doped Fe_3O_4 particles. Moreover, over 500 °C temperature, all the samples were thermodynamically stable in phase [55].

The morphologies of Ce-doped Fe_3O_4 system were confirmed by TEM images (Fig. 4(a)–(e)) and the average diameters of the particles are listed in Table 1. It was revealed that the particle

Fig. 4. TEM images of Ce-doped $_{(x)}$ Fe_3O_4 samples: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.3$, (d) $x=0.4$, and (e) $x=0.5$.

Fig. 5. Magnetization versus applied magnetic field for Ce-doped Fe_3O_4 system at 300 K.

size decreased (e.g. the mean diameter of $\text{Ce-doped}_{(0.0)}\text{Fe}_3\text{O}_4$ estimated by TEM was about 528.9 nm and it was only 80.9 nm for $\text{Ce-doped}_{(0.4)}\text{Fe}_3\text{O}_4$) with the increased amount of cerium doped, the surface rougher, and irregular shapes from spherical. This result suggested that doping of cerium hampered the precipitation process in the synthesis process and changed the form of the products. The samples synthesized by solvothermal method were nearly 5–10 times higher diameter than conventional co-precipitated samples. Larger magnetic particles could be separated from water more easily, because they had high response to an external magnetic field [Eq. (S1)]. Therefore, solvothermal method was more applicable to prepared magnetic adsorbents. Moreover, the morphology of $\text{Ce-doped Fe}_3\text{O}_4$ showed some crystal structure (Fig. 4e). It could be concluded from the XRD and XPS analysis that the crystal structure should be the compound of Ce_2O_3 .

The saturation magnetization, M_s , was an important parameter of magnetic materials, which reflected the ability of magnetic materials to respond to an external magnetic field and quickly separated from the aqueous solution. Fig. 5 compared the magnetic field-dependent behaviors of $\text{Ce-doped Fe}_3\text{O}_4$ in an applied magnetic field from -10 to 10 kOe. All samples showed typical hysteresis loops in their magnetic behavior and their magnetic coercivities ranged from 84.5 Oe to 287.3 Oe, suggesting the presence of ferromagnetic rather than the superparamagnetic properties. This phenomenon could be ascribed to the size range of particles, which were larger than the superparamagnetic critical size (25 nm). Lower coercivity of $\text{Ce-doped Fe}_3\text{O}_4$ could enhance their dispersion in solution because no residual magnetic attraction existed when removal of external magnetic field. Therefore, the $\text{Ce-doped Fe}_3\text{O}_4$ could be categorized magnetically soft. The non-doped sample [$\text{Ce-doped}_{(0.0)}\text{Fe}_3\text{O}_4$] exhibited the highest M_s of 66.19 emu/g, which is slightly lower than the reported value for the bulk samples (73.9 emu/g) [56]. Apparently, $\text{Ce-doped Fe}_3\text{O}_4$ particles had lower magnetic values than that of non-doped Fe_3O_4 and the M_s value decreased as a result of doping more Ce into Fe_3O_4 . To understand the mechanism behind this magnetism, it could be well explained with a structural perspective. Magnetite (Fe_3O_4) showed inverse spinel structure with iron in two valence states (Fe^{II} and Fe^{III}) and these ions were distributed in octahedral and tetrahedral sites. The magnetization could be varied over a wide range by synthesis methods associated with impurity addition, disrupting the crystal structure of magnetic materials [57]. Furthermore, the sublattices

Fig. 6. Zeta potential curve of $\text{Ce-doped Fe}_3\text{O}_4$ suspension versus pH.

were antiferromagnetically coupled, and the nonmagnetic Ce^{III} ions would prefer to occupy the magnetic sites (shown in Fig. 1). A decrease in occupation fraction of Fe^{III} would reduce the magnetic moment and consequently decrease the M_s . In other words, these Ce^{III} ions were non-magnetic and they replaced partly the magnetic Fe-ion and may destroy the original magnetic structure. Generally, the obtained $\text{Ce-doped Fe}_3\text{O}_4$ (7.7–66.2 emu/g) showed relatively M_s as compared with some other magnetic adsorbents (Table 4). Although a relative low M_s was observed in $\text{Ce-doped}_{(0.5)}\text{Fe}_3\text{O}_4$, the value of 7.7 emu/g was enough for the efficiently capture (10 min) of those micro-sized materials using a 70.6 mT magnetic field (Fig. S3). Comparatively, some high-gradient magnetic separation (HGMS) system used magnetic intensity greater than 1 T for ferric suspension separation from water [58,59].

The point of zero charge (pH_{pzc}) is an important adsorbent parameter and the adsorption of charged species onto charged surfaces could be influenced by electrostatic attraction or repulsion forces. The zeta potentials of the samples suspensions before and after doping Ce were measured and illustrated in Fig. 6. Non-doped Fe_3O_4 was found to be an isoelectric point of about 4.5 and the value increased 6.5–7.3 when Ce doped. It was obvious that the presence of Ce ions makes the adsorbent surface more positively charged and it has contributed to attract the negative adsorbate [e.g. $\text{Sb}^V(\text{OH})_6^-$]. Antimony could be adsorbed on $\text{Ce-doped Fe}_3\text{O}_4$ through non-specific and specific adsorption. Nonspecific adsorption involved the Coulombic force [Eq. (S8)], and was mainly limited to pH-dependent sites below pH_{pzc} of the adsorbent. The specific adsorption, however, involved ligand exchange reactions where the anions displace $-\text{OH}$ and/or H_2O from the surface.

3.2. The adsorption performance

3.2.1. Adsorption kinetics

The effect of contact time for the removal of aqueous Sb(III) and Sb(V) by $\text{Ce-doped Fe}_3\text{O}_4$ adsorbent was investigated and the results are shown in Fig. 7. The kinetic results showed adsorption reaction was rapid initially within 2.0 h for both of adsorbate and slow down after 2.0 h. Researchers often interpreted the initial rapid reaction as adsorption by high affinity sites or the precipitation of adsorbate on adsorbent surface. In the following step, intraparticle diffusion dominated and the adsorption slowed down. Over 90% of the maximum adsorption had taken place at 4.0 h and the adsorption equilibrium was achieved after 6.0 h. As shown

Table 2
Adsorption kinetics constants for the adsorption of Sb(III) and Sb(V) onto Ce-doped Fe_3O_4 .

Condition		Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation		
		$q_{\max}$ (mg/g)	k_1	R^2	$q_{\max}$ (mg/g)	k_2	R^2	C	k_3	R^2
Sb (III)	Ce-doped _(0.0) Fe_3O_4	31.87	0.043	0.996	35.29	0.0016	0.983	−0.147	6.229	0.938
	Ce-doped _(0.2) Fe_3O_4	39.66	0.052	0.871	43.45	0.0017	0.943	5.264	6.835	0.991
	Ce-doped _(0.3) Fe_3O_4	50.03	0.061	0.920	54.41	0.0016	0.968	6.507	8.784	0.975
	Ce-doped _(0.4) Fe_3O_4	51.42	0.048	0.927	56.65	0.0012	0.975	5.336	9.049	0.994
	Ce-doped _(0.5) Fe_3O_4	64.21	0.025	0.931	73.60	0.0004	0.967	−3.998	12.484	0.974
Sb (V)	Ce-doped _(0.0) Fe_3O_4	3.99	0.062	0.801	4.41	0.0188	0.870	0.622	0.685	0.921
	Ce-doped _(0.2) Fe_3O_4	36.42	0.037	0.958	40.62	0.0012	0.972	−0.230	7.026	0.957
	Ce-doped _(0.3) Fe_3O_4	37.52	0.117	0.907	40.57	0.0039	0.960	9.740	5.963	0.959
	Ce-doped _(0.4) Fe_3O_4	56.41	0.031	0.971	64.41	0.0060	0.987	−5.122	11.675	0.976
	Ce-doped _(0.5) Fe_3O_4	81.34	0.018	0.964	97.22	0.0002	0.982	−10.217	15.962	0.950

Fig. 7. Adsorption kinetics of (a) Sb(III) and (b) Sb(V) on Ce-doped Fe_3O_4 (Initial $[\text{Sb(III)}] = [\text{Sb(V)}] = 50 \text{ mg/L}$, adsorbents doses = 200 mg/L , $\text{pH} = 7.0$).

in Table 2, the non-linear fit between q_t versus contact time (t) and the regression coefficients (R^2) for the kinetics models showed that the Sb(III) and Sb(V) removal kinetics could be approximated as Elovich and Pseudo-second-order equation, respectively. It was inferred that the predominantly chemical uptake on highly heterogeneous adsorbents for Sb(III) and the adsorption process was controlled by chemical reaction for Sb(V) adsorption [60,61]. As the doped cerium amount increased, the calculated maximum adsorption capacity of Ce-doped Fe_3O_4 towards Sb(V) and Sb(III) increased from 4.14 to 85.05 mg/g and from 32.84 to 67.65 mg/g at neutral pH, respectively.

3.2.2. Adsorption isotherms

The Sb(III)/Sb(V) adsorption capacities of the Ce-doped Fe_3O_4 at pH 7.0 (25°C) were evaluated using the isotherms (Fig. 8). In contrast to the pure Fe_3O_4 , the sorption capacity for Sb(III) and Sb(V) exhibited a positive increasing in the presence of different amounts

Fig. 8. Adsorption isotherms for (a) Sb(III) and (b) Sb(V) by Ce-doped Fe_3O_4 adsorbent (Initial $[\text{Sb(III)}]/[\text{Sb(V)}]$ concentration from 10.0 mg/L to 100.0 mg/L , adsorbent dose = 200 mg/L , $\text{pH} = 7.0$).

of Ce. As shown in Table 3, the higher regression coefficient suggested that Langmuir model was more suitable for describing the sorption behavior of Sb(III) and Sb(V) by Ce-doped Fe_3O_4 . We concluded that the sorption reactions took place on the surface of adsorbent, which was regarded as monolayer adsorption [62]. The calculated maximal sorption capacities for Sb(III) and Sb(V) were

Table 3 Parameters of Langmuir and Freundlich models for the adsorption of Sb(III) and Sb(V) onto Ce-doped Fe₃O₄ at pH 7.0.

Adsorbent		Langmuir model			Freundlich model		
		$q_m(\text{mg/g})$	K_L	R^2	n	K_F	R^2
Sb(III)	Ce-doped _(0.0) Fe ₃ O ₄	111.380	0.037	0.996	2.168	11.411	0.987
	Ce-doped _(0.2) Fe ₃ O ₄	136.891	0.074	0.993	2.654	24.222	0.989
	Ce-doped _(0.3) Fe ₃ O ₄	167.953	0.058	0.977	2.312	22.632	0.963
	Ce-doped _(0.4) Fe ₃ O ₄	187.769	0.059	0.976	2.269	24.857	0.966
	Ce-doped _(0.5) Fe ₃ O ₄	224.168	0.046	0.995	2.068	23.375	0.981
Sb(V)	Ce-doped _(0.0) Fe ₃ O ₄	37.213	0.139	0.999	4.388	12.895	0.980
	Ce-doped _(0.2) Fe ₃ O ₄	97.865	0.109	0.988	3.422	25.527	0.937
	Ce-doped _(0.3) Fe ₃ O ₄	157.951	0.163	0.995	3.544	46.522	0.941
	Ce-doped _(0.4) Fe ₃ O ₄	170.523	0.272	0.984	3.982	60.577	0.934
	Ce-doped _(0.5) Fe ₃ O ₄	188.069	0.229	0.995	3.585	60.181	0.978

111.38–224.17 mg/g and 37.21–188.07 mg/g, respectively, which provided a significant potential for practical aqueous removal of Sb in comparison with some other sorbents in discussion (Table 4).

3.2.3. Effect of pH

Ions adsorption onto adsorbents strongly depends on the pH value of the water to be treated [79]. The adsorption of antimony on Ce-doped Fe₃O₄ as a function of pH from 3.0 to 10.0 is shown in Fig. 9. As can be seen, the adsorption of Sb(III) on Ce-doped Fe₃O₄ was evidently dependent on pH with the lowest adsorption occurring under acidic conditions and increased with pH value. At pH 7.0, the amount of adsorbed Sb(III) on Ce-doped_(0.5) Fe₃O₄ remained close to 75 mg/g, while the amount of adsorbed Sb(III) on Ce-doped_(0.5) Fe₃O₄ reduced to less than 10% at pH 3.0. The similar pH-dependence curve of Sb(III) adsorption on iron oxide has been reported in literatures [8,73]. However, Sb(V) adsorption onto the Ce-doped Fe₃O₄ was benefited from acidic condition. Such pH effect has been observed for the adsorption of Sb(V) onto kaolinite [80], ferrihydrite [81], and graphene oxide/schwertmannite nanocomposites [82], etc. It addressed aspect of the solution chemistry of Sb(V) and assumed that [Sb(OH)₆][−] was the main species of Sb(V) present over the wide range of pH 2–11 (Fig. S4). The p_HPZC value of Ce-doped Fe₃O₄ used in the study was up to 7.3. This maximum adsorption phenomenon of Sb(V) was a consequence of the increased of positive surface charge of Ce-doped Fe₃O₄ with decreasing pH, resulting in greater attraction for anions.

3.2.4. Influence of coexisting anions

The effect of commonly present anions (Cl[−], SO₄^{2−}, and PO₄^{3−}) on aqueous removal of Sb were then examined. As shown in Fig. 10, the presence of the three anions had no negative effect on the adsorption of Sb(III). Interestingly, a slight increase Sb(III) sorption

was observed in the presence of Cl[−] or SO₄^{2−}. For the Sb(V), a negligible decreased removal efficacy was observed in the presence of Cl[−] and SO₄^{2−}. However, the presence of PO₄^{3−} greatly impaired the sorption process, which was resulted from the strong competition by phosphate to binding sites. Both phosphate and antimony are located in the VA group, and the structure of phosphate ion is very similar to that of antimony ion [60].

3.2.5. Reusability of Ce-doped Fe₃O₄

In 3 cycle's adsorption-desorption process, 100% of Sb(III) can be desorbed using 0.5 M NaOH, and the Ce-doped Fe₃O₄ sorbent still kept a high removal performance to Sb after 2 cycle (Fig. 11), indicating its high stability and reusability. It can be explained in terms of competition adsorption between OH[−] ions and Sb ion on the surface of Ce-doped Fe₃O₄. This extraordinary efficiency of Sb desorption from the adsorbents created the removal process economical since both adsorbent and Sb were regenerated and recycled effectively.

3.3. Adsorption mechanisms

From above results, the preferred adsorption mechanisms between Sb(III)/(V) and Ce-doped Fe₃O₄ was concluded:

1. Comparing the results obtained from pseudo-first-order, pseudo-second-order, and the Elovich equations, the experimental data for the adsorption of Sb(V) ions onto Ce-doped Fe₃O₄ gave the best fitted to the pseudo-second-order model rather than other models. It could be concluded that the entire adsorption process of Sb(V) ions is controlled by chemical reaction at the solid/solution interface [83,84]. Simultaneously, the Elovich model fitted best for the adsorption of Sb(III) onto Ce-doped

Table 4

Comparison of saturated magnetization and maximum adsorption capacities of Sb(III) and Sb(V) on adsorbents.

Adsorbent	Saturated magnetization (emu/g)	Initial Sb con. range (mg/L)	Max. Sb(III) adsorption capacity (mg/g)	Max. Sb(V) adsorption capacity (mg/g)	pH	Refs.
Magnetic sludge composite	52.2 [63]	0.5	–	35.7	2.6	[63]
MnFe ₂ O ₄	24.4–68.2 [64]	894.3	10.66	–	2.0	[65]
Fe-Zr binary oxide	1.97–6.1 [66]	10	–	51	7.0	[67]
α-FeOOH	0.05–0.25 [68]	12	44.1	7.47	7.0	[8]
α-Fe ₂ O ₃	0.64 [69]	12	30.13	11.01	7.0	[8]
Hydrous ferric oxide	5.7 [70]	25	–	65.82	7.0	[8]
Cu-doped Fe ₃ O ₄	43.1 [71]	50	43.55	34.46	7.0	[71]
Bentonite	Non-magnetic	4	0.55	0.5	6.0	[72]
Zirconium oxide-carbon nano fibers	Non-magnetic	200	42	32	7.0	[73]
Merapto-functionalized hybrid sorbent	Non-magnetic	515.3	108.8	–	7.0	[74]
Plyamide-graphene composite	Non-magnetic	25	158.2	–	5.0	[36]
Fe(VI) decay product	Non-magnetic	10	129.9	–	4.0	[75]
Fe-Mn binary oxide	Non-magnetic [76]	242	212.9	–	3.0	[77]
		121	–	133.1	5.0	[78]
Ce-doped _(0.5) Fe ₃ O ₄	7.7	50	224.2	188.1	7.0	Present study

Fig. 9. Effect of pH on (a) Sb(III) and (b) Sb(V) adsorption onto Ce-doped Fe_3O_4 adsorbents.

Fig. 10. Effect of co-existing anions on (a) Sb(III) and (b) Sb(V) sorption (Initial $[\text{Sb(III)}] = [\text{Sb(V)}] = 50 \text{ mg/L}$, adsorbents doses = 200 mg/L , $\text{pH} = 7.0$).

Fe_3O_4 , which indicated the occurrence of heterosphere diffusion reactions [77]. Moreover, the un-doped Fe_3O_4 sample showed diverse fit model, attributed to the different adsorption pathway from Ce-doped samples.

Fig. 11. Variation of the adsorption capacity of the Ce-doped Fe_3O_4 in 3 cycle's adsorption-desorption process.

- The abundant surface hydroxyl groups played the major role in its superior antimony adsorption performance. The Ce-doped Fe_3O_4 was more negatively charged than un-doped Fe_3O_4 , which indicated that more surface hydroxyl groups existed on their surface and was in good agreement with the FTIR and TGA results [21]. Additionally, the larger specific surface area (S_{BET}) on Ce-doped Fe_3O_4 indicated that it could provide more adsorption site (include surface hydroxyl groups) and possess an even better antimony removal effect by adsorption. According to surface complexation modeling (SCM) studies [8], only the complexes of $\equiv\text{FeOSbO}(\text{OH})_4^{2-}$ and $\equiv\text{FeOSbO}(\text{OH})^-$ were appeared on the Fe-based sorbents. In addition to the conventional "Fe sites", Ce sites on the surface of Ce-doped Fe_3O_4 also played an important role for the removal of Sb oxyanions. Moreover, it was reasonable to speculate that the doping of Ce affected the chemical states of Fe, and ameliorated the formation of the as-mentioned two complexes on surface of the sorbent, so that the adsorption capacity was enhanced ultimately.
- The surface of Ce-doped Fe_3O_4 adsorbent was positively charged at $\text{pH} < 7.5$, which was favorable for nonspecific adsorption of Sb(V) through Coulombic attraction between anions and the

adsorbent. Since Sb(V) removal could be obtained at $\text{pH} > 7.5$, it was speculated that specific adsorption dominated in the adsorption of Sb(V) onto Ce-doped Fe_3O_4 adsorbent. Decreasing pH improved adsorption of Sb(V) but decreased adsorption of Sb(III). The reduction in Sb(III) adsorption at lower pH may be caused by competition between H^+ and $\text{Sb}(\text{OH})_2^+$ [74].

4. Conclusions

In summary, we herein fabricated the Ce-doped Fe_3O_4 particles from a modified solvothermal method, which was then applied as an effective sorbents for aqueous removal of Sb. According to the high resolution at Ce 3d and Fe 2p in XPS measurements, it was reasonable to conclude the successful doping of Ce into Fe_3O_4 . Furthermore, based on the results of the combined physical characterizations including BET surface area measurement, TEM, and zeta potential analysis, we found that the Ce doping resulting in the decreased particle size, increased the surface area, and isoelectric point. The excellent characters conferred by the Ce-doping increased in the adsorption capacity for Sb, from 111.4 to 224.2 mg/g and from 37.2 to 188.1 mg/g at neutral pH, respectively. More importantly, the Ce doping samples still have the high magnetic separation potential during water treatment. The results of adsorption kinetics along with zeta potential indicated that the adsorption process of Sb(V) ions was controlled by chemical reaction and Coulombic attraction, and that of Sb(III) indicated the occurrence of heterosphere diffusion reactions. With the help of doping Ce, the higher S_{BET} and more surface hydroxyl groups also played important roles in this superior performance. Moreover, the exhausted Ce-doped Fe_3O_4 could be readily regenerated using 0.5 M NaOH solution and be repeatedly used. The novel Ce-doped Fe_3O_4 particles with large adsorption capacity and magnetic separation potential could be used as a promising adsorbent for the removal of antimony from aqueous solutions.

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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.jhazmat.2017.01.007>.

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