TiO₂ incorporated in magnetic mesoporous SBA-15 by a facile inner-pore hydrolysis process toward enhanced adsorption–photocatalysis performances for As(III)

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GRAPHICAL ABSTRACT

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ABSTRACT

A facile inner-pore hydrolysis combining solvent evaporation method was used to decorate mesoporous silica, in which γ -Fe₂O₃ nanoparticles was preloaded onto mesoporous SBA-15 followed by decoration of TiO₂ nanoparticles. This decoration process exploited the homogeneous dispersivity of γ -Fe₂O₃ and TiO₂ nanoparticles in/on SBA-15 and inhibit aggregation of γ -Fe₂O₃ and TiO₂ nanoparticles, which in turn led to a synergistic photocatalytic oxidation and adsorption of As(III). It was found that the prepared nanocomposites had mesoporous structure, large specific surface area, high pore volume and super-paramagnetism according to SEM/TEM, N₂ adsorption–desorption isotherms, XRD and VSM analysis. Experimental results show that SBA-15/ γ -Fe₂O₃-TiO₂ can oxidize As(III) to As(V) efficiently in the photocatalysis reaction. At the same time, As(V) is effectively removed through adsorption by the composites. In addition, with the treatment of alkali solution, As(V) can be easily desorbed from SBA-15/ γ -Fe₂O₃-TiO₂. After reuse for 5 times, the composites still retain comparable catalysis and adsorption performance compared with that of first use, revealing the excellent stability of the composites.

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1. Introduction

Owing to high photocatalytic efficiency, chemical stability, commercial availability, environmental friendliness, and other properties, TiO₂ has been extensively applied in environmental improvement, many studies confirmed that TiO₂ is effective to

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eliminate contamination both in air and water [1]. TiO_2 is widely used as a photocatalyst for organic pollutants removal from water [2–5]. Moreover, some researches indicated that TiO_2 was also effective for oxidizing As(III) to As(V) in the presence of oxygen [1,6–8]. Because arsenite contamination in natural water is a great threat to human beings and other living organisms [1], World Health Organization (WHO) set a maximum arsenic contaminant level of 10 $\mu\text{g/L}$ in drinking water, many efforts have been made to developing effective methods to remove As(III) from drinking water. As(III) is the dominant arsenic species in groundwater, while As(V) is the main arsenic species in surface water. The toxicity of As(III) is about 25–60 times higher than that of As(V) [9], and it is more difficult to remove As(III) than that of As(V), because the adsorption capacity of As(III) is quite lower than that of As(V). Thus, a pretreatment for As(III) oxidation to As(V) before adsorption process is required for its effective removal from water [10].

It is well-established that the photocatalysts simultaneously adsorb contaminants (adsorption) and absorb photons (photoinduced redox reaction) in the photocatalytic oxidation [11]. Moreover the photocatalytic oxidation of contaminants substantially occurs at the surface of TiO_2 in the adsorbed phase and not in the solution [12]. In this regard, a lot of efforts have been made to improve the adsorption capability of TiO_2 based photocatalysts [13–19]. For example, zeolite, porous carbon materials, and mesoporous silica involving TiO_2 frequently used as adsorbent/photocatalyst composites for enriching the pollutants and enhancing the photocatalytic performance [14,15,18,19]. Therefore, it is promising to design a photocatalyst in terms of reasonable combination of photocatalytic sites and adsorption sites on nanoscale. There are many researches about the visible-light photocatalytic activity of TiO_2 , but the oxidation capacity may become lower. In UV/ TiO_2 system, anatase TiO_2 can absorb UV light ($\lambda < 400 \text{ nm}$) due to the energy band gap of 3.2 eV, As (III) can be oxidized to As (V) under UV light, but the adsorption capacity of TiO_2 is quite low, leading to the inefficient removal of As(V) [1]. This shortcoming could be remedied when a material with good adsorption performance was introduced in the system. Many studies proved that maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which is magnetic, possesses excellent adsorption property in water treatment [20–22], where the As (V) can be efficiently adsorbed onto the surface of maghemite and easily separated by magnetic separation method.

It is widely believed that the nature of support plays an important role in improving the catalytic oxidation efficiency [23]. Due to the high surface area, tunable pore diameter, and alignment, mesoporous silica structures have been considered as ideal supports for heterogeneous catalysts. In particular, the SBA-15 framework synthesized by Zhao et al. [24] has a highly ordered

hexagonal mesostructure with parallel channels and adjustable pore size in the range of 5–30 nm [25]. Compared with other mesoporous silica molecular sieve, such as MCM-41, SBA-15 possesses thick walls and better hydrothermal stability, and it is regarded as a good candidate of supporting matrix for photocatalysts [26,27]. SBA-15 can contain individual metallic oxide particles within its mesopores, and the reactants and products can diffuse easily through the pores. Immobilization of TiO_2 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on mesoporous silica can avoid agglomeration and enhance the adsorption and photocatalytic activity of TiO_2 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles [28–30].

In this study, we report the magnetic SBA-15/ TiO_2 nanocomposite synthesized by an inner-pore hydrolysis combining solvent evaporation method. A series of SBA-15 based nanocomposites have been prepared by tuning the decorated nanoparticles. A magnetic mesoporous SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$ composite prepared by an internal hydrolysis method is used as a carrier for supporting TiO_2 . TiO_2 nanoparticles are uniformly incorporated onto the mesoporous $\gamma\text{-Fe}_2\text{O}_3/\text{SBA-15}$ frameworks, and shows ignorable influence on the mesostructure ordering.

2. Experimental

2.1. Preparation of SBA-15, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$ and magnetic SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$

All chemicals used in the experiment were of analytic grade, and were used without further purification. Synthesis of SBA-15 follows Zhao's process [24]. Fe_3O_4 was incorporated into SBA-15 by using an internal hydrolysis combining solvent evaporation method, and then calcined at 250 $^\circ\text{C}$ to form magnetic mesoporous silica SBA-15. TiO_2 was incorporated into magnetic SBA-15 by using an inner-pore hydrolysis method, and then the dried powder was calcined at 400 $^\circ\text{C}$ for 1 h in air. A heating rate of 10 $^\circ\text{C}/\text{min}$ was used. A typical synthesis process is as follows: magnetic SBA-15 was first prepared by internal hydrolysis using $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.40 g) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.27 g) as the precursor and SBA-15 (0.5 g) as the support, the solvent was evaporate to dryness under continuous stirring at 40 $^\circ\text{C}$. The obtained powder was grinded and then calcined at 250 $^\circ\text{C}$ to form magnetic SBA-15. The calculated amount of titanium source titanium tetrabutoxide (TBOT, 0.55 ml) was dissolved in ethanol (20 ml). The clear solution was injected into the above magnetic SBA-15 powder in atmosphere, and the obtained suspension was stirred for 2 h to make the TBOT adsorb completely onto magnetic SBA-15. Then, deionized water was slowly injected into the above suspension under

Fig. 1. The small angle XRD (a) and wide angle XRD (b) patterns of SBA-15, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$, and SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$.

Fig. 2. TEM and FESEM images of SBA-15 (a and d), SBA-15/γ-Fe₂O₃ (b and e), and SBA-15/γ-Fe₂O₃-TiO₂ (c and f).

Fig. 3. Nitrogen adsorption-desorption isotherm (a) and the corresponding pore size distribution curve (b) for SBA-15, SBA-15/γ-Fe₂O₃, and SBA-15/γ-Fe₂O₃-TiO₂.

stirring to hydrolyze TBOT completely. Afterward, the samples were collected by external magnetic field and washed by ethanol and deionized water, followed by drying at 80 °C overnight, and then the samples were calcined at 400 °C for 1 h, the obtained powder was SBA-15/γ-Fe₂O₃-TiO₂. Synthesis of SBA-15/γ-Fe₂O₃ follows the process of magnetic SBA-15, excepting using 0.60 g FeCl₂·4H₂O and 0.41 g FeCl₃·6H₂O as the precursor.

2.2. Characterization techniques

The phase composition of the products was determined by X-ray diffraction on a Philips X'Pert Pro diffractometer, equipped with a Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The particle morphology was

analyzed using a transmission electron microscope (TEM JEOL 2010) at an acceleration voltage of 200 kV and a scanning electron microscope (SEM, Shimadzu SS-550) operated at 200 kV. Nitrogen physisorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 system. The samples were degassed for 180 min at 250 °C in the degas port of the adsorption analyzer. The pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 Versaprobe system, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 150 W. All binding energies (B.E.) were referenced to the C1s peak at 284.6 eV. The magnetic hysteresis (BH) loop was measured via vibrating specimen magnetometer (VSM, BHV-50HTI, Riken Keiki) at ambient temperature. The zeta potentials of the samples were determined under various pH conditions by Zetasizer 2000 (Malvern, U.K.).

2.3. Batch removal experiments

A stock solution of 50 mg/L As(III) was prepared by dissolving NaAsO₂ into deionized water, and stored in the dark in a

Table 1
The BET surface area, pore volume and average pore size of catalysts.

Sample	S _{BET} (m ² /g)	V _{BJH} (cm ³ /g)	D _{BJH} (nm)
SBA-15	719.64	1.18	6.31
SBA-15/γ-Fe ₂ O ₃	397.99	0.67	5.39
SBA-15/γ-Fe ₂ O ₃ -TiO ₂	431.24	0.86	6.02

Fig. 4. Fully scanned spectra (a), O 1s XPS spectra (b), Ti 2p XPS spectra (c), Fe 2p XPS spectra (d) of SBA-15/ γ -Fe₂O₃-TiO₂.

refrigerator. The initial As(III) concentration was fixed at 1.01 mg/L in the removal experiment, which is in the high range of arsenic concentrations appeared in natural water around the world. The pH value of the reaction solution was adjusted with NaOH or HCl solution. A fixed dosage of 1.0 mg photocatalyst per 1.0 mL arsenic solution was used in this study. During the experiment, the suspension was stirred vigorously to disperse photocatalyst to ensure a good contact of photocatalyst with the arsenic species. A 20 W UV lamp through a water filter (UV light ($\lambda < 360$ nm) intensity of surface of the reaction mixture was 1.0 mW/cm²) was used as a light source. The distance between the lamp and fluid level was maintained as 10.0 cm. The photocatalyst was added to a 500 ml quartz photoreactor (diameter $\approx$ 11.2 cm) that contained aqueous

solution of arsenic. The photocatalytic reactor was open to ambient air to reach the air-equilibrated condition. Before the photocatalytic oxidation experiments, the suspension was stirred 2 h and stirred continuously during the irradiation. To examine both the adsorption capability and photocatalytic oxidation performance of the catalyst, the experiments were carried out in the dark and under UV light illumination, respectively. For comparison, As(III) solution was also treated by UV light illumination alone. For the desorption experiments, photocatalysts were added to NaOH (0.01 M) solution for arsenic desorption. After adsorption and desorption, the photocatalysts were recovered by magnetic separation with a permanent magnet. The concentration of As(tot) and As(III) was determined by Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) (Beijing Ruili Analytic Instrument corporation AF-610A) after 0.45 μ m membrane filtration.

3. Results and discussion

3.1. Phase structures and morphology

The small angle XRD was used to examine pore structure of the prepared products. Fig. 1a shows that the small angle XRD pattern of SBA-15 exhibits a strong peak at 0.94° and weak peaks at 1.64° and 1.88°, which can be indexed as the (100), (110) and (200) reflections associated with the p6mm hexagonal symmetry [31]. The small angle XRD patterns of SBA-15/ γ -Fe₂O₃ and SBA-15/ γ -Fe₂O₃-TiO₂ are similar to that of SBA-15, confirming that the hexagonal mesoporous structure was kept after γ -Fe₂O₃ and TiO₂ nanoparticles orderly decorated onto SBA-15. It can be also seen from Fig. 1a that, for SBA-15/ γ -Fe₂O₃ and SBA-15/ γ -Fe₂O₃-TiO₂, the reflection intensity decreased obviously, indicating the effect of γ -Fe₂O₃ and TiO₂ supported on the support. The wide angle XRD was carried out to detect the crystallinity of the oxides on

Fig. 5. Magnetic hysteresis loop at 300 K of SBA-15/ γ -Fe₂O₃-TiO₂.

Fig. 6. Effect of pH on (a) zeta potential (0.01 M KNO_3) and (b) arsenite removal by $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ and SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ nanocomposites.

Table 2

BET surface area and adsorption property of As(III) and (V) on adsorbents (reaction time 2 h, initial arsenic concentration at 1.01 mg/L and solution pH at 7.0).

Catalysts	Surface area ($\text{m}^2 \text{g}^{-1}$)	Adsorbed As(III) (%)	Adsorbed As(V) (%)
SFT	431.24	68.53	97.43
SF	397.99	63.27	85.27
ST	386.37	36.48	51.64
TiO_2	58.36	30.26	47.35
Mixture	259.15	27.59	41.82

SFT: SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$; SF: SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$; ST: SBA-15/ TiO_2 ; Mixture: mixture of SBA-15, $\gamma\text{-Fe}_2\text{O}_3$ and TiO_2 .

the SBA-15, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$, and SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$. As can be seen from Fig. 1b, the broad diffraction peak appeared at $2\theta = 22.30^\circ$ in all the samples confirmed the presence of silica, which is attributed to the amorphous framework of SBA-15 [32]. For SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$, the strong diffraction peaks at $2\theta = 30.16, 35.50, 43.22, 53.62, 57.11$ and 62.72 can be indexed to the (220), (311), (400), (422), (511) and (440) reflections, respectively, which are the characteristic peak of cubic structure of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS No. 19-629). For SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$, besides the diffraction peaks caused by the $\gamma\text{-Fe}_2\text{O}_3$ component, the strong diffraction peaks at $2\theta = 25.28, 37.86, 48.09, 53.94, 62.78, 69.26, 70.03$, and 75.73 can be ascribed to anatase phase TiO_2 (A).

Morphologies of SBA-15, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$, and SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ were characterized by TEM and FESEM. The TEM image of SBA-15 clearly exhibits the well developed uniform hexagonal mesoporous structure with long range orders (Fig. 2a). In Fig. 2b and c, the places with darker contrast could be ascribed to the

presence of metal oxide nanoparticles which located into the channels of SBA-15 and come into being small crystallites resulting from calcinations. The growth of these crystallites that embedded into the mesostructured framework was controlled by the walls of mesoporous silica, with the rodlike crystallites formed after calcination. For SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$ (Fig. 2b), $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles aggregated and led to blockage of the pores. As can be seen in Fig. 2c, the aggregation of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ is improved, indicating that the existence of TiO_2 makes the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles avoid aggregation and disperse homogeneously on the pore walls of the SBA-15 framework. Images of FESEM of the prepared samples further evidences the abovementioned discussions. Fig. 2d shows FESEM image of the SBA-15, clearly demonstrating the porous structure. As illustrated by Fig. 2e, modification of $\gamma\text{-Fe}_2\text{O}_3$ alone leads to bigger particles and the structure becomes coarser due to the embedded $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. As can be seen from Fig. 2f, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ remains the uniform structure as SBA-15, and the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles are smaller than that being solely modified on the substrate SBA-15.

3.2. BET surface area and pore structure

The N_2 adsorption–desorption isotherm of SBA-15, SBA-15/ $\gamma\text{-Fe}_2\text{O}_3$, and SBA-15/ $\gamma\text{-Fe}_2\text{O}_3\text{-TiO}_2$ are depicted in Fig. 3. All the samples exhibited type IV isotherms with a H1-type hysteresis loop, resulting from the capillary condensation of N_2 in the mesopores, which was the characteristic of mesoporous materials having cylindrical mesostructure [33]. The isotherm of SBA-15 exhibited

Fig. 7. Arsenic species concentrations vs treatment time under various conditions with initial As(III) concentration at 1.01 mg/L and solution pH at 7.0.

Fig. 8. Regeneration studies of SBA-15/ γ -Fe₂O₃-TiO₂ composites after five cycles.

a sharp jump at the relative pressure of 0.6–0.8, suggesting the typical mesostructure with uniform pore size distribution in the sample. After introduction of γ -Fe₂O₃ and TiO₂, the hysteresis loop closed around $p/p^0 = 0.45$ with an obvious two-step capillary evaporation. The phenomenon is typical of pore-plugging [34,35], indicating that partial channels are filled by guest species. The location of γ -Fe₂O₃ and TiO₂ in the mesopores can be also concluded from the pore size distribution results. It can be seen from Fig. 3b that after introduction of γ -Fe₂O₃ and TiO₂, the pore sizes are decreased compared with pristine SBA-15. The average pore diameter of SBA-15/ γ -Fe₂O₃-TiO₂ was estimated to be ca. 6.02 nm which was smaller than that of pristine SBA-15, but bigger than that of SBA-15/ γ -Fe₂O₃ (Table 1). The distribution peak became lower after loading γ -Fe₂O₃ and TiO₂ due to the decreased pore volumes. As can be seen from Table 1, the surface area, pore volume and pore diameter of SBA-15/ γ -Fe₂O₃-TiO₂ are bigger than that of SBA-15/ γ -Fe₂O₃, which further confirms that the existence of TiO₂ makes the γ -Fe₂O₃ nanoparticles avoid aggregation, and relieves the blocking of mesoporous.

3.3. XPS spectra

XPS is used to analyze the surface element composition and chemical state of the elements existing in catalysts. The XPS spectrum shown in Fig. 4 reveals that the sample includes four elements, Si, O, Fe and Ti, in which C came from the measuring solvent. The binding energies of Si were at 2p 103 eV and 2s 154 eV [36]. For O 1s spectra, it is evident that two O 1s peaks are contained in SBA-15/ γ -Fe₂O₃-TiO₂ (Fig. 4b), the main peak at 532.8 eV can be attributed to -OH existing on the surface of SBA-15, and the shoulder peak at 529.7 eV can be attributed to the characteristic lattice oxygen of metal oxides [37]. As can be seen in Fig. 4c, two peaks appears at the binding energies of 464.4 and 458.6 eV in the Ti 2p XPS spectrum, which can be assigned to Ti 2p_{1/2} and Ti 2p_{3/2} respectively, indicating that titanium exists as Ti⁴⁺ in anatase TiO₂. For the survey of Fe 2p (Fig. 4d), two feature peaks of Fe 2p_{1/2} and Fe 2p_{3/2} emerged clearly at round 725.01 eV and 710.91 eV, respectively, this implies that Fe element exists as Fe³⁺ in SBA-15/ γ -Fe₂O₃-TiO₂.

3.4. VSM

The magnetism is an important performance which determining the practical separability of SBA-15/ γ -Fe₂O₃-TiO₂. The magnetic separation was carried out by placing a permanent magnet (2300 G) close to the beaker which contained well dispersed

SBA-15/ γ -Fe₂O₃-TiO₂ nanocomposite in water. It was observed that most of the nanocomposites could be rapidly separated from water (within 3 min) upon magnetic attraction. After removing the magnet, SBA-15/ γ -Fe₂O₃-TiO₂ could be easily dispersed again in water with slight stir. Though the saturation magnetization of SBA-15/ γ -Fe₂O₃-TiO₂ (6.57 emu/g) (Fig. 5) was weaker than that of γ -Fe₂O₃ (58.83 emu/g), the remaining magnetism of SBA-15/ γ -Fe₂O₃-TiO₂ was still sufficient to achieve fast solid-liquid separation under an external magnetic field.

3.5. Adsorption and photocatalytic oxidation of arsenite

Before photocatalytic oxidation, the adsorption property of As(III) on SBA-15/ γ -Fe₂O₃-TiO₂ was investigated first. The effect of solution pH on As(III) adsorption onto γ -Fe₂O₃-TiO₂ and SBA-15/ γ -Fe₂O₃-TiO₂ is shown in Fig. 6. The initial As(III) concentration was 1.01 mg/L and the reaction time was 2 h. As can be seen from Fig. 6a, the zero point of zeta potential of γ -Fe₂O₃-TiO₂ and SBA-15/ γ -Fe₂O₃-TiO₂ are round 6.8 and 4.4, respectively. The adsorption of As(III) is not obviously affected by solution pH values for SBA-15/ γ -Fe₂O₃-TiO₂ (Fig. 6b), which is consistent with previous report [1]. As for γ -Fe₂O₃-TiO₂, the maximum adsorption amount for As(III) is about 60.50% (pH = 8.0), which is lower than that of SBA-15/ γ -Fe₂O₃-TiO₂ (68.53%, at pH = 7.0). It can be ascribed to the special surface properties and the high surface area (431.24 m² g⁻¹) of the composites, which possesses of the uniform dispersion of γ -Fe₂O₃ and TiO₂ nanoparticles in the channels and on the surface of SBA-15. In this work, the photocatalytic oxidation of As(III) is studied at pH = 7.0.

In order to evaluate As(III) removal efficiency of SBA-15/ γ -Fe₂O₃-TiO₂, control experiments were carried out. Experimental results show that, under the same experimental conditions, As(III) could also be oxidized to As(V) by TiO₂, but the removal efficiency of As(V) is only 47.35% (Table 2), therefore, As(III) cannot be completely eliminated by one time. Furthermore, the adsorption efficiency of As(III) for SBA-15/ γ -Fe₂O₃, SBA-15/TiO₂, and the mixture of γ -Fe₂O₃, TiO₂, SBA-15 are 63.27, 36.48, 27.59% (Table 2), respectively, which are lower than that of SBA-15/ γ -Fe₂O₃-TiO₂. These phenomena indicate that the mesoporous framework of SBA-15 is necessary for dispersing and anchoring the γ -Fe₂O₃ and TiO₂ phase because of the large specific surface area and good affinity of silanol surface which is favorable for the nucleation of γ -Fe₂O₃ and TiO₂.

Fig. 7a shows the concentration of residual As(III) after three different treatments. As can be seen, with only UV light illumination, little As(III) could be oxidized to As(V) [10]. Although SBA-15/ γ -Fe₂O₃-TiO₂ nanocomposites possess good adsorption capability for As(III), the remaining As(III) concentration was still 0.29 mg/L after 3 h treatment, which is much higher than the WHO standard (10 μ g/L) for drinking water. Further decrease of As(III) concentration could be observed when both SBA-15/ γ -Fe₂O₃-TiO₂ and UV light illumination were present. After 12 h illumination of UV light, the residual As(III) concentration decreased to 3.65 μ g/L, which is lower than the limit of 10 μ g/L. The changes of As(V) concentration under three different treatments are shown in Fig. 7b. With UV light only, the concentration of As(V) increased slightly due to the oxidation of As(III) to As(V) when exposed to the air. When SBA-15/ γ -Fe₂O₃-TiO₂ existed without UV light, the concentration of As(V) decreased quickly due to its adsorption onto SBA-15/ γ -Fe₂O₃-TiO₂ and decreased from 30.1 to 5.2 μ g/L after adsorption for 12 h. Under the presence of both SBA-15/ γ -Fe₂O₃-TiO₂ and UV light, the As(V) concentration decreased initially, which could be attributed to the combination impacts from both As(III) oxidation (increasing the As(V) concentration) and As(V) adsorption (decreasing the As(V) concentration), while at the beginning of the reaction, As(V) adsorption plays the dominant

Scheme 1. Schematic representation of the formation of SBA-15/γ-Fe₂O₃–TiO₂ composites, the procedure of PCO of As(III) under UV irradiation and simultaneous adsorption of As(V).

role. With continuous illumination, a slight increase of As(V) concentration could be observed. This increase could be attributed to the continuous photocatalytic oxidation of As(III) to As(V) by SBA-15/γ-Fe₂O₃–TiO₂, which exceeds the decrease of As(V) concentration caused by adsorption. Thus, in our experiment, it can be clearly seen that in the presence of both SBA-15/γ-Fe₂O₃–TiO₂ nanocomposites and UV light, As(III) can be oxidized to As(V) by dissolved O₂, and As(V) can be eliminated by the adsorption of SBA-15/γ-Fe₂O₃–TiO₂ nanocomposites.

Desorption experiments were performed in NaOH (0.01 M) solution, the surface of nanocomposites presents negative charges and yet As(V) predominately exists as AsO₄^{3–}, As(V) can be desorbed easily from photocatalysts because of the strong electrostatic repulsion. Fig. 8 shows the removal efficiency of As(III) during five regeneration cycles. The As(III) removal efficiency is all above 90% for SBA-15/γ-Fe₂O₃–TiO₂ and the structure of the nanocomposites is not destroyed. This confirms that the photocatalyst is very stable and possesses good performance of adsorption and desorption.

3.6. Formation mechanism, the photocatalytic oxidation procedure (PCO) and adsorption of arsenite

The possible mechanism for the formation of SBA-15/γ-Fe₂O₃–TiO₂ nanocomposites, the photocatalytic oxidation of As(III) and the adsorption of As(V) is demonstrated in Scheme 1. At first, SBA-15 is synthesized follow Zhao's process [24]. And then, Fe³⁺, Fe²⁺, and Ti⁴⁺ are impregnated into SBA-15. After internal hydrolysis process, Fe³⁺, Fe²⁺, and Ti⁴⁺ are enriched in/onto SBA-15 and then SBA-15/γ-Fe₂O₃–TiO₂ nanocomposites are formed after calcinations. Here, SBA-15 plays dual roles, where SBA-15 not only serves as a supporter, but also serves as a dispersant of γ-Fe₂O₃ and TiO₂. The accumulation of γ-Fe₂O₃ and TiO₂ nanoparticles is inhibited efficiently by SBA-15. The uniform dispersion of γ-Fe₂O₃ and TiO₂ in the channels and on the surface of SBA-15 is desirable for efficient arsenite adsorption. It is well-known that γ-Fe₂O₃ is an excellent arsenic adsorbent [22]. Therefore, in comparison with TiO₂ and γ-Fe₂O₃, SBA-15/γ-Fe₂O₃–TiO₂ composites can possess of more adsorption sites for arsenic because of its high surface area and special surface property. When SBA-15/γ-Fe₂O₃–

TiO₂ composites are added into the arsenite contained water, arsenite is adsorbed onto the surface of the composites. When the photons reach the TiO₂ photocatalytic sites under UV light irradiation, the charge separation produces electron/hole pair (h⁺ and e[–]). The conduction band e[–] transfers to the surface of TiO₂ to reduce the dissolved oxygen and then forms the OH[–] radicals, the valence band h⁺ reacts with the H⁺/H₂O and also produces the OH[–] radicals [38]. The resulting OH[–] can oxidize the As(III) adsorbed on the TiO₂ surface and then adsorbed by γ-Fe₂O₃. The adsorbed As(III) on TiO₂ surface can be immediately supplied by the As(III) enriched on γ-Fe₂O₃ adsorption sites near or on the TiO₂ nanoparticles, which can effectively shorten the diffusion distance of As(III) from adsorption sites to photocatalytic sites. Finally, As(V) can be efficiently adsorbed by SBA-15/γ-Fe₂O₃–TiO₂ composites. In addition, As(V) can be easily desorbed from the composites by treating in alkali solution because of the strong electrostatic repulsion. Therefore, the recycle utilization of SBA-15/γ-Fe₂O₃–TiO₂ composites is possible.

4. Conclusions

In summary, γ-Fe₂O₃ and TiO₂ incorporating SBA-15 nanocomposites were synthesized through an inner-pore hydrolysis combining solvent evaporation method employing SBA-15 as the support and FeCl₃·6H₂O, FeCl₂·4H₂O and TBOT as the precursors, respectively. The obtained composites possess an ordered mesopore structure, large specific surface area (397.99–719.64 cm²/g), and uniform pore size (5.39–6.31 nm). The adsorption capability of the SBA-15/γ-Fe₂O₃–TiO₂ composites for As(III) and As(V) are much higher than that of SBA-15/γ-Fe₂O₃, SBA-15/TiO₂, TiO₂, and the mixture of γ-Fe₂O₃, TiO₂, and SBA-15. The enhanced photocatalytic oxidation performance of As(III) under UV irradiation is ascribed to the high surface area, high dispersivity of γ-Fe₂O₃ and TiO₂ on SBA-15 and the combination of γ-Fe₂O₃ and TiO₂ on the nanoscale. Moreover, the photocatalyst can be easily regenerated by treating in alkali solution without destroying the structure of the composites. The resulting composites that possessed the excellent photocatalytic oxidation, adsorption and desorption property were very stable even after 5 times recycle. Therefore, the obtained novel SBA-15/γ-Fe₂O₃–TiO₂ composites may be an

potentially attractive photocatalyst for water treatment, especially for the arsenite contaminated water.

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